

Mechanistic Elucidation of Oxygen Evolution and Reduction Reactions via X-ray Absorption Spectroscopy

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Chapter 1. General Introduction

1.1 Overview of Hydrogen Energy

Hydrogen, the most abundant element in the universe and a fundamental Earth component, is increasingly recognized for its potential as a clean energy source to support global sustainable development efforts (Figure 1-1).¹ Due to its unique physical and chemical properties, hydrogen is playing an expanding role in the energy landscape. It can be produced from various sources, including fossil fuels, industrial by-products, and water. Among these, water electrolysis offers a promising method for green hydrogen production by splitting water into hydrogen and oxygen with electricity, resulting in zero direct carbon emissions.^{2, 3}

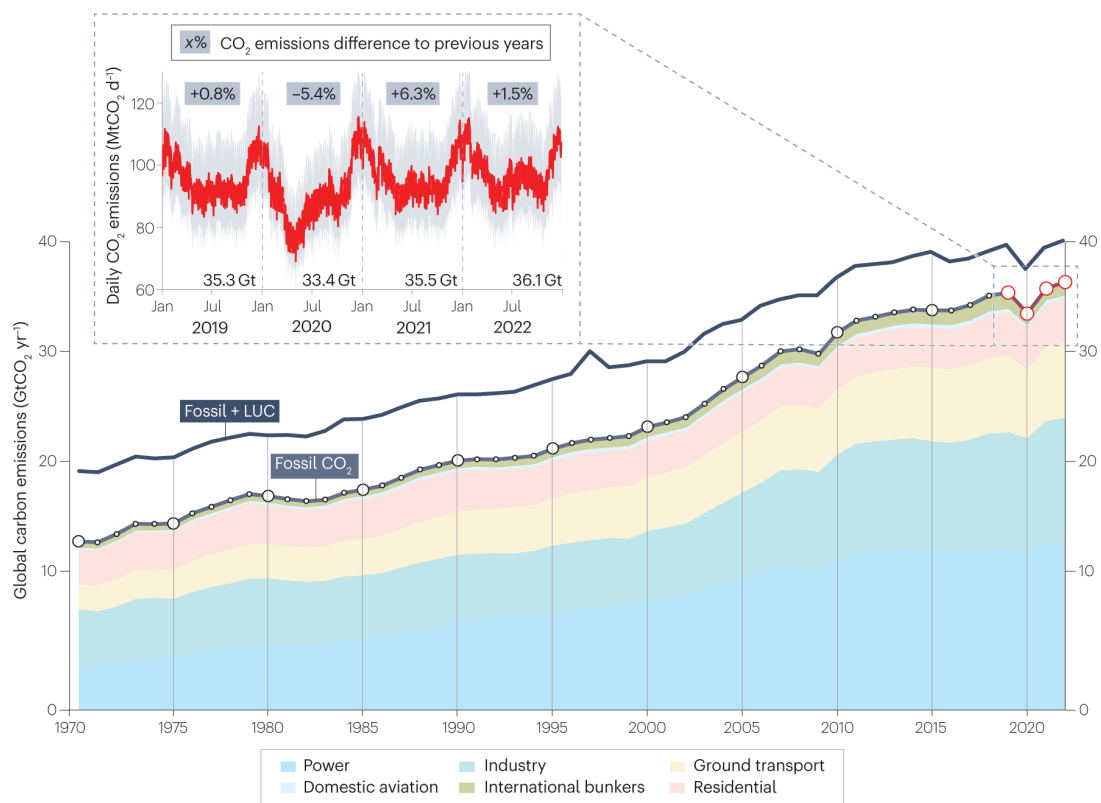


Figure 1-1. Historical CO₂ emissions.¹

However, water electrolysis faces significant challenges: alkaline and proton exchange membrane electrolyzers are costly due to materials like platinum-group metals and require

durable, corrosion-resistant components.⁴ Efficiency is further constrained by overpotentials in the hydrogen and oxygen evolution reactions (HER and OER),⁵ creating a need for advancements in catalyst performance and energy efficiency to reduce costs and scale up production. To address these issues, research is advancing with solid oxide electrolyzers and improved catalyst materials, aiming to boost electrolysis efficiency and cost-effectiveness.⁶ When powered by renewable sources, electrolysis could enable fully carbon-free hydrogen production, seamlessly integrating into sustainable energy systems.⁷

Additionally, hydrogen's high energy density (140.4 MJ/kg) and fuel cell efficiency (over 90%) make it an exceptional energy carrier.^{8,9} Its versatility allows it to serve as a bridge among various forms of energy—electricity, gas, and heat—supporting cross-sector applications and optimizing energy networks (Figure 1-2).^{10,11}

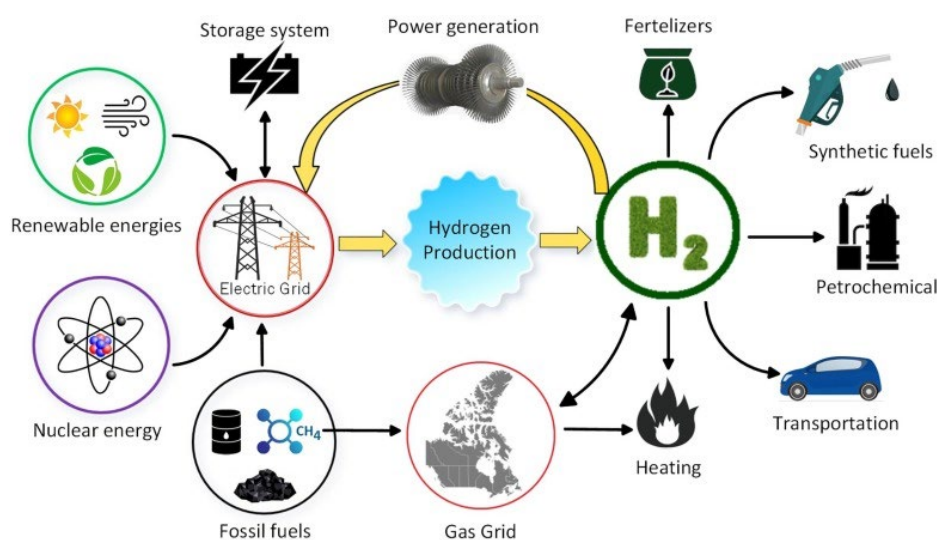


Figure 1-2. The wide range of uses for hydrogen.¹¹

Hydrogen safety has historically raised concerns due to its properties like low ignition energy and wide flammability range.¹² However, advancements have made production, storage, and transportation much safer, with modern hydrogen systems incorporating over-temperature alarms, fire protection, pressure controls, and leak detection mechanisms.¹³ For example, hydrogen storage tanks use aluminum liners with carbon fiber wraps to prevent embrittlement, while pipelines are constructed from stainless steel for increased durability.¹⁴

Fuel cell vehicles (FCVs), a major application of hydrogen, exemplify both efficiency and safety. The Toyota Mirai, launched in 2014, showcases the potential of hydrogen-powered vehicles with a driving range exceeding 500 km, quick refueling, and operability at extreme temperatures.¹⁵ Studies indicate that FCVs may have a lower explosion risk compared to gasoline and electric vehicles due to advanced safety measures in fuel cell systems, including regulations for onboard hydrogen systems.¹⁶

Globally, hydrogen is becoming integral to energy strategies. Its role as an efficient energy carrier and enabler of fuel cell technology highlights its potential in carbon neutrality efforts, supporting both climate change mitigation and energy security. With continued advancements in safety and infrastructure, hydrogen is poised to contribute substantially to a cleaner, sustainable energy future.

1.2 Fuel Cell Introduction

Fuel cell technology dates back to 1839, when William R. Grove invented the first hydrogen-oxygen cell.¹⁷ This foundation was later refined by W.F. Ostwald and saw practical application in the 1960s as auxiliary power sources in space missions.¹⁸ The first FCV was developed in 1967 in the United States, paving the way for commercialization.¹⁹ Today, countries like the United States, Japan, and South Korea are leaders in fuel cell development, with applications spanning power generation, transportation, aerospace, and marine industries.

Fuel cells generate electricity through an electrochemical reaction between hydrogen and oxygen, providing an efficient and clean alternative to combustion-based systems. Unlike conventional power generation, fuel cells are not limited by the Carnot cycle, allowing them to achieve high energy conversion efficiencies—up to 90% in combined heat and power (CHP) systems. Practical efficiencies range from 40-60%, still surpassing many traditional sources.⁹

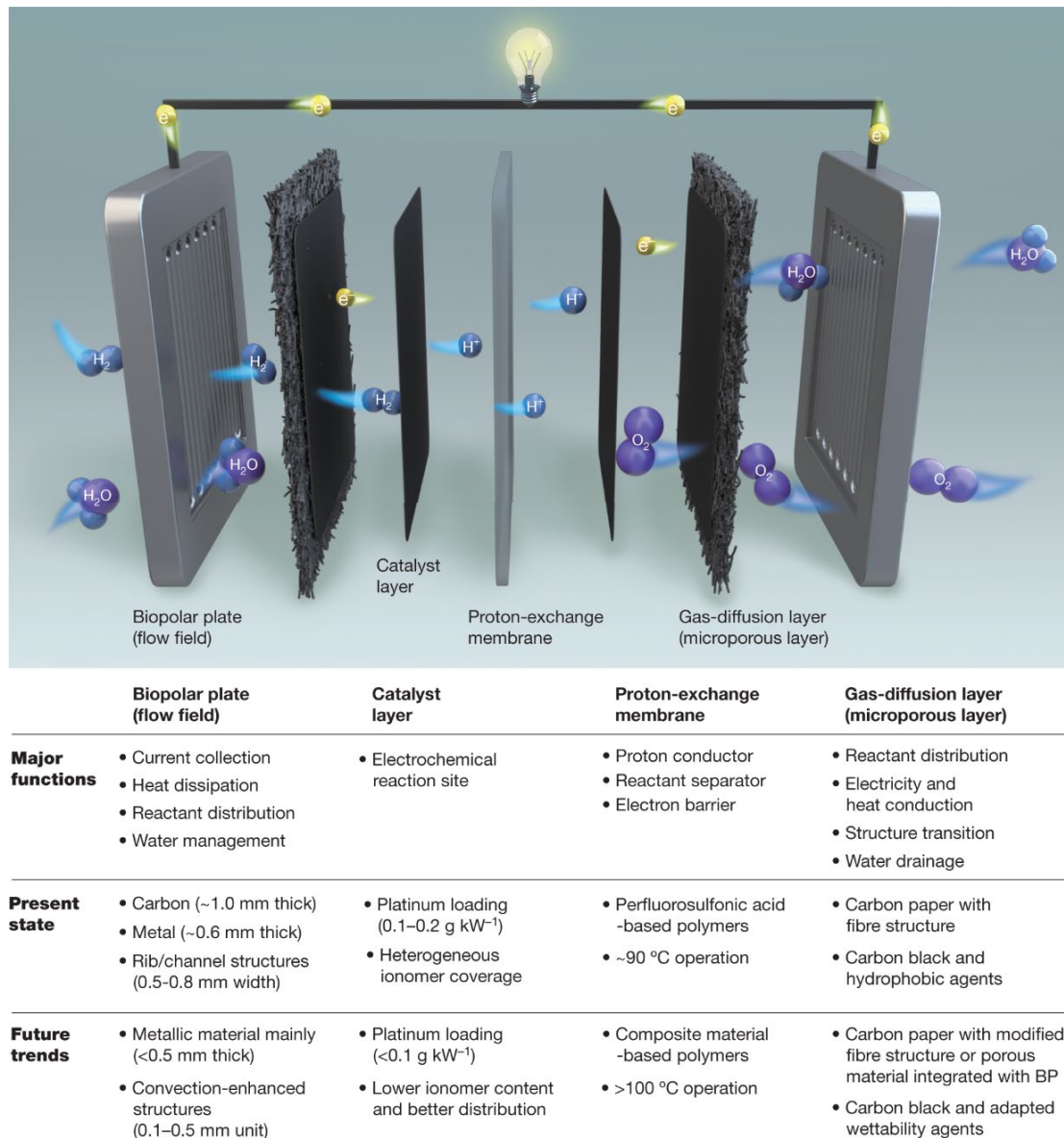


Figure 1-3. Seven components of a PEMFC are presented, including BPs with flow channel/field, GDLs and CLs at the anode and cathode, respectively, and the central PEM. ²⁰

For instance, in Proton-Exchange Membrane Fuel Cells (PEMFCs), hydrogen at the anode is split into protons and electrons. The protons pass through a membrane to the cathode, where they combine with oxygen to form water, the only emission when pure hydrogen is used. Electrons travel through an external circuit, generating a clean, quiet power source well-suited to applications demanding low emissions (Figure 1-3). ²⁰

1.2.1 Classification of fuel cells

Fuel cells come in various types, each suited for different applications and operating environments. The primary way to classify fuel cells is based on the type of electrolyte they use, which determines their operating temperature, fuel flexibility, and specific applications.

Below are the key types of fuel cells (Table 1-1).²¹ Each type of fuel cell has its unique advantages and application areas, ranging from high-efficiency stationary power generation to portable and transportation-related uses. Recent advances in fuel cell technologies, especially in improving power density, durability, and cost reduction, have paved the way for broader commercial adoption across multiple sectors.

Table 1-1. The types of the fuel cell devices.²¹

	Alkaline Fuel Cells	Phosphoric Acid Fuel Cells	Molten Carbonate Fuel Cells	Solid Oxide Fuel Cells	Proton Exchange Membrane Fuel Cells
Electrolyte	KOH	H ₃ PO ₄	Li ₂ CO ₃ /K ₂ CO ₃	Composite oxide (e.g., zirconia)	Proton exchange membrane (Nafion)
Electrolyte Form	Liquid	Liquid	Liquid	Solid	Solid
Conducting Ions	OH ⁻	H ⁺	CO ₃ ²⁻	O ²⁻	H ⁺
Anode Catalyst	Pt/Au, Pt	Pt	Ni/ZrO ₂	Ni/ZrO ₂	Pt/Pd
Cathode Catalyst	Pt/Au, Pt	Pt/Cr/Co, Pt/Ni	LaSrMnO ₃	LaSrMnO ₃	Pt
Conversion Efficiency (%)	60	40	45–60	50–60	40–60
Specific Power (W/kg)	35–105	120–180	30–40	15–20	340–3000
Operating Temperature (°C)	60–200	160–220	600–650	800–1000	20–120
Fuel	Hydrogen	Natural gas, methanol	Natural gas, methanol, oil, coal	Natural gas, methanol, oil, coal	Hydrogen

1.2.2 PEMFC working principle

PEMFCs consist of key components such as the endplate, bipolar plate, sealing gasket, and membrane electrode assembly (MEA).²² The endplate acts as a current collector and maintains compression, while the bipolar plates, made from materials like graphite or metal, channel gas flow and remove water, ensuring proper gas distribution and water management. The sealing gasket, typically silicone, prevents gas leaks. The MEA, the core of PEMFCs, consists of a proton exchange membrane (PEM) between electrodes. The PEM, usually made of

perfluorosulfonic acid, allows proton transfer while blocking electrons to prevent short circuits. The electrodes include a gas diffusion layer (GDL) that distributes gases and supports the catalytic layer (CL), facilitating the fuel cell's electrochemical reactions.

The working principle of PEMFCs relies on an electrochemical reaction between hydrogen and oxygen (Figure 1-4). At the anode, hydrogen is introduced and split into protons (H^+) and electrons (e^-) with the help of a platinum catalyst. The protons move through the PEM to the cathode, while the electrons are directed through an external circuit, producing electrical power.²³

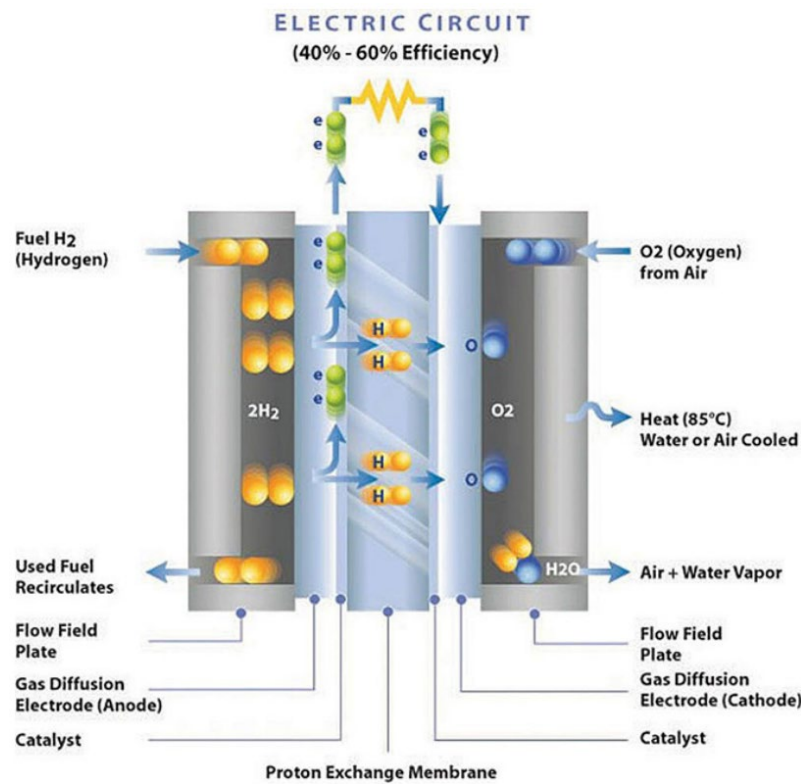
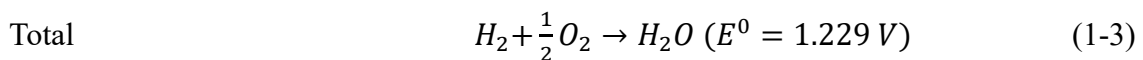
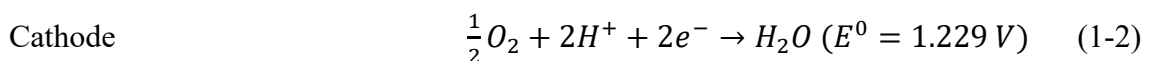
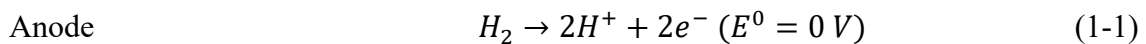


Figure 1-4. Schematic diagram of PEMFC working principle.²³

The cell electrode reaction equation is:



While Pt-based catalysts are employed for both the HOR at the anode and the ORR at the cathode, a substantially larger amount of Pt is needed for the cathode. This is due to the ORR being a kinetically slower reaction, which makes it the rate-limiting step in fuel cell performance.²⁴ As a result, the overall performance of the PEMFC is highly dependent on the reaction rate at the cathode, making the electrocatalytic study of the ORR critical for improving fuel cell efficiency.

Unlike the relatively straightforward HOR at the anode, the ORR involves multiple intermediate reactions and radical species, with various potential reaction pathways. Despite extensive research, a detailed understanding of the ORR mechanism remains elusive, which continues to limit the optimization of catalyst design and fuel cell performance.

1.2.3 Present issues for PEMFC

Proton-Exchange Membrane Fuel Cell (PEMFC) hold substantial potential as a clean energy solution but face challenges that limit widespread adoption. The high cost, mainly due to the reliance on Pt catalysts, poses a significant barrier.²⁵ Efforts are underway to develop cost-effective alternatives, including non-Pt catalysts or designs that reduce Pt usage without compromising efficiency (Figure 1-5). Additionally, the lack of comprehensive hydrogen infrastructure, particularly for production, storage, and distribution, hinders the adoption of PEMFC, especially in the transportation sector. However, increased attention on renewable energy sources for hydrogen production is expected to help address these limitations over time.

Operationally, PEMFC require meticulous water and heat management to maintain efficiency. The proton-conducting membrane must be well-hydrated to function, but excess water can cause flooding, while insufficient water risks membrane dehydration, both of which degrade performance. The durability of PEMFC is also challenged by membrane degradation, catalyst deactivation, and corrosion under dynamic conditions, as in automotive uses. Advances in materials science and design—such as high-performance membranes, novel catalysts, and improved structural designs—are essential to enhance stability and support PEMFC deployment on a larger scale

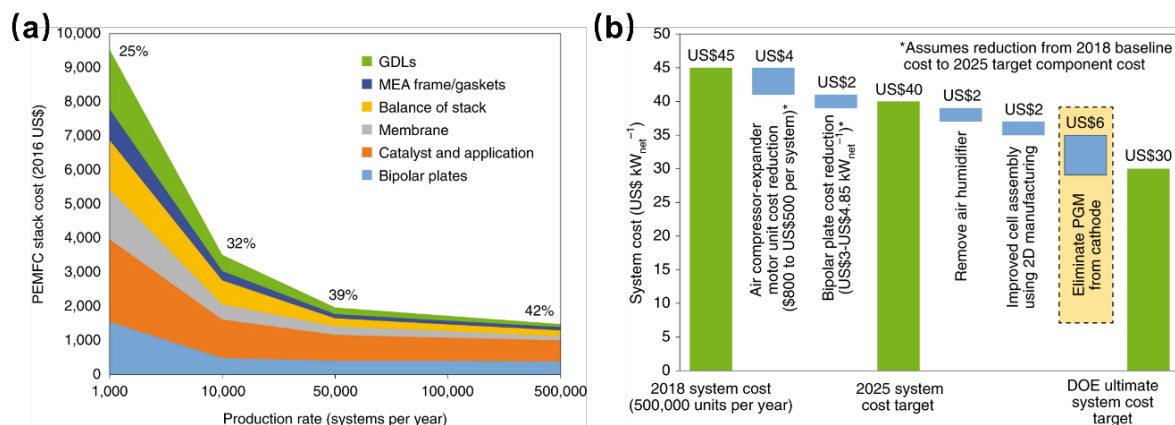


Figure 1-5. (a) Breakdown of projected stack costs for a modern 80 kW net fuel cell system. (b) The most crucial step toward achieving the final system cost goal is removing PGMs from the PEMFC cathode.²⁵

1.3 Overview of Pt-based ORR Catalysts

1.3.1 Reaction mechanisms for ORR in PEMFCs

The ORR in PEMFCs can proceed through two main pathways, as illustrated in Figure 1-6.²⁶ In the four-electron pathway, O_2 is directly reduced to H_2O without the formation of H_2O_2 , with a rate constant of k_1 . In the two-electron pathway, O_2 is first reduced to an adsorbed hydrogen peroxide intermediate (H_2O_{2ad}) with a rate constant of k_2 , which can either decompose into water via the catalytic surface (k_3), or dissociate back into oxygen and adsorbed oxygen species (O_{2ad}) with rate constant k_4 . Additionally, H_2O_2 can desorb from the catalyst surface into the electrolyte with a rate constant of k_5 .

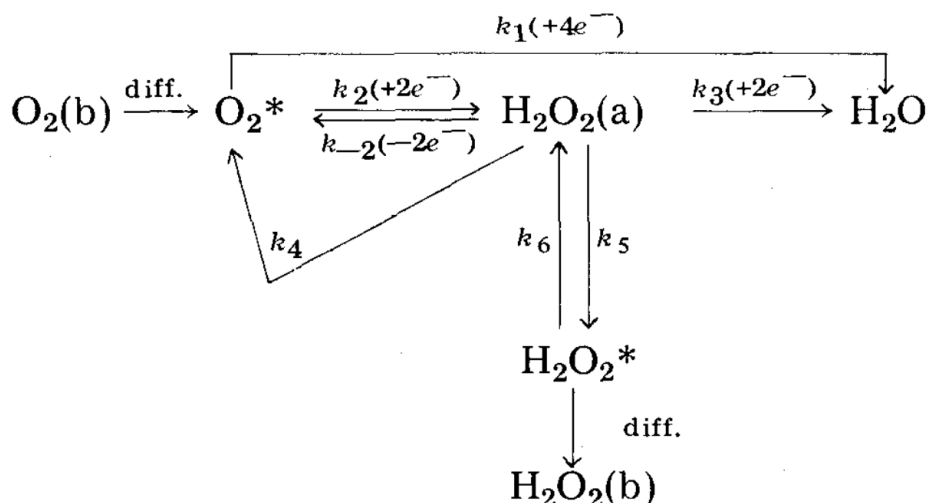


Figure 1-6. ORR mechanism diagram.²⁶

The critical step controlling the reaction rate in ORR is generally considered to be the adsorption and desorption of oxygen reduction intermediates, particularly hydroxyl (-OH) species, on the catalyst surface. This adsorption is closely linked to the metal-oxygen binding energy, which is a key determinant of the catalytic activity. Studies by Nørskov et al. using density functional theory (DFT) calculations demonstrate a volcano plot relationship between the metal-oxygen binding energy and ORR activity.²⁷ Pt and Pd have moderate binding energies, making them some of the most effective monometallic catalysts for the ORR (Figure 1-7).

For optimal performance, the metal-oxygen binding energy should be approximately 0.2 eV lower than that of Pt to maximize ORR activity.²⁸ If the binding energy is too high, the oxygen intermediates bind too strongly to the catalyst, hindering desorption and reducing the number of active sites available for the reaction. Conversely, if the binding energy is too low, the O-O bond in the oxygen molecule cannot be sufficiently weakened, which slows the transfer of protons and electrons to the adsorbed oxygen species, limiting the overall catalytic activity.

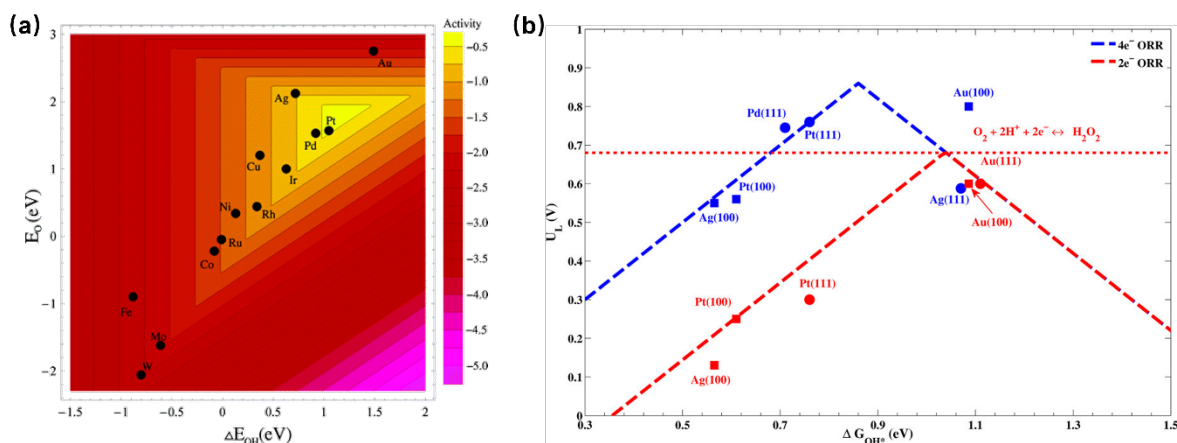


Figure 1-7. (a) The relationship between ORR activity and the binding energies of O and OH is depicted.²⁹ (b) Volcano curve relationship between catalytic activity and hydroxide bond energy for four- and two-electron pathways of ORR.²⁷

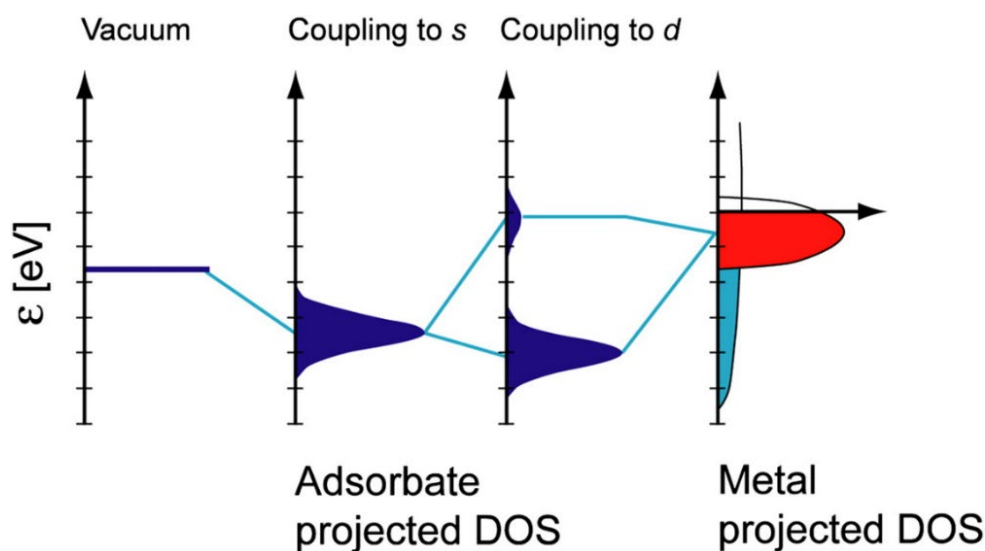


Figure 1-8. Diagram depicting how a chemical bond forms between the valence level of an adsorbate and the s and d orbitals of a metal surface.³⁰

Additionally, adjusting the d-band center of the catalyst can fine-tune its binding energy with oxygen intermediates (Figure 1-8). A higher d-band center strengthens oxygen binding, while a lower d-band center weakens it. Optimizing the d-band center of Pt or other catalysts could theoretically enhance ORR activity by balancing the binding energy of oxygen species.

1.3.2 Pt-based catalyst design principles

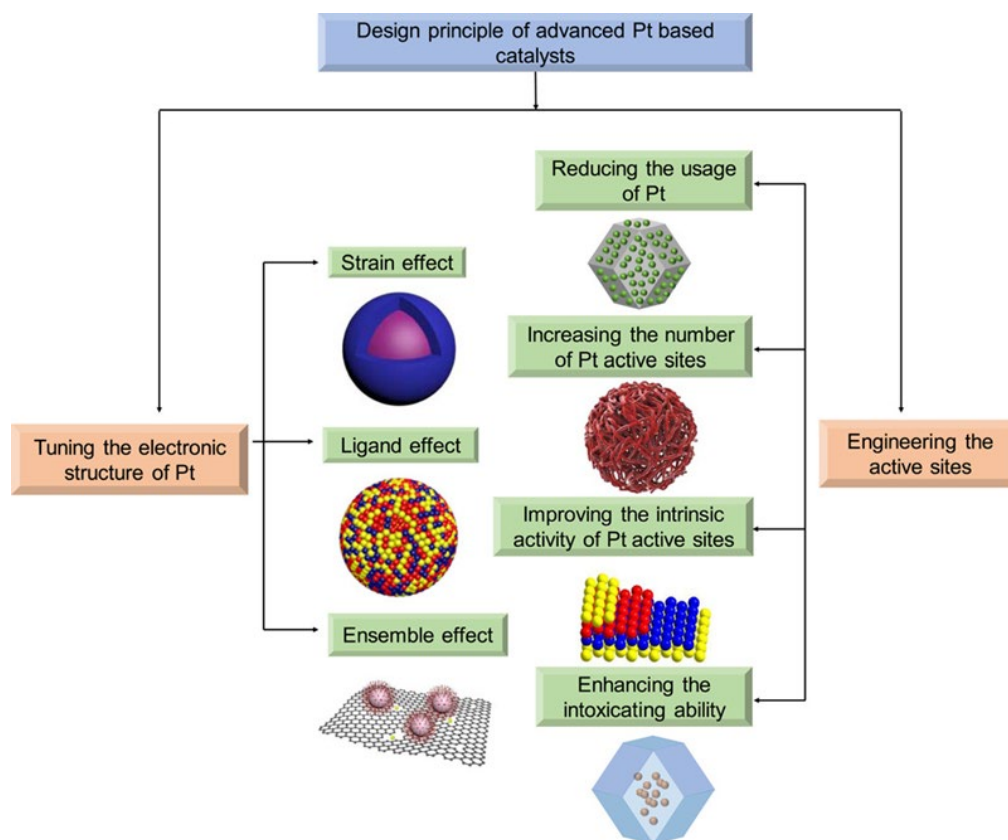


Figure 1-9. Diagram illustration of fundamental design principles for developing advanced Pt-based electrocatalysts for ORR.³¹

Pt-based catalysts are widely recognized as the most effective catalysts for the ORR in fuel cells. However, due to the sluggish kinetics of ORR, it is essential to develop novel Pt-based electrocatalysts with improved performance. To achieve this, two key principles guide catalyst design: (i) increasing the number of active Pt sites and (ii) enhancing the intrinsic activity of each active site (Figure 1-9). Additionally, the poisoning effect of adsorbed species on Pt surfaces in practical applications significantly reduces the activity and stability of the catalyst, necessitating strategies to mitigate these effects.³¹

To enhance the activity and durability of Pt-based catalysts, researchers have developed various strategies, including tuning the electronic structure and modifying the coordination environment of Pt active sites. Three major effects—strain effect, ligand effect, and ensemble effect—have been identified as critical in enhancing the catalytic behavior of Pt-based

materials.

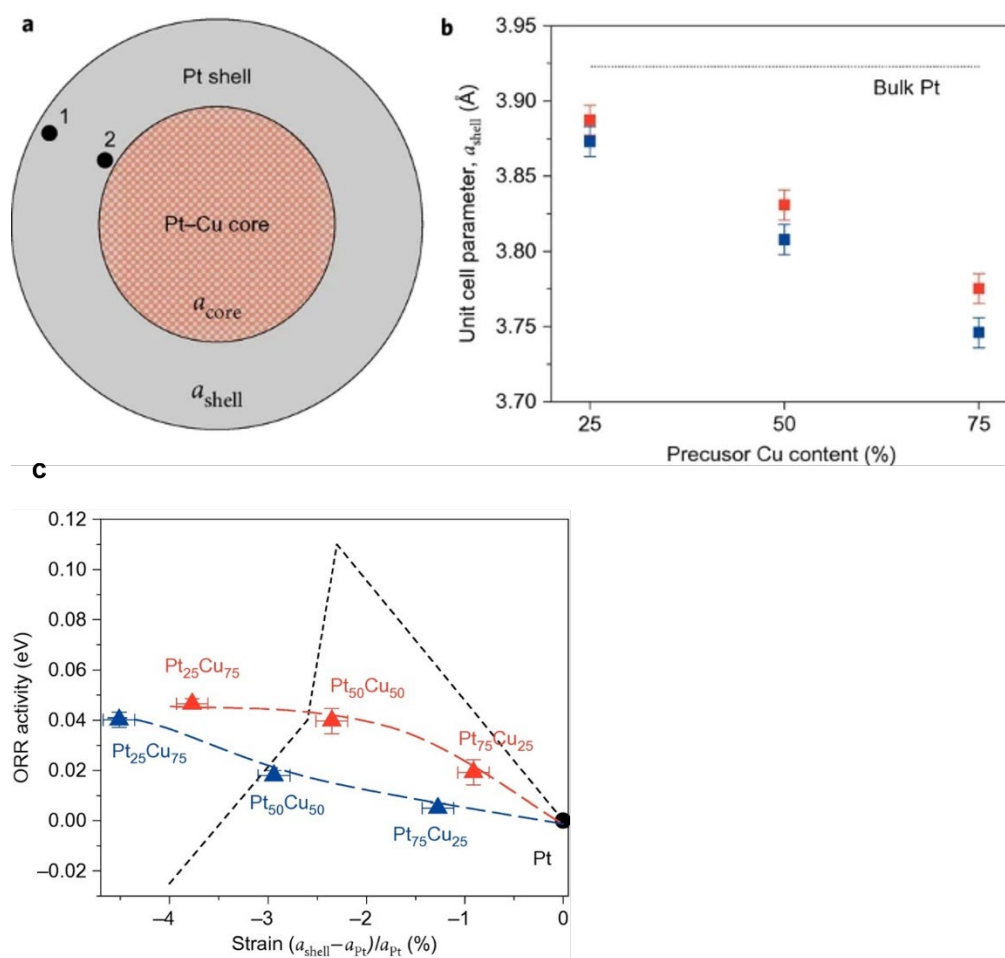


Figure 1-10. A core-shell structure model and evaluation of their lattice parameters changed by strain effect.³⁵

Strain engineering has emerged as a crucial approach for enhancing the electrocatalytic efficiency of Pt-based catalysts.³² The strain effect arises from lattice mismatch when external metals are incorporated into Pt-based nanocatalysts, typically deeper than 1 nm into the material.^{33, 34} This lattice mismatch modifies the Pt lattice structure (Figure 1-10),³⁵ influencing the position of the d-band center and, as a result, altering the adsorption and desorption energies of Pt to oxygenate species. This change in electronic structure directly impacts catalytic activity, making strain engineering a promising strategy for catalyst improvement.

Maria et al. explored the impact of strain on ORR activity in Pt-based catalysts by

synthesizing eight Pt-M alloys (M = La, Ce, Sm, Tb, etc.), using lanthanide contraction to induce surface strain (Figure 1-11).³⁶ After acid treatment, the lanthanides were removed, leaving a strained Pt surface with shortened Pt-Pt bond lengths due to combined ligand and strain effects, enhancing both activity and stability. Their findings showed a volcano-shaped relationship between ORR activity and lattice parameters, indicating that optimal strain can significantly improve catalytic performance, providing a theoretical basis for further catalyst design through strain modulation.

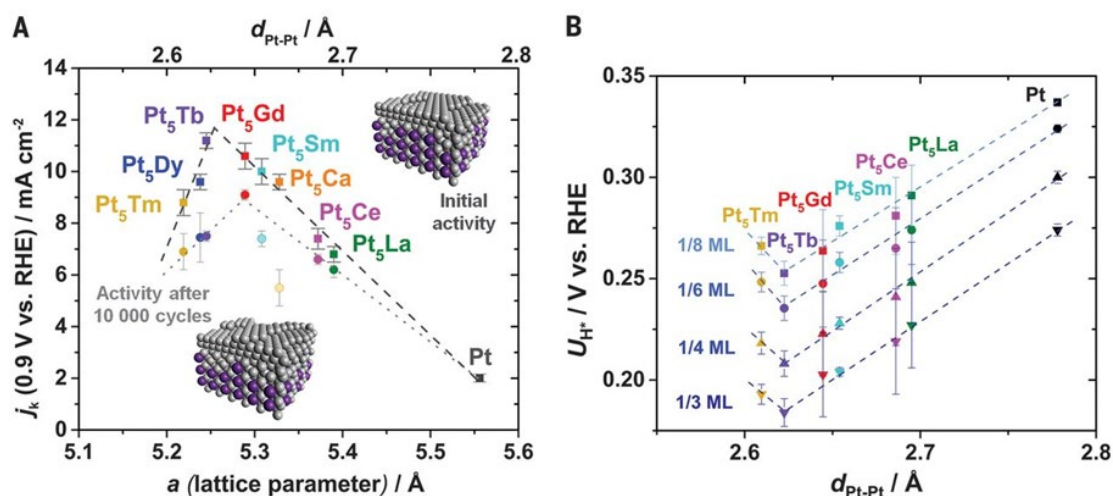


Figure 1-11. Volcano-shape relationships between ORR activity, U_{H^+} with $d_{\text{Pt-Pt}}$ for different alloys.³⁶

The strain effect is commonly accompanied by ligand and synergistic effects, all of which influence the d-band center. Compressive strain, which reduces the lattice spacing, downshifts the d-band center, weakening the interaction between Pt active sites and adsorbed species, thus facilitating ORR by improving the desorption of intermediates (Figure 1-12).³² On the other hand, tensile strain expands the lattice, upshifting the d-band center, which can strengthen adsorption but may hinder desorption, often reducing catalytic efficiency.³⁷ However, the effect of tensile strain on ORR remains debated, with some theoretical studies suggesting that it could also enhance performance under certain conditions.³⁸

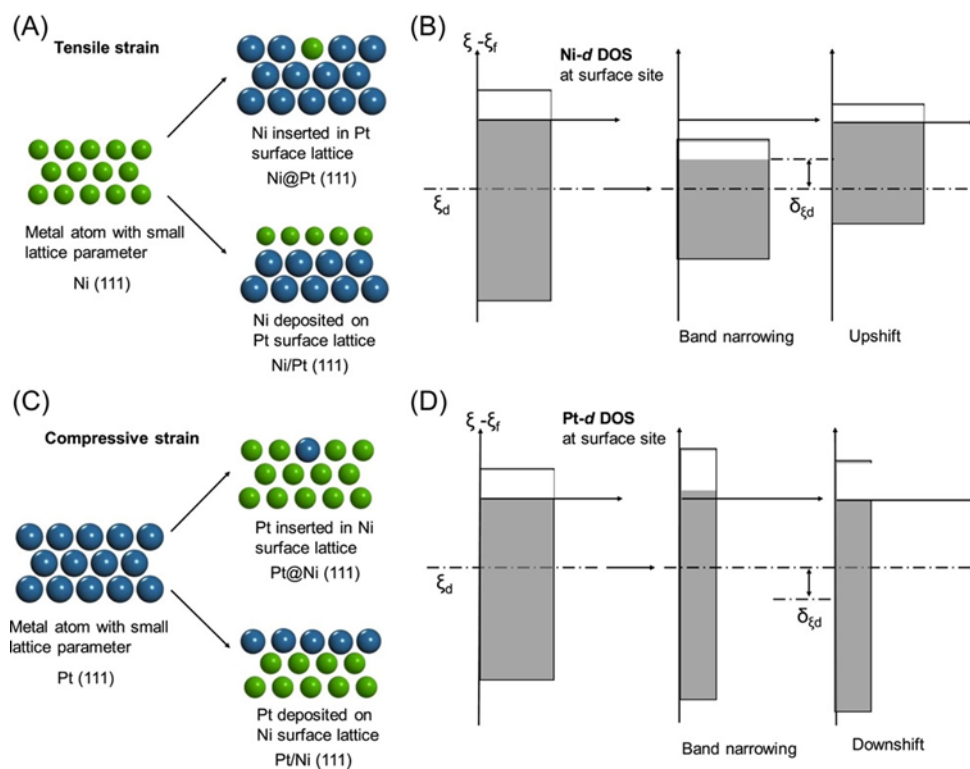


Figure 1-12. Schematic diagram of the change in d-band structure due to lattice strain when the lattice is stretched or compressed.³⁹

The ligand effect involves changes in the electronic properties of a catalyst due to interactions between atoms with varying electronegativities, commonly observed in alloyed or multi-metal systems.⁴⁰ This effect arises when atoms with dissimilar d-band centers transfer electronic charge, altering the electronic environment of the catalyst surface.⁴¹ Incorporating transition metals like Ni, Fe, or Co into Pt catalysts modifies the d-band center, enhancing the efficiency of oxygen intermediate interactions during the ORR.

The ligand effect can significantly enhance catalytic activity, as seen in the example of Pt₃Ni(111), which has been shown to be much more active in ORR than pure Pt due to its modified electronic structure and surface atom arrangement (Figure 1-13).⁴² By adjusting the electronic environment, the interaction between the catalyst's active sites and reactants is optimized, allowing for more efficient ORR.

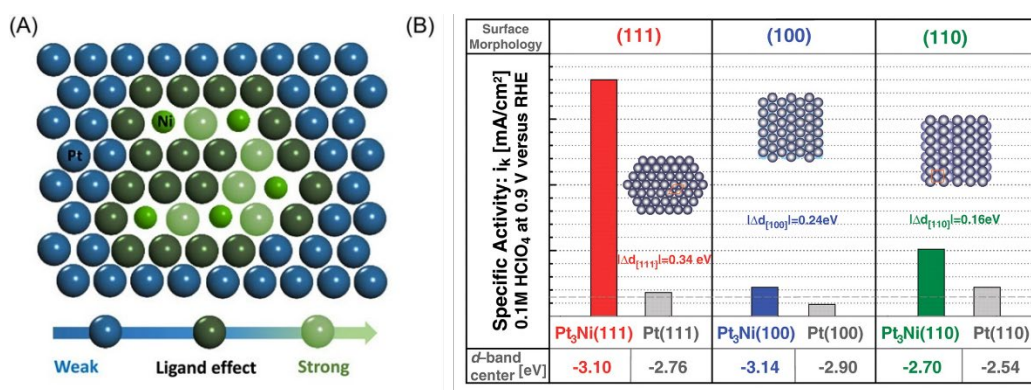


Figure 1-13. (a) Diagram illustrating the electronic interaction between Pt and Ni atoms in a Pt₃Ni alloy. (b) Illustration showing how lattice strain alters the d-band structure in Pt₃Ni catalyst.⁴²

The ensemble effect in Pt-based catalysts refers to how the spatial arrangement of atoms, particularly in multi-metal systems, influences catalytic performance by creating distinct reaction environments on the surface. This effect becomes especially important when Pt atoms form atomic groupings (ensembles) with other metals or non-metals, improving interactions with reactants like oxygen during the ORR. By optimizing the arrangement of atoms, the ensemble effect enhances adsorption, bond cleavage, and desorption of oxygen-containing species, improving overall catalyst efficiency and reducing the amount of Pt required. Not only like strain and ligand effects, which alter the electronic properties, affecting surface interactions based on the Langmuir-Hinshelwood (L-H) principle, particularly in nanomaterials with rich interfaces such as Pt-O or Pt-OH.^{43, 44}

The ensemble effect also contributes to improved antitoxicity in electrocatalysis. For instance, introducing more oxygenophilic elements like Ru, Mo, or Sn into Pt alloys has been shown to enhance resistance to poisoning, a common issue for ORR catalysts (Figure 1-14).⁴⁵ Additionally, the use of oxide supports, such as SnO_x, can further enhance the ensemble effect. For instance, in SnO_x/Pt-Cu-Ni catalysts, dual active sites at the oxide and Pt interfaces allow ORR to proceed more efficiently, reducing energy barriers and increasing activity by up to 40%, as demonstrated through DFT calculations (Figure 1-15).⁴⁶ These findings highlight the importance of optimizing atomic ensembles to improve both ORR activity and durability.

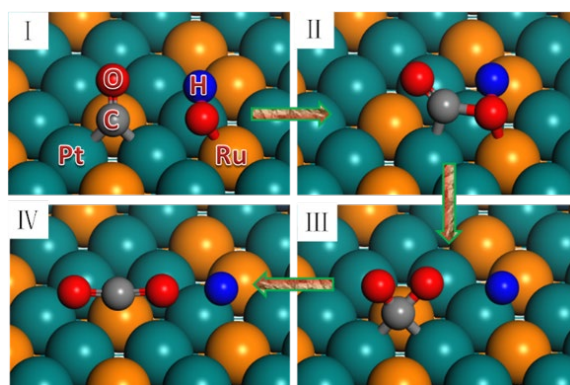


Figure 1-14. (a) Schematic diagram of resistance to CO poisoning in Pt-Ru alloys based on the L-H pathway.⁴⁵

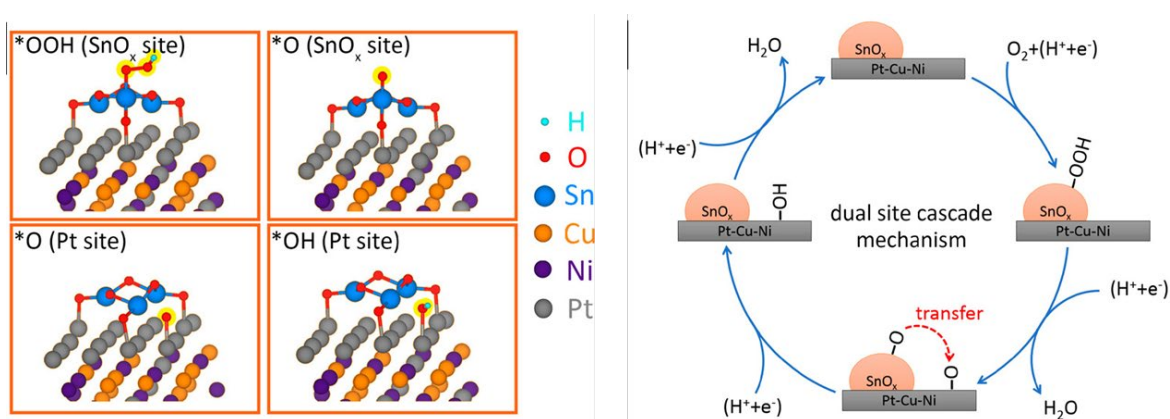


Figure 1-15. DFT models depicting the adsorption of O, OH, and OOH on $\text{SnO}_x/\text{Pt-Cu-Ni}$, alongside a schematic representation of the dual-site cascade mechanism occurring on $\text{SnO}_x/\text{Pt-Cu-Ni}$.⁴⁶

1.3.3 Advances in Pt-based catalyst

Recent advances in Pt-based catalyst research have emphasized the development of PtM alloys (intermetallic compounds), core-shell structures, and morphology control strategies to enhance ORR performance. PtM alloys, where Pt is alloyed with transition metals like Ni, Co, or Fe, have shown great promise in tuning the electronic structure and improving catalytic activity due to their optimized d-band center and stability from intermetallic formation.⁴⁷ Core-shell structures, with a Pt-rich shell and a less expensive metal core, have effectively reduced Pt loading while maintaining high catalytic efficiency.⁴⁸ Additionally, morphology control,

including tuning the shape and size of nanocatalysts, has been pivotal in maximizing the surface area, exposing more active sites, and enhancing the interaction with reactants.⁴⁹ These strategies collectively push Pt-based catalysts toward higher activity, durability, and cost-effectiveness for fuel cell applications.

Pt metal alloys, particularly intermetallic compounds, are structural materials formed by alloying Pt with transition metals (M) such as Ni, Co, or Fe. These intermetallic compounds exhibit highly ordered atomic arrangements, which enhance their stability and catalytic activity in fuel cell applications (Figure 1-16).⁵⁰ The A1 phase, a disordered structure, is commonly found during the early stages of alloying in PtM alloys. Although it shares a face-centered cubic (FCC) structure (space group $Fm\bar{3}m$), the atomic arrangement of Pt and transition metals is random. The major drawback of the A1 phase is its susceptibility to metal dissolution and phase separation during electrochemical reactions, particularly in high-temperature or acidic environments, which compromises catalyst stability.

In contrast, the L1₀ and L1₂ phases, which are ordered intermetallic compounds, significantly improve the stability and durability of catalysts through specific atomic arrangements.⁵¹ The L1₀ phase is a highly ordered face-centered tetragonal (fct) structure (space group $P4/mmm$) typically formed in Pt alloys with transition metals like Co and Ni. Its alternating layers of platinum and transition metal atoms along the crystal plane enhance corrosion resistance and electrochemical stability.

Similarly, the L1₂ phase is an ordered FCC structure (space group $Pm\bar{3}m$) commonly found in ternary or multi-component Pt alloys with metals.⁵² In this structure, each Pt atom is surrounded by 12 transition metal atoms, forming a three-dimensional arrangement. L1₂-Pt₃Co alloys exemplify this structure and exhibit excellent electrochemical activity and stability.⁵³

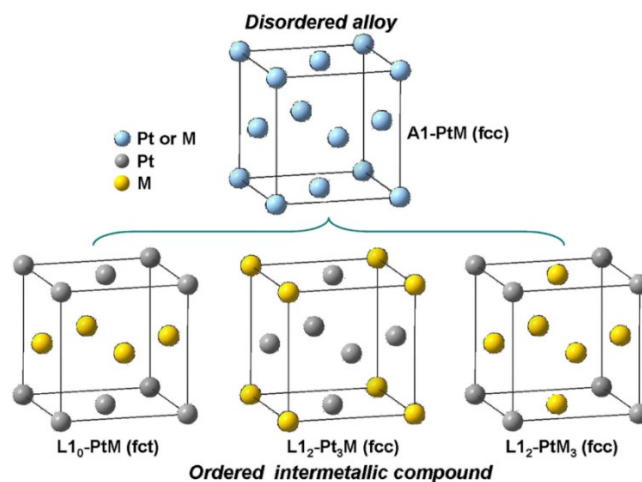


Figure 1-16. Comparison of the crystal structures of PtM alloys.⁵⁰

The synthesis of Pt intermetallic compounds typically requires high-temperature annealing, which facilitates the desired atomic ordering. As shown in Figure 1-17, understanding the phase transition temperature (T_{PT}) and chemical composition from binary alloy phase diagrams is essential for forming various PtM intermetallic compounds.⁵⁴ However, the high annealing temperatures ($>600^{\circ}\text{C}$) needed for ordering often result in particle agglomeration and uneven sizes, negatively impacting catalytic performance.

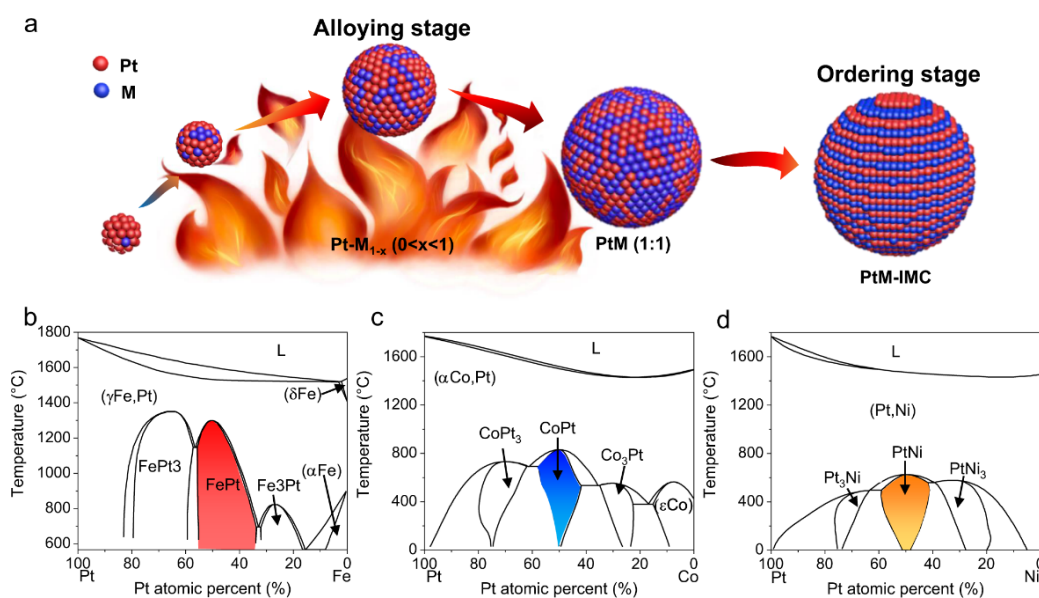


Figure 1-17. (a) Diagram illustrating the synthesis process of ordered Pt–M (M = Fe, Co, and Ni) intermetallic compounds. (b–d). Colored regions indicate the formation of $L1_0$ alloys in Pt–Fe, Pt–Co, and Pt–Ni.⁵⁴

To address these challenges, researchers have developed strategies such as carefully controlling the Pt loading (≤ 20 wt%) to minimize agglomeration.⁵⁵ Another approach involves enhancing the strong metal-support interaction (SMSI) to prevent metal ion aggregation while simultaneously optimizing catalytic activity.⁵⁶ Liang et al. introduced a novel concept by incorporating low-melting-point metals ($M' = \text{Sn, Ga, In}$) into Pt alloys, which lowers the activation energy (E_a) and enables atomic ordering at reduced temperatures ($\leq 450^\circ\text{C}$) (Figure 1-18).⁵⁷ These methods help avoid agglomeration and improve synthesis efficiency, resulting in more stable and active catalysts. Recent studies have demonstrated the effectiveness of core-shell structures, where a thin Pt layer is formed over an intermetallic core, reducing Pt usage while maintaining high catalytic activity. For example, the $\text{Pt}_1\text{Co}_3@\text{Pt}$ core-shell nanostructure catalysts have shown excellent ORR performance than Pt_1Co_3 catalyst, with significantly enhanced durability.⁵⁸

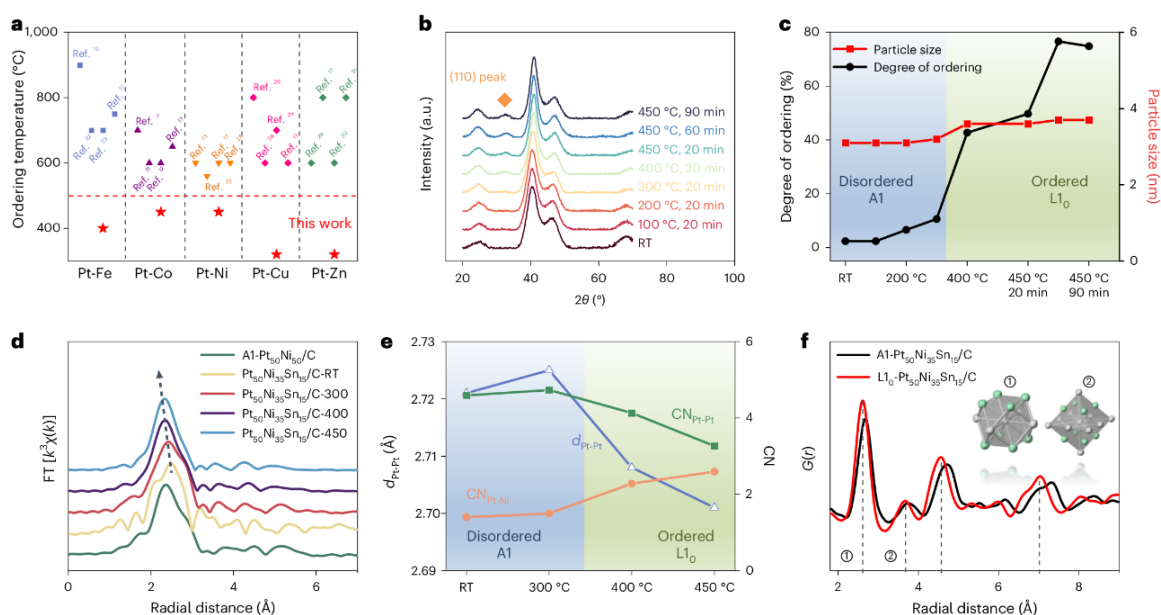


Figure 1-18. XRD and XAS spectrum of $\text{Pt}_{50}\text{Ni}_{35}\text{Sn}_{15}/\text{C}$ NCs catalyst during the phase transition process.⁵⁷

Design of Pt-based core-shell catalysts is considered as one of the most promising strategies to control the cost by effectively reducing the Pt content. These catalysts feature a core made of non-Pt or low-Pt metals, surrounded by a thin shell of Pt.⁵⁹ This structure not only reduces Pt usage but also improves the utilization of surface Pt atoms, resulting in higher catalytic

efficiency and stability. The Pt shell protects the core metal from dissolution in electrochemical environments, significantly enhancing the overall durability of the catalyst. Additionally, the strain effect and ligand effect generated by the interaction between the non-Pt core and Pt shell further improve catalytic performance by optimizing the surface Pt cativity.⁶⁰

The choice of core material plays a critical role in the ORR performance of core-shell catalysts. For instance, Adzic et al. studied Pt monolayers (Pt_{ML}) deposited on different substrates, such as Au, Pd, Rh, Ru, and Ir. Among these, only $\text{Pt}_{\text{ML}}/\text{Pd}$ (111) exhibited superior ORR activity compared to Pt (111), due to its electronic structure being closer to that of Pt (111) (Figure 1-19). This highlights the importance of selecting appropriate core materials to modulate the electronic properties of the Pt shell, enhancing ORR activity.⁶¹

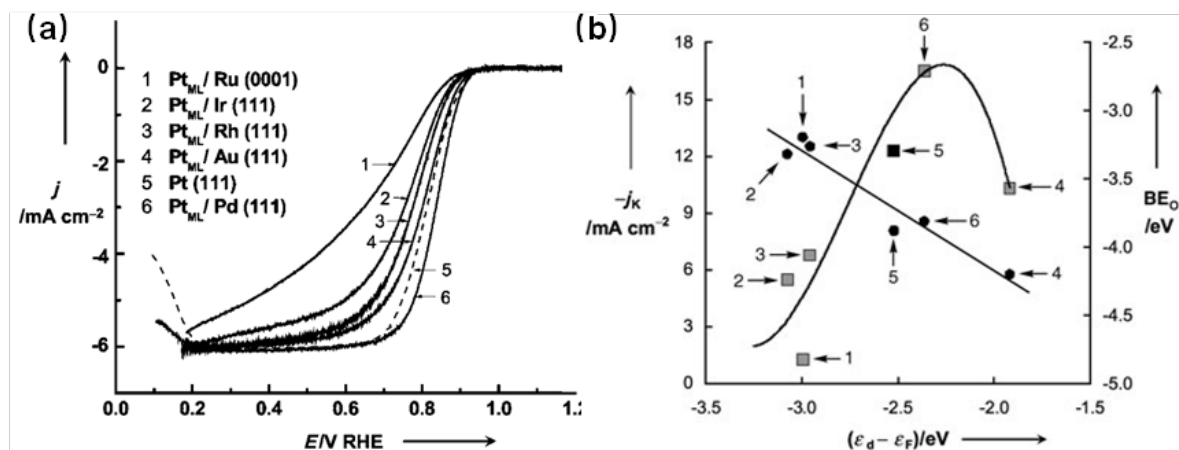


Figure 1-19. (a) Oxygen reduction catalytic polarization curves of the six catalysts; (b) Graphs of the relationship between ORR activity, oxygen binding energy, and d-band center position.⁶¹

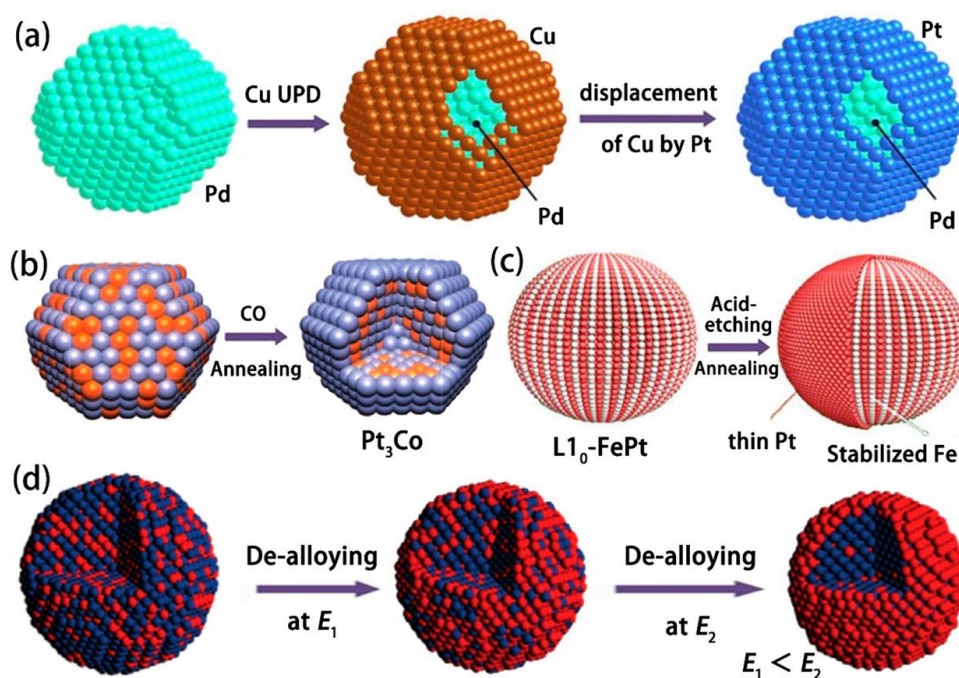


Figure 1-20. Schematic representation of the synthesis approaches for Pt-based core-shell catalysts.⁶⁴

Several synthesis methods have been developed for Pt-based core-shell nanocrystals (Figure 1-20), including underpotential deposition (UPD), which replaces a sacrificial Cu layer with Pt,⁴⁸ and de-alloying/chemical leaching, where non-Pt metals are selectively removed from Pt alloy surfaces to create a rough Pt-rich shell.⁶² Other methods include seed-mediated overgrowth, where non-Pt metal seeds are used for Pt epitaxial growth, and heat treatment, which induces Pt segregation in Pt alloy nanocrystals to form core-shell structures.⁶³ These methods offer various approaches to optimizing the composition and shell thickness, which are key factors in maximizing ORR performance and catalyst stability.

Some advancements in Pt catalyst design have focused on the morphological and structural modulation of catalysts to enhance their performance for fuel cells (Figure 1-21). Moving beyond traditional zero-dimensional Pt-based nanoparticles, researchers have explored anisotropic nanostructures such as nanoplates,⁶⁵ nanoflowers, nanowires,⁶⁶ nanoframes and so on.⁶⁷ These self-supported structures exhibit enhanced catalytic performance due to their high surface area and the presence of highly reactive features like edges, corners, and stepped

surfaces. These unique geometries not only increase the number of accessible active sites but also improve the overall catalytic efficiency for ORR.

Pt-based nanowire catalysts are a major advancement in PEMFC due to their one-dimensional structure and high aspect ratio, which provide a larger surface area and more exposed active sites than traditional Pt nanoparticles.⁶⁸ This structure promotes efficient electron transport and enhances stability by minimizing aggregation and dissolution during operation.⁶⁹ Jagged Pt nanowires, formed through a surfactant-induced method followed by Ni leaching, exhibit significantly increased electrochemically active surface areas (up to 120 m²/g_{Pt}) due to the formation of coordination-unsaturated Pt sites with high lattice strain (Figure 1-22). These characteristics significantly enhance ORR performance, with simulations suggesting up to a 212-fold improvement over traditional Pt catalysts, highlighting their strong potential for use in fuel cell applications.⁷⁰

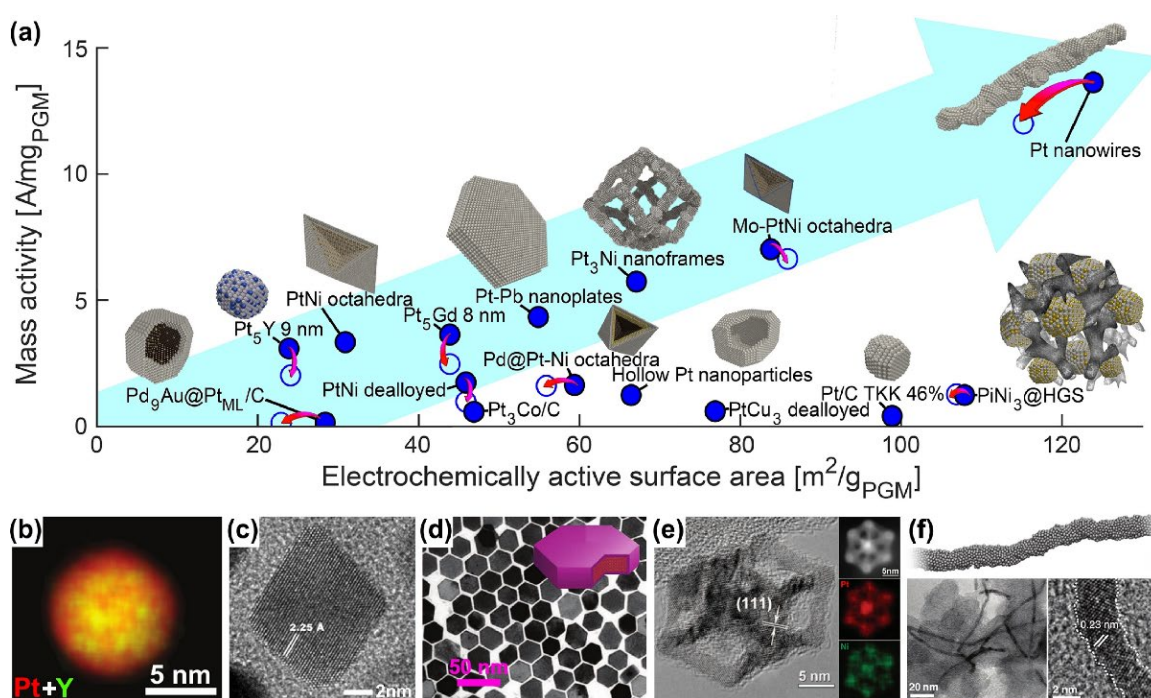


Figure 1-21. Catalysts with different morphologies and their mass activity.⁷¹

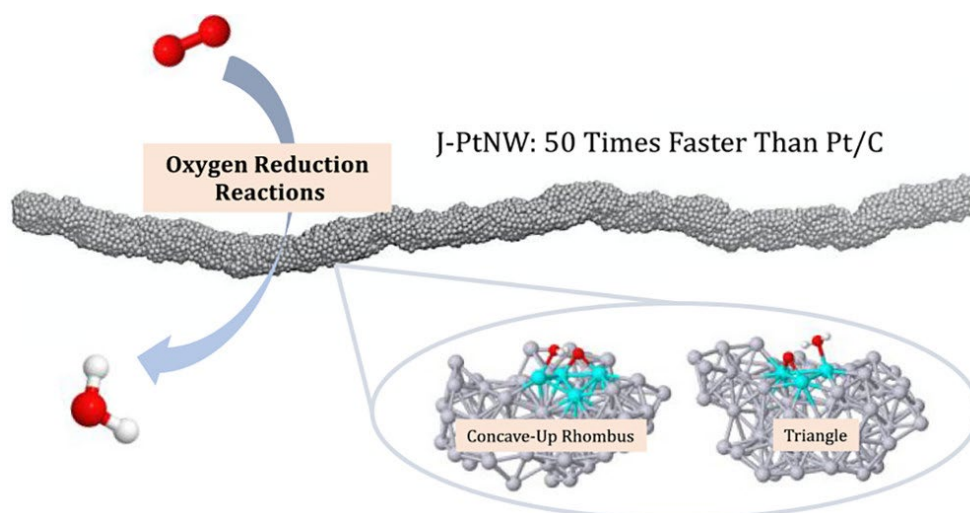


Figure 1-22. Illustration explaining the significantly enhanced ORR performance of jagged Pt nanowires.⁷²

1.4 Water electrolysis Introduction

Water electrolysis is a vital process that uses electrical energy to split water into hydrogen and oxygen, providing a clean and sustainable energy source.⁷³ The main types of water electrolysis are alkaline water electrolysis (AWE) and proton exchange membrane (PEM) electrolysis, each with unique characteristics, advantages, and challenges (Table 1-2).⁷⁴

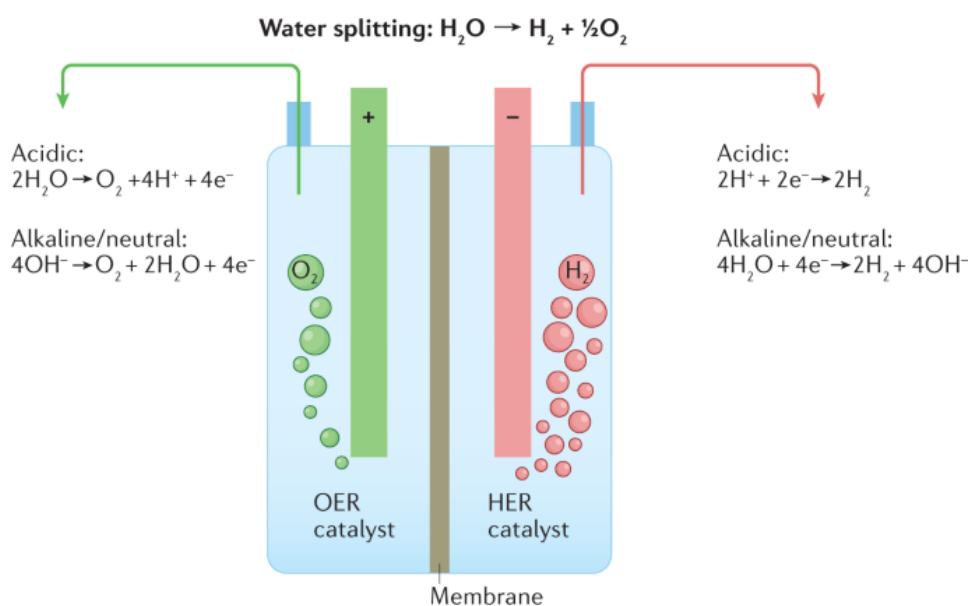


Figure 1-23. Schematic diagram of water electrolysis.⁷³

1.4.1 Classification of water electrolysis

AWE is the most established method for industrial hydrogen production, utilizing an alkaline electrolyte like KOH or NaOH and non-precious metal electrodes, typically Ni.⁷⁵ Operating between 70°C and 90°C, AWE systems are valued for their simplicity, durability, and cost-effectiveness, making them ideal for large-scale applications. However, AWE's limitations include lower current density and the need for careful gas separation to maintain hydrogen purity, which can be less efficient compared to other methods.

Table 1-2. Development status and typical operating condition/components of AWE and PEM.

Feature	Alkaline Water Electrolysis (AWE)	Proton Exchange Membrane Electrolysis (PEM)
Membrane	ZrO ₂ stabilized with PPS mesh	PFSA membrane
Feed stock	30 wt% KOH	DI water
Operating Temperature	70° C - 90° C	50° C - 80° C
Catalysts	Non-precious metals (Ni)	Precious metals (Pt, Ir)
Charge carrier	OH ⁻	H ⁺
Cost	250 \$/kW	450 \$/kW
Hydrogen Purity	Lower, requires gas separation	High
Current Density	Lower	Higher
System Size	Larger	Compact
Startup Time	Slower	Higher
Applications	Large-scale industrial hydrogen production	Small-scale, decentralized production, renewable energy integration
Advantages	Cost-effective, reliable, mature technology	High hydrogen purity, fast response, compact design
Challenges	Lower hydrogen purity, larger size, slower startup	High cost due to precious metal catalysts

PEM electrolysis, a newer technology, offers advantages in efficiency and hydrogen purity, using a solid polymer membrane that allows protons to move from anode to cathode while

blocking electrons.⁷⁶ PEM operates at 50°C to 80°C and achieves higher current densities than AWE, making it suitable for compact systems and fast hydrogen production, particularly in applications like renewable energy integration and hydrogen refueling stations. Despite its benefits, PEM electrolysis faces high costs due to reliance on precious metal catalysts, such as Pt and Ir, which drive up the overall expense.⁷⁷

Both AWE and PEM electrolysis are essential to hydrogen production, each with unique strengths and challenges. Research efforts focused on improving materials, catalyst efficiency, and system integration are expected to enhance performance and reduce costs for both technologies, positioning water electrolysis as a cornerstone in the transition to a hydrogen-based energy economy.

1.4.2 Economic feasibility

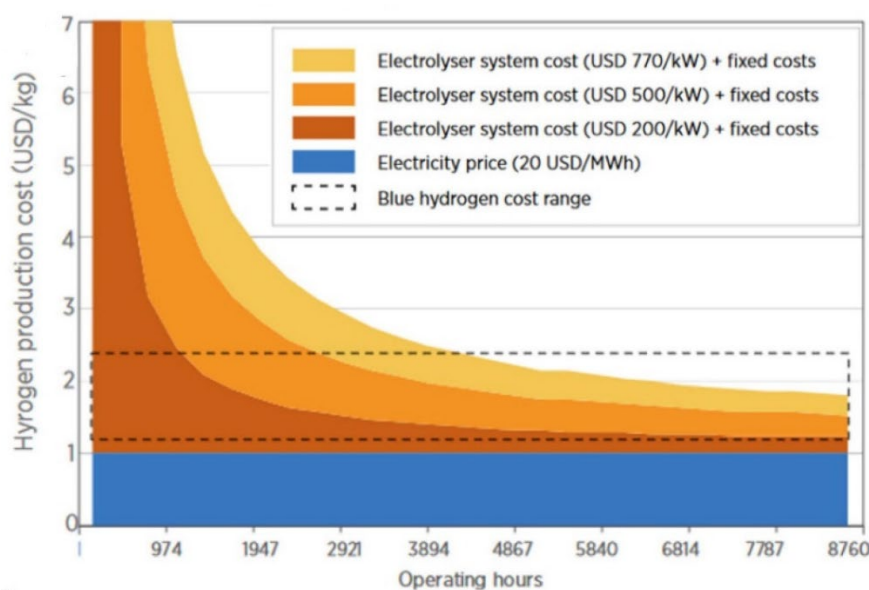


Figure 1-24. Cost analysis in (a) PEM and (b) AWE from International Renewable Energy Agency (IRENA) report.^{74, 80}

Achieving cost-effective hydrogen production through water electrolysis requires reducing both system and electricity costs (Figure 1-24). Currently, AWE is the most affordable option, with production costs around \$2/kgH₂, followed by PEM electrolysis at over \$3/kgH₂.⁷⁸ In PEM systems, nearly 45% of costs come from the stack, especially the costly PGM catalysts

and bipolar plates, while in AWE, non-precious materials help reduce costs. Reducing the balance of plant (BOP) expenses is critical in both systems, and innovations such as seawater electrolysis are being explored to lower water treatment costs.

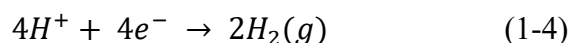
Long-term durability and performance improvements are essential for reducing hydrogen production costs over time. The U.S. DOE targets an 80,000-hour stack lifetime, though this is assessed through accelerated stress tests (ASTs).⁷⁹ Increasing current density to 2–3 A/cm² and minimizing PGM content in PEM electrolysis systems can significantly cut costs. Additionally, factors like heat generation, gas crossover, and cell optimization need to be addressed to enhance system efficiency, maximize hydrogen output, and lower the overall cost of green hydrogen production.

1.4.3 Principles of water electrolysis

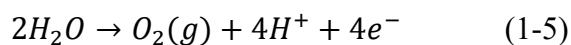
Water splitting is an endothermic reaction that requires an energy input of $\Delta G = 237.1$ kJ/mol under standard conditions (25°C, 1 atm).⁸¹ The reaction pathways of HER and OER differ depending on the pH of the electrolyte used (Figure 1-23).⁸²

In PEM electrolysis, a solid polymer membrane (proton exchange membrane) serves as the electrolyte, conducting protons (H⁺). The reactions occur as follows:

Cathode (Hydrogen Evolution Reaction):

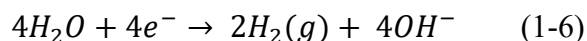


Anode (Oxygen Evolution Reaction):

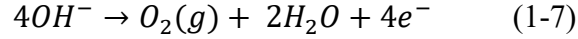


In alkaline water electrolysis, the electrolyte is typically an aqueous solution of KOH or NaOH, which conducts hydroxide ions (OH⁻). The reactions differ as follows:

Cathode (Hydrogen Evolution Reaction):



Anode (Oxygen Evolution Reaction):



Although the thermodynamic potential for water splitting is 1.23 V, a higher applied voltage is generally required due to several factors, including kinetic barriers, overpotentials for HER and OER, and system resistances such as electrolyte, contact, and membrane resistances.⁸³ The total voltage (E_{total}) needed to drive water electrolysis is influenced by the overpotential of both reactions and additional resistances from factors like reactant diffusion and gas evolution at the electrodes.^{84, 85}

$$E_{total} = 1.23 V + \eta_{HER} + \eta_{OER} + \eta_{other} \quad (1-8)$$

In ideal conditions, 3.55 kWh of electricity is required to produce one liter of hydrogen, but this value rises to 4.26 kWh when accounting for system losses.⁸⁶ Overpotentials, especially for OER, are significant because the reaction requires breaking strong O-H bonds and forming O-O bonds, which involves multiple electron transfers and high overpotentials, significantly affecting the efficiency of the entire system.⁸⁷ Reducing the activation energy for these reactions using efficient electrocatalysts is crucial. Improving OER electrocatalysts is vital for enhancing the overall efficiency of water splitting, as this step is the primary bottleneck in the process.

To increase reaction efficiency, strategies like optimizing ion diffusion through stirring or increasing the temperature of the electrolyte can be employed. Ultimately, developing highly active and stable OER catalysts is key to advancing large-scale hydrogen production for sustainable energy systems.

1.5 Overview of OER Catalysts

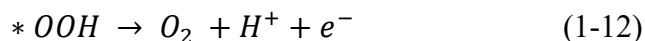
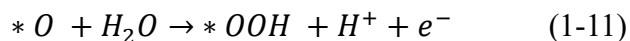
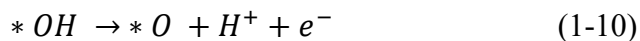
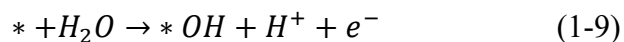
1.5.1 Proposed OER mechanism

OER is a key process in electrochemical water splitting, directly affecting oxygen production at the anode and overall energy consumption. Since OER involves multiple electron transfers

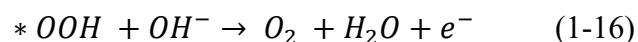
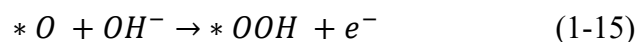
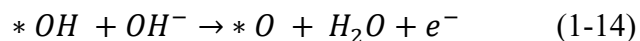
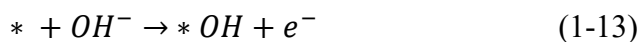
and bond formations, efficient and stable catalysts are essential for improving the reaction's efficiency.⁸⁷ Two primary mechanisms describe the OER process: the Adsorbate Evolution Mechanism (AEM) and the Lattice Oxygen Mechanism (LOM), each with distinct pathways for oxygen generation.⁸⁸

AEM, the more traditional and extensively studied pathway, involves a sequence of adsorption and desorption steps (Figure 1-25). In this mechanism, hydroxyl species (OH^-) first adsorb onto the catalyst surface, where they are oxidized to form oxygenated intermediates like O or O-OH . Following oxygen-oxygen bond formation, molecular oxygen (O_2) is generated and desorbs from the catalyst. This mechanism relies heavily on the catalyst surface's ability to facilitate intermediate adsorption and desorption efficiently.⁸⁸ Catalysts that support these interactions, such as noble metals like Ir and Ru, demonstrate high OER effectiveness through AEM.⁸⁹

In acidic media:⁹⁰



In alkaline or neutral media:⁹⁰



Where * represents active sites of the catalyst.

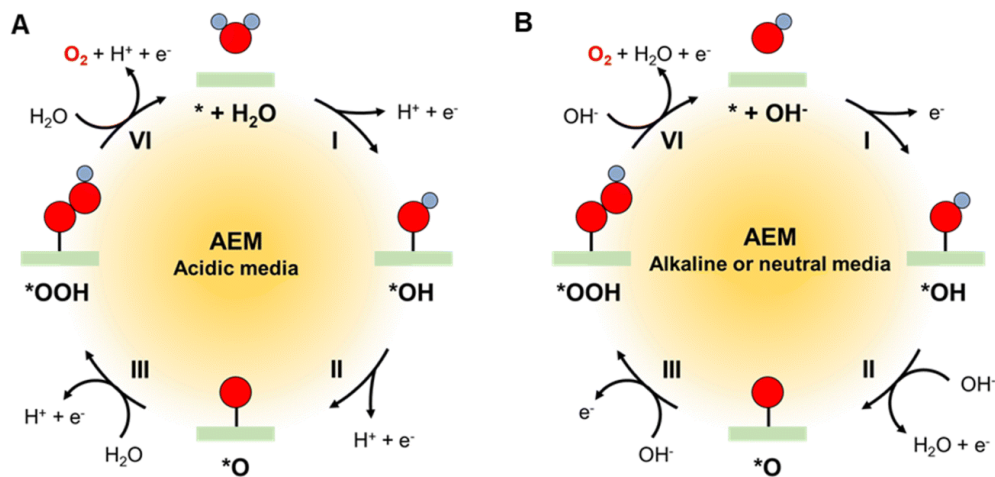
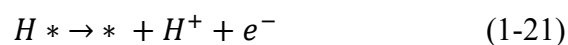
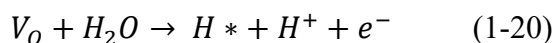
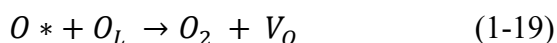
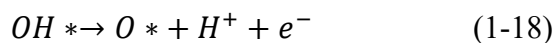
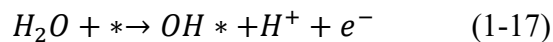


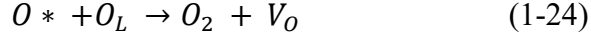
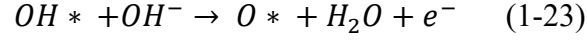
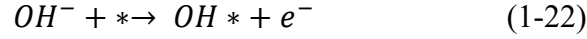
Figure 1-25. Diagram depicting the AEM pathways for OER in (A) acidic and (B) alkaline/neutral environments.⁹⁰

The LOM presents an alternative pathway for the OER by proposing that oxygen atoms from the catalyst lattice directly contribute to oxygen gas formation.⁹¹ This mechanism differs from the traditional AEM, which relies solely on oxygen from water or hydroxide ions. In LOM, the reaction involves the oxidation of lattice oxygen atoms, which form oxygenated intermediates that then couple to generate O_2 . Following gas release, the lattice oxygen vacancies are replenished by oxygen atoms from the electrolyte, restoring the lattice structure (Figure 1-26). The LOM has garnered attention as it accounts for the high OER activity observed in certain non-precious metal oxides like perovskite and spinel structures, which possess mobile lattice oxygen capable of participating directly in the reaction.

In acidic media:⁹²



In alkaline or neutral media:⁹³



where $*$, O_L , and V_O represent the metal active site, lattice oxygen, and surface oxygen vacancy, respectively.

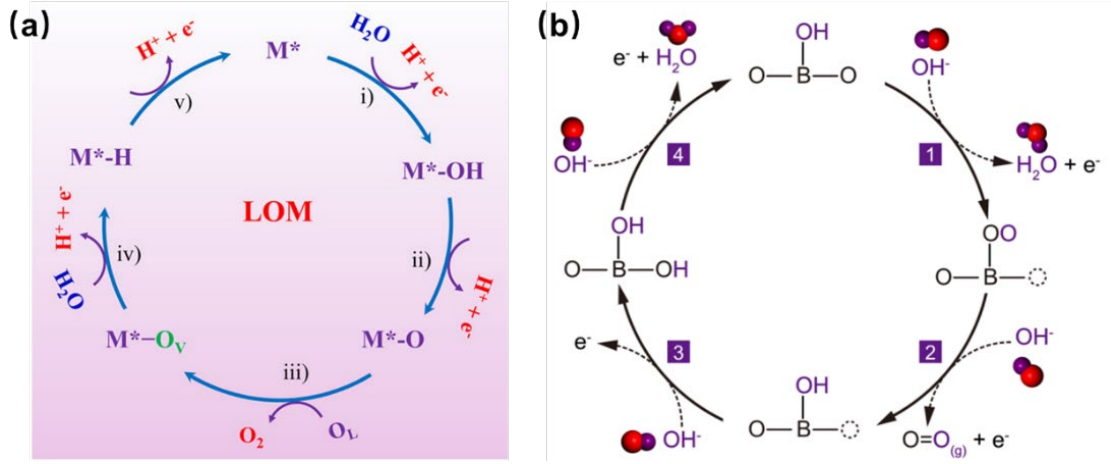


Figure 1-26. Diagram showing the LOM pathways for OER in (a) acidic and (b) alkaline conditions.^{92, 93}

The AEM and LOM offer distinct approaches to oxygen evolution in OER, impacting both catalyst design and performance. AEM primarily focuses on catalyst surface chemistry, where adsorption and desorption of intermediates are crucial, favoring noble metals like Ir and Ru oxides. LOM, however, engages the bulk structure, especially the lattice oxygen mobility, which is advantageous for high OER activity in perovskites and spinels without relying on precious metals.⁹⁴ While LOM can reduce the energy barriers for O-O bond formation, making it potentially more efficient, it may also lead to structural degradation over time due to oxygen vacancy formation.⁹⁵

In the AEM, the adsorption energies of intermediates such as $^*\text{OH}$, O , and OOH on the catalyst surface are key determinants of OER performance,⁹⁶ as represented by the volcano plot using energy differences like $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$ (Figure 1-27b).⁹⁷ Ideally, in a single-site AEM, the energy gap between $^*\text{O}$ and $^*\text{OH}$ should be around 1.6 eV to achieve optimal catalytic activity.⁹⁸ If the binding strength is too strong or too weak, it may either hinder the formation of $^*\text{OOH}$ or affect the deprotonation of $^*\text{OH}$, thus determining the potential determining step (PDS) of water oxidation.⁹⁹

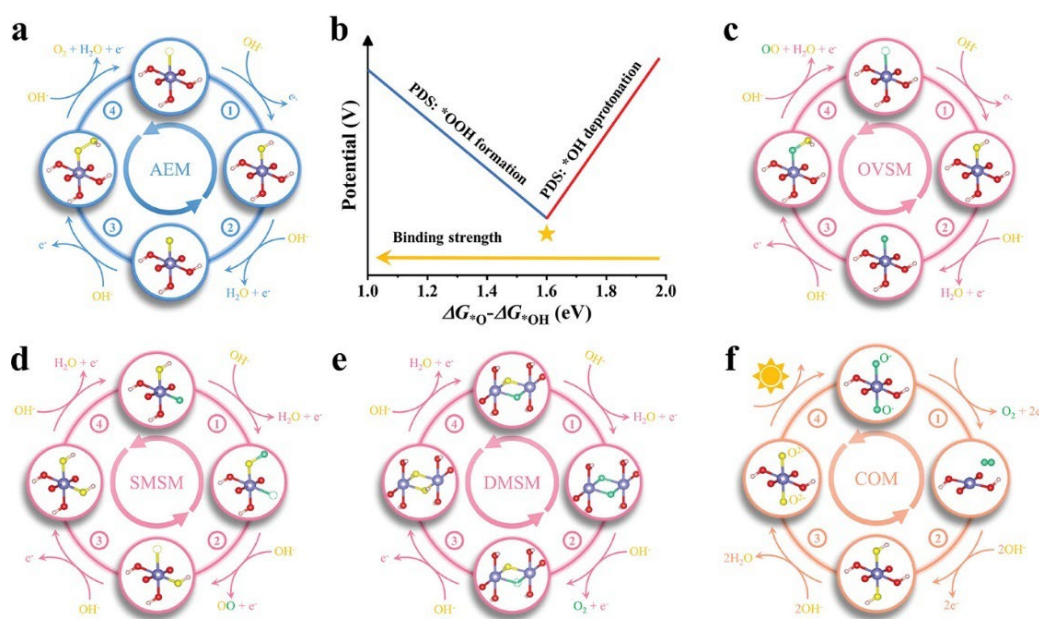


Figure 1-27. (a) Diagram of the mononuclear AEM pathway. (b) Depiction of the OER volcano plot with $\Delta G_{^*\text{O}} - \Delta G_{^*\text{OH}}$ used as a reference for the mononuclear AEM. (c–f) Schematics of (c) oxygen-vacancy-site mechanism (OVSM), (d) single-metal-site mechanism (SMSM), (e) dual-metal-site mechanism (DMSM), and (f) COM pathways. The inactive lattice oxygen, active lattice oxygen involved in OER, and oxygen from the electrolyte are shown in red, cyan, and yellow, respectively.⁹⁷

To overcome these limitations, researchers have explored different strategies to modify the reaction pathways and enhance catalytic performance. For instance, Liu et al. introduced Os into RuO_2 as a proton acceptor, facilitating the dissociation of water molecules through a dual-function mechanism.¹⁰⁰ Similarly, Rossmeisl et al. optimized the donor-acceptor functionality at bridge sites by incorporating Ni and cobalt Co into Ru-based catalysts, improving the

catalytic efficiency for OER.¹⁰¹ In addition, a binuclear mechanism has been proposed in which two water molecules in solution are oxidized in parallel at two adjacent active sites.¹⁰² Therefore, the translation as well as the prioritization of multiple mechanisms needs to be considered when studying the AEM pathway.

The LOM engages lattice oxygen as an active site. Mechanisms like the Oxygen Vacancy Site Mechanism (OVSM) involve lattice oxygen reacting with OH^- to form $^*\text{OOH}$, which then deprotonates to produce O_2 , sustaining a catalytic cycle (Figure 1-27c).¹⁰³ In contrast, Single Metal Site (SMSM) and Dual Metal Site (DMSM) pathways utilize under-coordinated metal sites or adjacent oxygen atoms to form $\text{M}-\text{OO}-\text{M}$ structures, bypassing rate-limiting steps found in AEM (Figure 1-27d).^{104, 105} Additionally, the recently proposed Coupled Electrochemical Oxidation Mechanism (COM) suggests oxygen atoms from the catalyst surface interact directly with intermediates during OER, forming O_2 through electrochemical coupling steps (Figure 1-27f).¹⁰⁶ This mechanism highlights the complexity and variability in OER pathways, underscoring the potential for enhanced efficiency through tailored catalyst designs.

1.5.2 Progress in acidic OER catalyst

In acidic water electrolysis, particularly PEM electrolysis, the development of efficient and durable catalysts is crucial due to the harsh operating conditions. Ir and Ru-based catalysts have emerged as the most effective materials for the OER at the anode, given their superior stability and activity in acidic environments (Figure 1-28).^{89, 95} However, the high cost and scarcity of these precious metals drive ongoing research efforts aimed at optimizing their usage, improving performance, and extending catalyst lifespan.

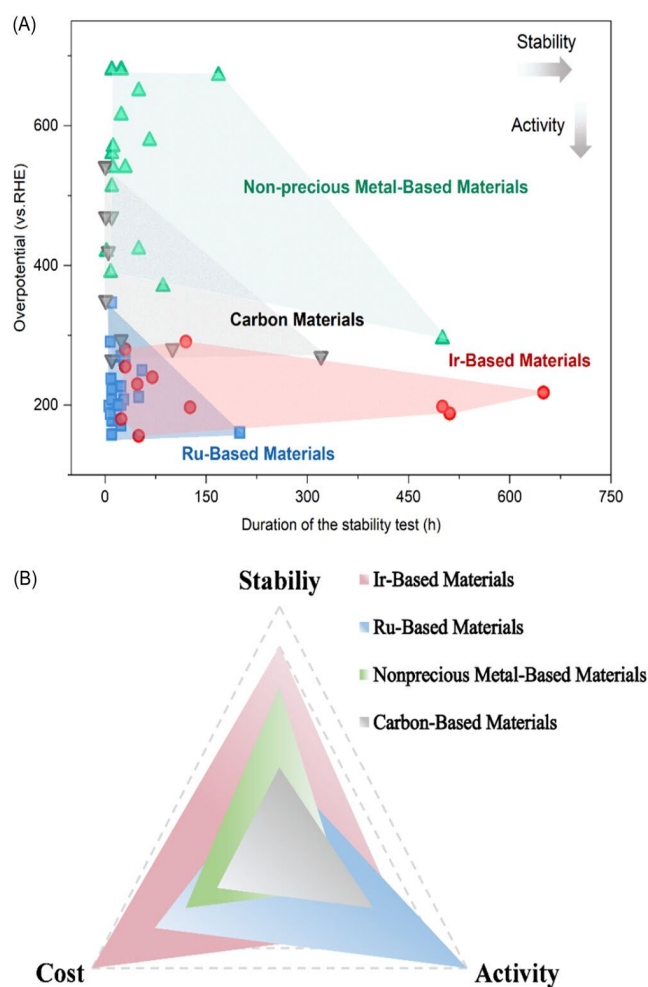


Figure 1-28. (A) Duration of stability tests and the corresponding overpotential of catalysts reported in recent years, and (B) comparison of stability, activity, and cost among Ir-, Ru-, non-precious metal-, and carbon-based materials.⁹⁵

Ir-based catalysts are widely recognized for their excellent stability and resistance to corrosion in acidic media. Researchers have focused on enhancing the performance of monometallic Ir-based catalysts by modifying their morphology to increase surface active sites and improve structural stability. Approaches such as designing one-dimensional nanowires, two-dimensional nanosheets, and three-dimensional nanoclusters have been effective in increasing the electrochemically active surface area (ECSA) of Ir catalysts (Figure 1-29a and b).^{107, 108} In addition, commercially available rutile IrO_2 is currently the most widely used OER catalyst, but it is less active in acidic media. It has been shown that amorphous IrO_x provides more reactive active sites (μ_1 and μ_1), and surface and subsurface deprotonation reduces the

OER potential barrier, thereby increasing the catalytic activity, but also exacerbates the dissolution of Ir and exhibits poor stability (Figure 1-29c).^{109, 110}

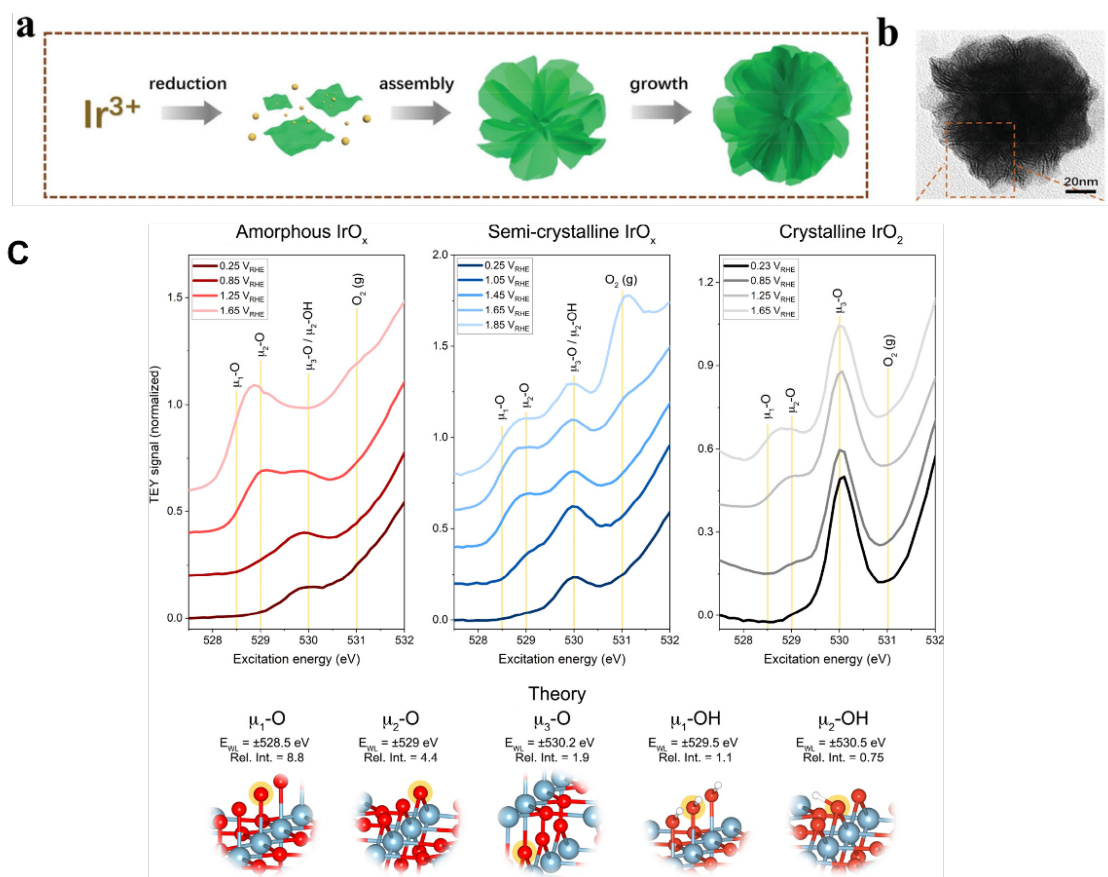


Figure 1-29. (a, b) Diagram showing the growth process of the 3D Ir superstructure and corresponding HAADF-STEM image. (c) *In situ* O K-edge spectra of IrO_x with different crystallinity.^{107, 110}

Some research has aimed to reduce Ir loading while maintaining or even improving catalytic activity. A promising strategy involves creating Ir-based alloys, like IrNi and IrCo, which not only decrease Ir content but also adjust Ir's electronic structure for improved efficiency. This tuning of the electronic structure optimizes the adsorption and desorption energies of oxygen intermediates ($\ast\text{O}$ and $\ast\text{OOH}$) on the catalyst surface, leading to improved OER performance. Additionally, the use of conductive oxides like SnO_2 and TiO_2 as support materials has proven effective in dispersing IrO_x more uniformly, enhancing both activity and durability in electrochemical applications.^{112, 113} A method for oxidizing Ir catalysts to the +6 oxidation state using MnO_2 as an oxidizing agent has been reported by Li et al.¹¹¹ The high activity and

stability of $\text{Ir}^{\text{VI}}\text{-ado}$ demonstrates its promise as an anode material for PEM electrolysis (Figure 1-30).

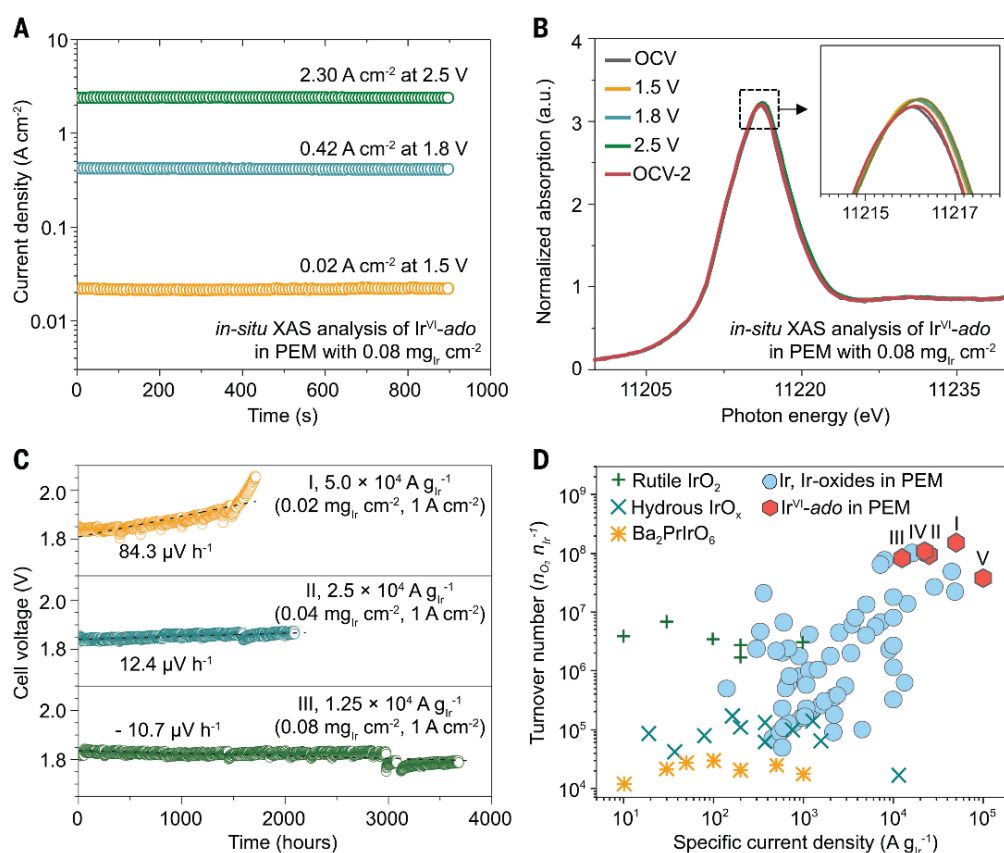


Figure 1-30. Stability of $\text{Ir}^{\text{VI}}\text{-ado}$ analyzed by *in situ* XAS and long-term electrolysis.¹¹¹

Ru-based catalysts are also highly active for OER in acidic conditions but face challenges related to stability. Ru is prone to oxidation and dissolution under OER conditions, which limits its practical application. To address this, researchers are exploring Ru alloys (e.g., RuCu, RuNi) and RuO_2 -based mixed oxides to improve durability (Figure 1-30 a-c).¹¹⁴⁻¹¹⁶ Deka et al. demonstrated that the entire oxygen lattice, both at the surface and bulk, is influenced in RuO_x , as shown by O K-edge spectra.¹¹⁷ The activation of the oxygen lattice by amorphous RuO_x is much more pronounced compared to polycrystalline RuO_2 (Figure 1-30d). This agrees with the conclusions obtained from IrO_x .

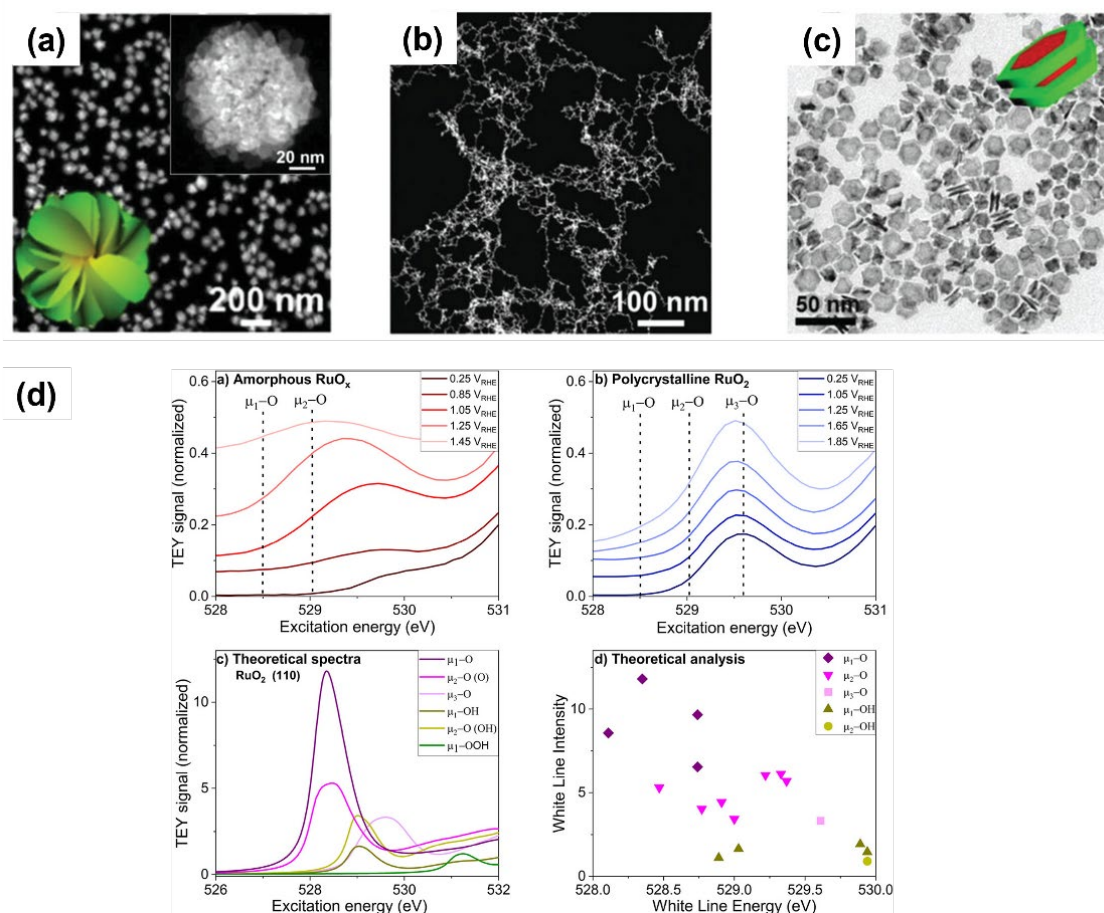


Figure 1-30. (a) HAADF-STEM images of Ru₃Ni₃ nanosheet assemblies.¹¹⁴ (b) STEM image of Ru-Pb wavy nanowires.¹¹⁵ (c) TEM image of Ru₂Ni₂ sandwiched nanoplates.¹¹⁶ (d) *Operando* O K-edge XAS of amorphous and polycrystalline RuO_x.¹¹⁷

In addition to alloying precious metals with non-precious metals and metal oxides to lower precious metal usage, another promising approach is the design and synthesis of complex oxides like perovskites. These materials provide a viable path to reduce dependence on costly metals while maintaining high performance. Perovskites, with the general formula ABO₃, have attracted significant attention due to their tunable structure, flexibility in composition, and ability to incorporate various transition metals into the lattice.¹¹⁸ In the context of acidic OER, Ir or Ru-based perovskites offer a highly adaptable framework for optimizing catalytic performance while reducing precious metal loading.

In perovskites, the A-site typically hosts larger cations like rare earth or alkaline earth metals

(e.g., Ba, La, Sr), while the B-site accommodates smaller transition metal cations, including Ir and Ru.¹¹⁹ The flexibility in substituting different elements at the A and B sites allows researchers to fine-tune the electronic structure, optimize oxygen vacancy formation, and enhance OER activity.¹²⁰ One of the key advantages of perovskite structures lies in their structural diversity. By adjusting synthesis parameters such as temperature and pressure, Ir-based perovskite catalysts with the same composition can adopt entirely different crystal structures, including cubic, hexagonal, and monoclinic forms.¹²¹ This flexibility in structure provides significant opportunities for tailoring perovskite materials for various catalytic applications. In the OER, surface reorganization often occurs due to the dissolution of B-site metals, and $[\text{IrO}_6]$ or $[\text{RuO}_6]$ octahedral units are typically considered the active sites in the reaction.¹²²

For example, Li et al. reported that after acid treatment, BaIrO_3 catalysts formed a 1 nm IrO_x surface active phase ($\text{IrO}_x/9\text{R-BaIrO}_3$), which exhibited a monoclinic structure with face-sharing $[\text{IrO}_6]$ trimers octahedra (Figure 1-31a).¹²³ This configuration demonstrated excellent electrochemical activity and stability. Similarly, Yang et al. investigated another perovskite structure, 6H-SrIrO_3 , where the presence of face-sharing $[\text{IrO}_6]$ octahedral dimers was identified as the main factor behind its high OER activity (Figure 1-31b). These dimers helped reduce the binding energy of Ir-O bonds, thereby facilitating the formation of the $^*\text{OOH}$ intermediate, which is crucial for efficient oxygen evolution.¹²⁴ The ability to manipulate the crystal structure and active site configuration in perovskites makes them promising candidates for advanced OER catalysts.

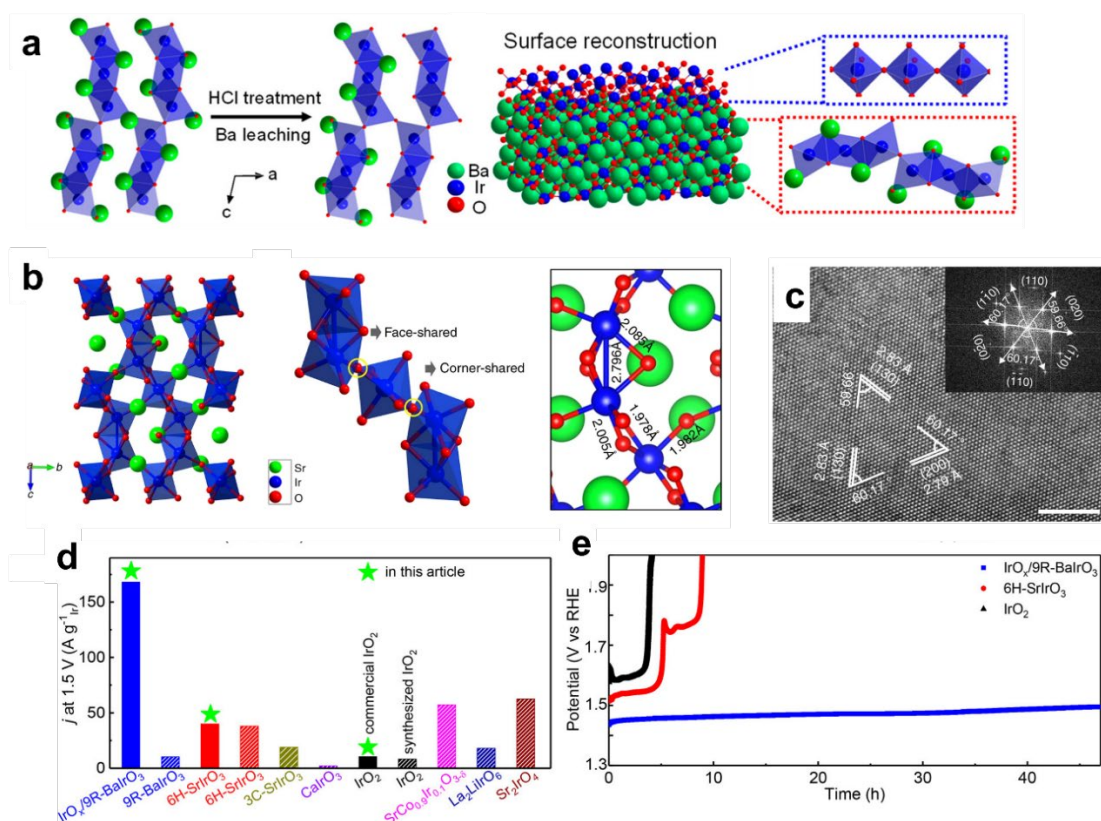


Figure 1-31. (a) Structure of $\text{IrO}_x/\text{9R-BaIrO}_3$ catalyst. (b) Crystal and electronic structure of 6H-SrIrO_3 . (c) HRTEM image of 6H-SrIrO_3 . (d) Comparison of Ir mass activity at 1.5 V for various recently reported Ir-based perovskite OER catalysts in acidic media. (e) Stability measurement results.^{123, 124}

1.5.3 Progress in alkaline OER catalyst

In the context of alkaline water electrolysis, transition metal (TM) oxides are mostly used among the promising OER catalysts due to their abundance, cost-effectiveness, and excellent catalytic properties.¹²⁵ TM such as Mn, Ni, Co, Fe, and others have been widely studied for their performance in alkaline conditions, with many exhibiting notable OER activity in their oxide states. Moreover, these elements have been incorporated into various catalyst structures, including perovskite and spinel, both of which are known to influence catalytic performance.¹²⁶ Understanding the key factors affecting the intrinsic OER activity of TM-based catalysts is crucial for optimizing their design and efficiency.

Several intrinsic factors have been identified as the primary influences on the OER activity

of transition metal oxides. Among them, the following factors are considered to be the most dominant.

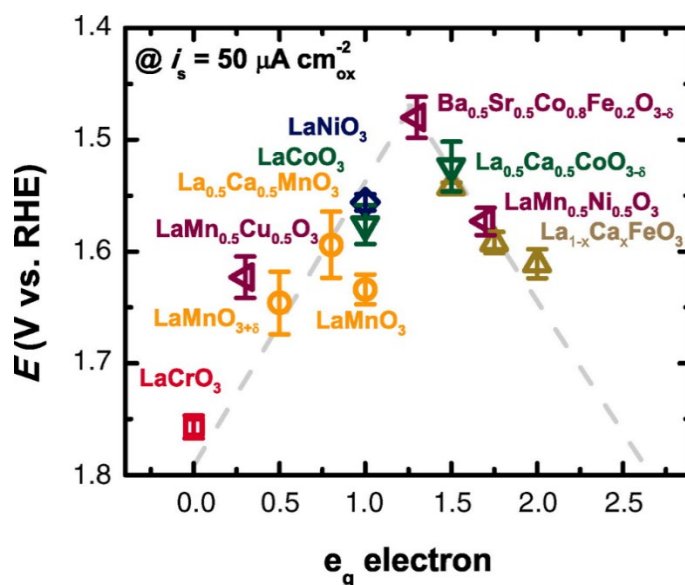


Figure 1-32. The correlation between OER catalytic activity and the e_g -symmetry electron occupancy of the transition metal at the B-site in the ABO_3 perovskite structure.¹²⁷

The occupancy of the e_g orbitals of transition metal ions in octahedral coordination plays a critical role in determining OER activity. Studies have shown that half-filled e_g orbitals are particularly favorable for OER because they optimize the interaction between the metal center and oxygen-containing intermediates.¹²⁸ For example, the BSCF catalyst shown in Figure 1-32, the surface Co atoms are in the intermediate spin state, and thus its intermediate configuration, $t_{2g}^5 e_g^{1.2}$ (+2.8 in the oxidation state), exhibits the highest OER activity.¹²⁷

The covalency of the transition metal-oxygen (TM-O) bond also significantly affects the binding strength of oxygen intermediates on the catalyst surface. A stronger covalent interaction between the metal and oxygen enhances the ability of the metal center to facilitate the adsorption and desorption of oxygen intermediates (*O, *OH, and *OOH), which are critical steps in the OER process.¹²⁹ Higher TM-O covalency typically correlates with higher OER activity because it improves the electron transfer between the metal and oxygen, enabling a more efficient reaction pathway (Figure 1-33).^{128, 130} Therefore, improved hybridization is the key to designing future water decomposition catalysts.

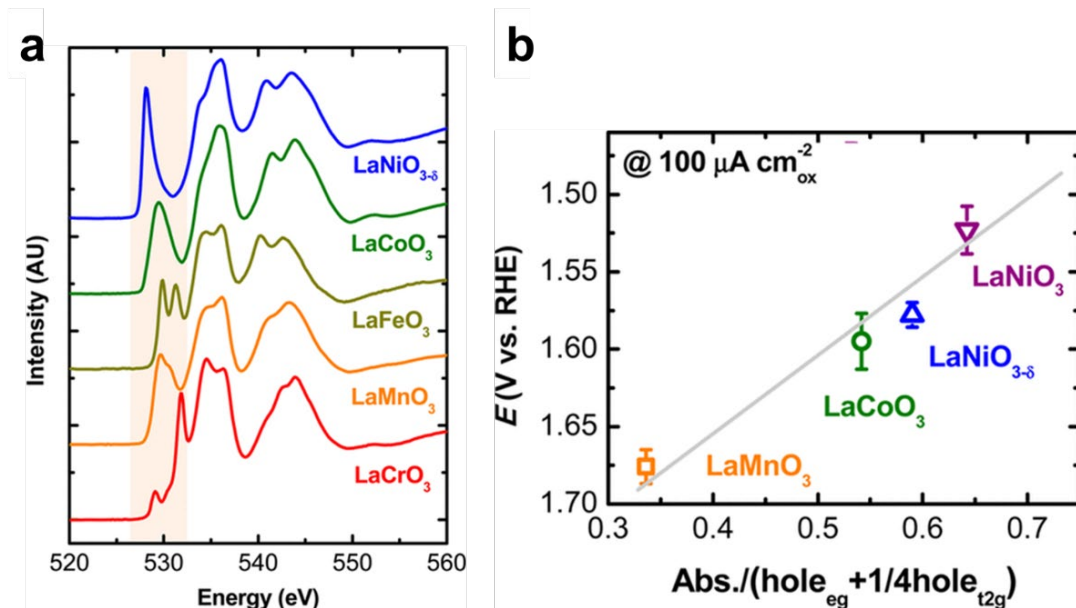


Figure 1-33. (a) O K-edge XAS spectra of LaBO_3 . (b) The effect of covalency on oxygen evolution activity. (Abs refers to the pre-edge area of the O K-edge XAS, hole_{eg} indicates the number of unoccupied e_g orbitals, and hole_{t2g} represents the number of unoccupied t_{2g} orbitals).

130

The d-band center theory provides a framework for understanding the electronic properties of transition metal catalysts and their OER activity.¹³³ The position of the d-band center relative to the Fermi level influences the binding energy of oxygen intermediates (Figure 1-34).¹³² A d-band center that is too high results in overly strong binding of oxygen species, which inhibits their desorption, while a d-band center that is too low results in weak binding, reducing activity.^{131, 134} Transition metal oxides with an optimized d-band center can achieve a balance that allows for effective adsorption and desorption of oxygen intermediates, leading to higher OER efficiency.

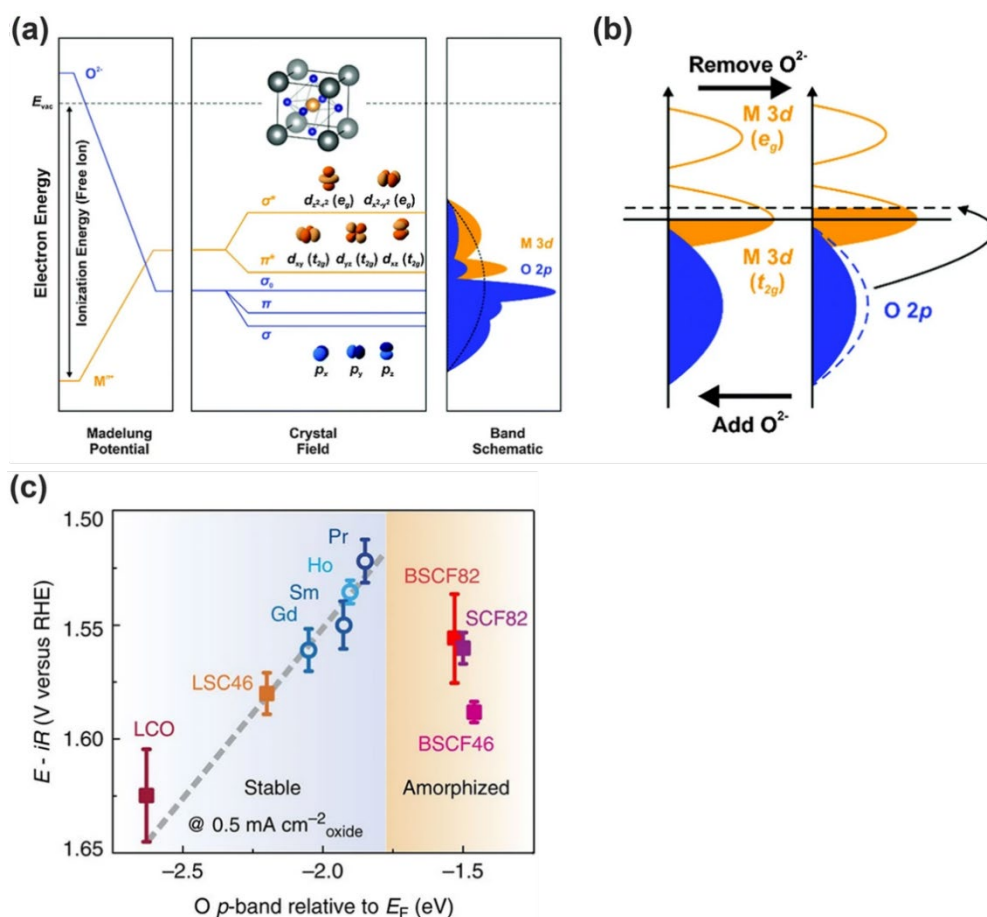


Figure 1-34. Bulk O 2p-band center relative to Fermi level (ϵ_{O-2p}) as a descriptor for OER.^{131,}

132

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) stands out as an efficient and stable catalyst for the oxygen evolution reaction in alkaline conditions, benefiting from its tunable perovskite structure, oxygen vacancies, and favorable electronic properties.¹³⁵ During the OER, the dissolution of Sr and Ba cations facilitates the formation of a surface-active Co(Fe)OOH layer. Shen et al. observed through TEM analysis that perovskite structures tend to first form Co/Fe spinel phases, which then transition into Co(Fe)OOH during OER (Figure 1-35).¹³⁶ This transformation is reversible, reflecting the dynamic nature of the catalyst structure under reaction conditions.

In an innovative approach by Guan et al., a mixed catalyst based on BSCF was developed to tackle ion leaching.¹³⁷ By integrating BaCl₂ and SrCl₂ into the BSCF structure, the normally harmful leaching of Ba²⁺ and Sr²⁺ ions during OER was used to an advantage. These leached ions enter the electrolyte early, stabilizing the catalyst surface while maintaining the integrity

of the perovskite structure. This leads to the formation of stable edge/face coplanar structures with enhanced OER activity.

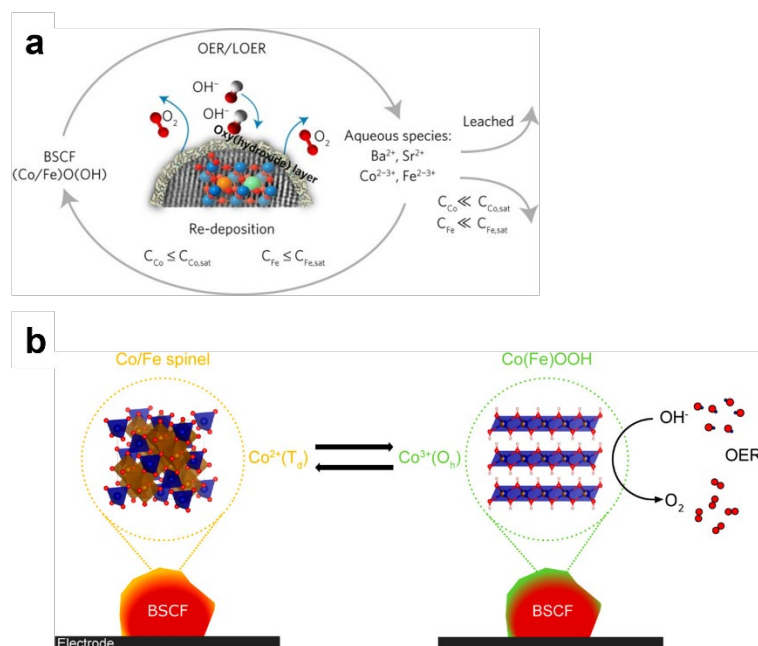


Figure 1-35. Proposed model illustrating the surface reconstruction process leading to the formation of Co/Fe oxyhydroxide in BSCF during the OER.^{81, 136}

1.6 X-ray Absorption Spectroscopy Introduction

X-ray Absorption Spectroscopy (XAS) is a highly flexible and effective method for studying the local atomic arrangement and electronic properties of different materials. It provides critical insights into oxidation states, bonding environments, and coordination numbers by measuring how X-rays are absorbed by specific elements within a sample. XAS is element-specific and non-destructive, making it suitable for a diverse scientific discipline such as materials, chemistry, catalysis, and biology.

1.6.1 Theoretical framework of XAS

The fundamental principle of XAS is based on the interaction between X-rays and matter, where X-rays are absorbed by an atom as their energy matches the binding energy of core electrons (Figure 1-36).^{138, 139} The absorption coefficient, denoted as $\mu(E)$, is measured as a

function of the X-ray energy E . The Beer-Lambert Law governs the relationship between the incident X-ray intensity I_0 and the transmitted intensity $I(E)$ through the sample:

$$I(E) = I_0 e^{-\mu(E)t} \quad (1-27)$$

where t represents the sample thickness, and $\mu(E)$ is the energy-dependent absorption coefficient. This absorption coefficient is related to the X-ray absorption cross-section $\sigma(E)$, which reflects the probability of an X-ray photon being absorbed by an atom:

$$\mu(E) \propto \sigma(E) \quad (1-28)$$

The XAS spectrum can be divided into two primary regions: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS).¹⁴⁰

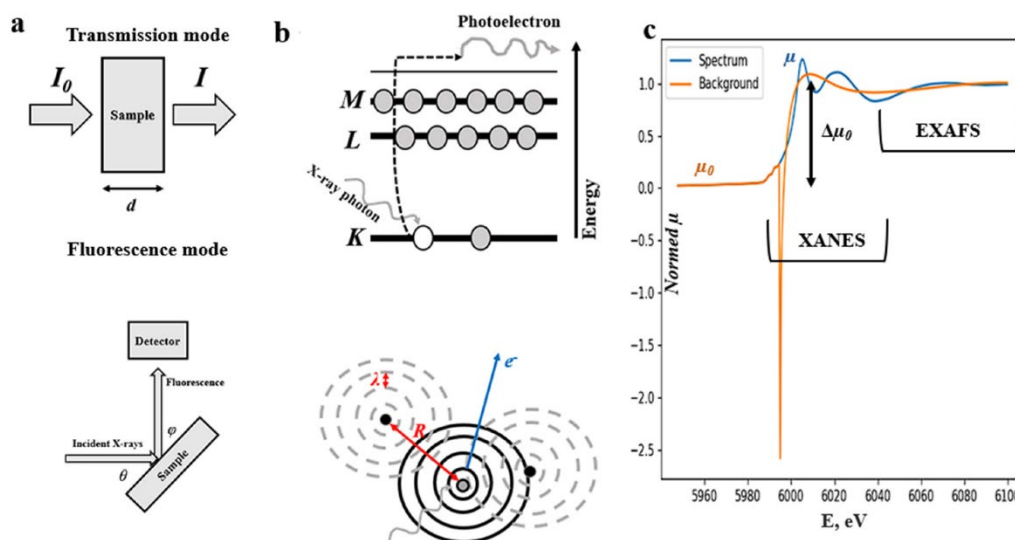


Figure 1-36. (a) Diagram showing transmission and fluorescence experimental mode; (b) graphical representation of the underlying physical principles of the XANES (top) and EXAFS (bottom) regions; and (c) a typical XAS spectrum.¹³⁹

XANES provides information about the oxidation state and electronic structure of the absorbing atom, revealing details about the local chemical environment. The absorption edge's energy position and the spectral features near the edge can be used to determine oxidation states. EXAFS contains information about the local atomic arrangement surrounding the absorbing atom. The oscillatory features observed beyond the absorption edge are caused by the

interference between the outgoing photoelectron wave and waves scattered by neighboring atoms. These oscillations are highly sensitive to the bond lengths, coordination numbers, and types of neighboring atoms.¹⁴¹

The EXAFS oscillations $\chi(k)$ are described as:

$$\chi(k) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \quad (1-29)$$

where $\mu(E)$ is the measured absorption coefficient, and $\mu_0(E)$ is the background absorption function. The wave number k of the photoelectron is given by:

$$k = \sqrt{\frac{2m}{\hbar} (E - E_0)} \quad (1-30)$$

with m being the electron mass, E_0 the edge energy, and $\hbar$ the reduced Planck constant.

The EXAFS equation is used to model the experimental data, providing quantitative information about the local structure of the material. The equation is expressed as:

$$\chi(k) = \sum_j \frac{N_j S_0^2}{k R_j^2} f_j(k) e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda(k)} \sin(2kR_j + 2\delta_j(k)) \quad (1-31)$$

where: N_j is the coordination number of the j -th shell, S_0^2 is the amplitude reduction factor, $f_j(k)$ is the scattering amplitude, R_j is the bond length between the absorbing atom and the j -th neighboring atom, σ_j^2 is the Debye-Waller factor, representing the disorder or thermal motion, $\lambda(k)$ is the electron mean free path, $\delta_j(k)$ is the phase shift.

Through fitting the EXAFS data using this equation, the structural parameters, such as bond lengths, coordination numbers, and the extent of structural disorder, can be determined. The Debye-Waller factor accounts for variations in the bond distances due to thermal and static disorder.

1.6.2 Applications of XAS in catalysts

XAS is a widely applicable technique used in numerous scientific disciplines. Some of its major applications include catalysis, battery, biology and so on. In OER and ORR catalyst study,

XAS is frequently employed to study *operando* catalytic systems, providing real-time information about the oxidation states and coordination environments of catalytic active sites.

¹⁴² This helps in understanding how catalysts behave under actual reaction conditions, leading to the design of more efficient catalytic materials.

In ORR, XAS plays a critical role in understanding how the electronic structure of the catalyst influences its activity. The d-band center theory is often employed to explain the catalytic activity of transition metals in ORR, and XAS provides a direct way to explore this by revealing how the electronic structure of the metal changes as oxygen species are adsorbed and reduced. For instance, XANES can show shifts in the Pt L₃-edge during ORR, indicating changes in the electronic structure that correlate with the binding strength of oxygen intermediates, which is critical for optimizing ORR efficiency (Figure 1-37 and 1-38).^{143, 144}

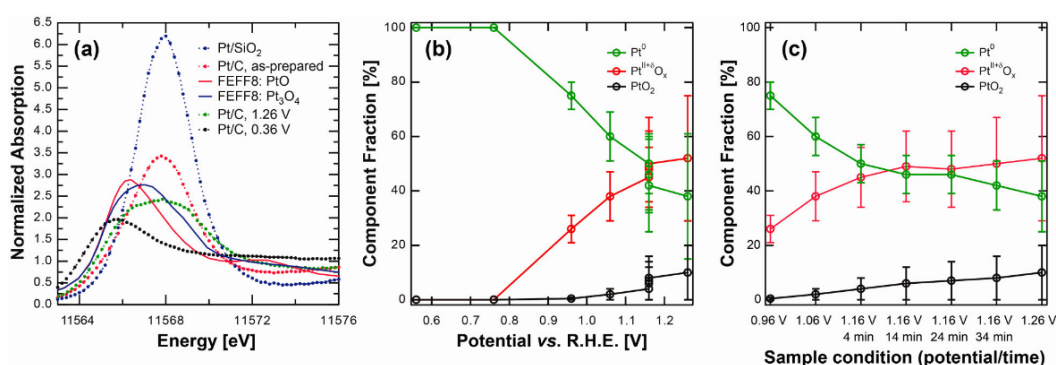


Figure 1-37. (a) Pt L₃ XANES spectra of some Pt-based samples.¹⁴³

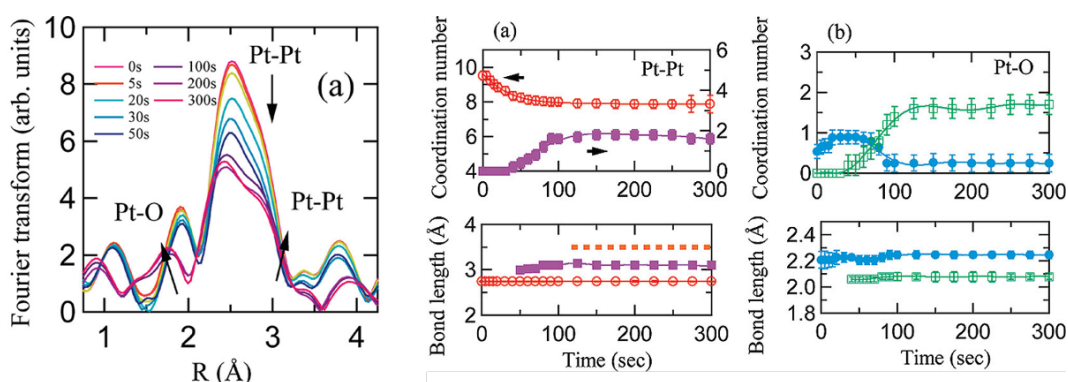


Figure 1-38. Time variations in k³-weighted of Pt-L₃ FT-EXAFS at potential of 1.4 V and corresponding possible Pt-Pt and Pt-O bonds information.¹⁴⁴

One of the significant challenges in ORR catalysis is the long-term degradation of catalysts. XAS allows for monitoring of catalyst stability by tracking the dissolution and restructuring of metal centers during ORR. Imai et al. reported Pt-based catalysts in PEMFCs can undergo dissolution and agglomeration under *operating* conditions, leading to performance loss (Figure 1-38). EXAFS studies have been able to monitor these processes, providing valuable information of Pt-Pt bond distance on how to mitigate degradation mechanisms and improve the longevity of ORR catalysts.¹⁴⁵

Additionally, XAS has been used to study the corrosion resistance of Pt alloys, where the dissolution of less noble metals (e.g., Ni or Co) from the alloy is a significant issue. By tracking the oxidation states and local structure of these metals during ORR, XAS provides insights into the design of more robust ORR catalysts that can resist dissolution while maintaining high activity (Figure 1-39).^{58, 146}

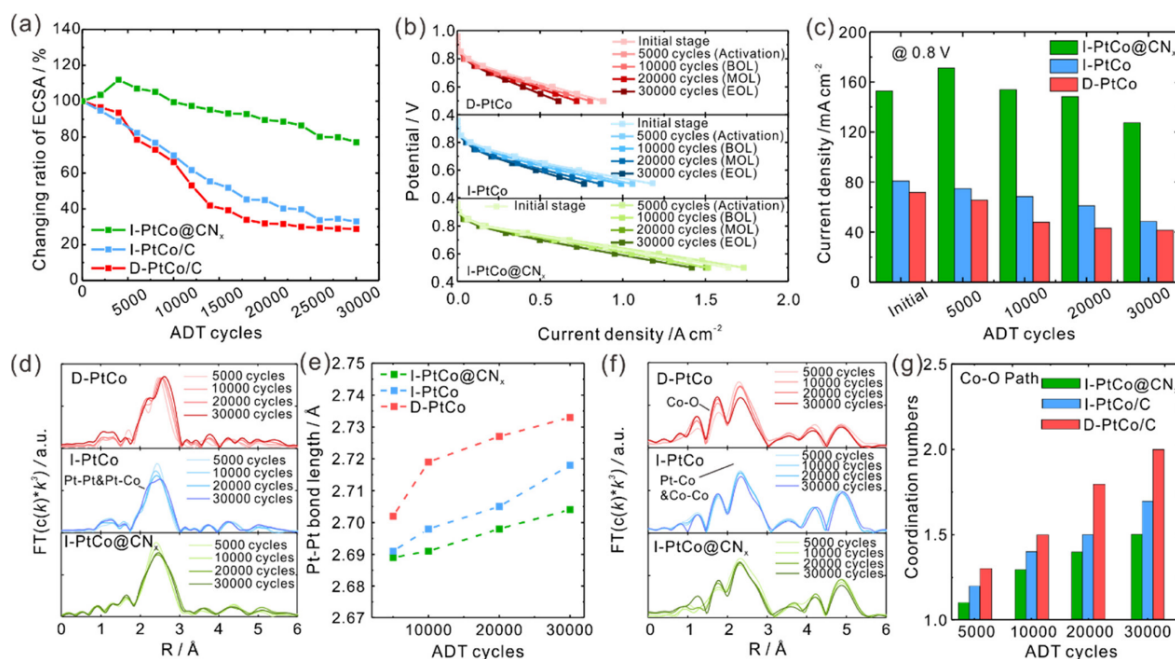


Figure 1-39. Pt L₃-edge XAS analysis of I-PtCo@CN_x, I-PtCo/C, and D-PtCo/C during the ADT cycles tested in the MEA operation conditions (80 °C, 80% RH).¹⁴⁶

OER is a crucial step in electrochemical water splitting, and it typically requires catalysts based on precious and transition metals, such as Ir, Ru, Co, and Ni, which exhibit multiple oxidation states during the reaction. XAS provides a direct method to monitor changes in the

oxidation states during OER, offering insight into the active species and reaction intermediates. In Zhao et al. study, Ir-based catalysts, considered among the most efficient OER catalysts in acidic media, have been extensively studied using XANES to track the formation of higher-valence Ir species (e.g., Ir^{4+} and Ir^{6+}) under reaction conditions. At the same time, EXAFS analysis gives us a better finding of the changes in the catalyst structure and the formation of the active phase (Figure 1-40).¹⁴⁷ Such studies help in understanding the redox behavior and stability of the catalyst during prolonged OER operation.

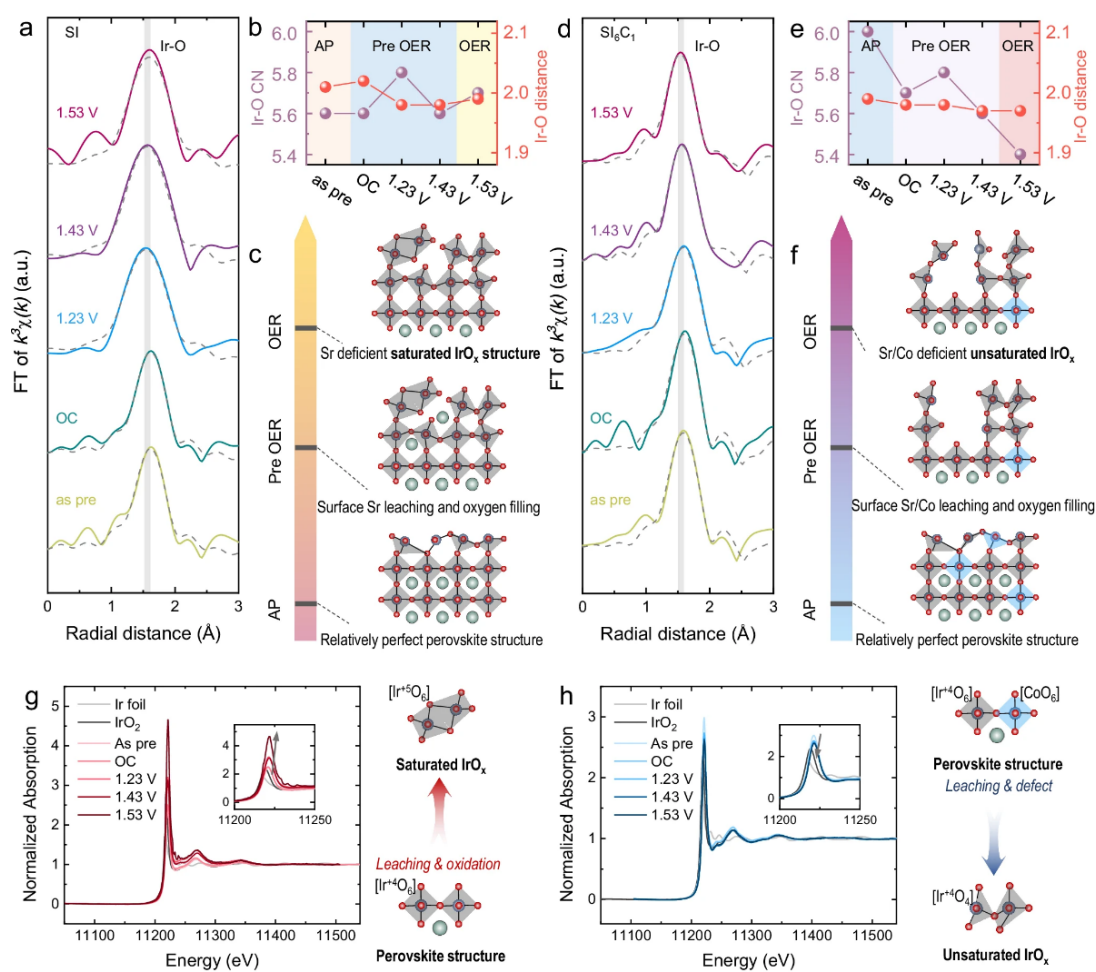


Figure 1-40. In situ XAS characterization of SrIrO_x (SI) and $\text{Sr}_7\text{Ir}_6\text{CoO}_x$ (SI_6C_1) samples.¹⁴⁷

In Co-, Fe- and Ni-based catalysts used for alkaline OER, XAS has been employed to investigate the structural reorganization and oxidation state changes that occur during the reaction. Especially, perovskite oxides (BSCF) have been investigated using XAS to observe the formation of surface-active species such as Co(Fe)OOH during OER. XAS studies have

revealed that the A-site cations (Ba and Sr) may dissolve during OER, while the B-site transition metals reorganize into more catalytically active phases.¹⁴⁸ The EXAFS region further provides details on the local bonding environment, revealing how changes from edge-sharing polyhedral from to Co/Fe-OOH construction correlate with catalytic performance (Figure 1-41).¹⁴⁹ This highlights the dynamic nature of the catalyst surface and provides valuable insights into designing more stable and efficient OER catalysts.

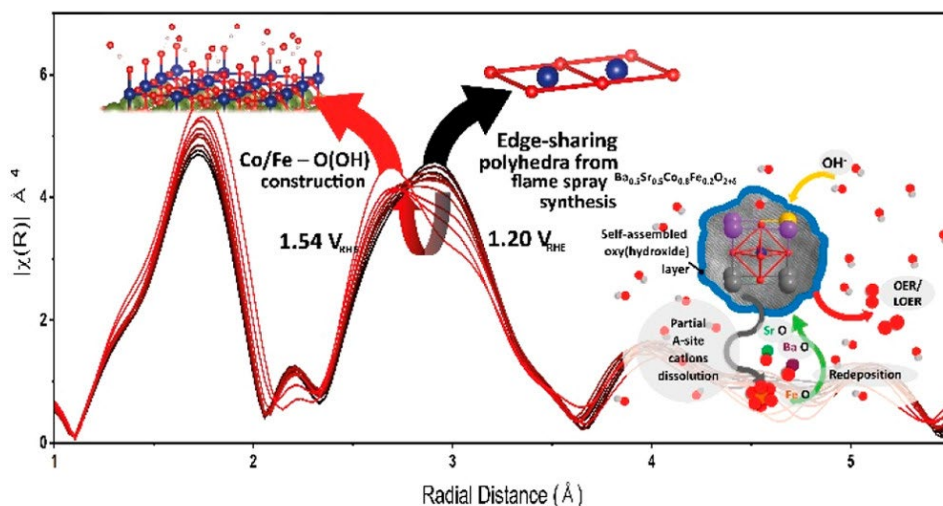


Figure 1-41. *operando* Co K-edge FT-EXAFS spectra of BSCF catalyst.¹⁴⁹

Operando O K-edge XAS has emerged as a powerful technique for investigating the local electronic and chemical environment of oxygen in water electrolysis catalysts during the OER.¹⁵⁰ By probing the O K-edge, which corresponds to the transition of core-level oxygen 1s electrons to unoccupied states, researchers can gain direct insight into the oxygen-related species and their role in catalysis.¹⁵¹

The O K-edge provides information on the oxygen bonding environment and the interaction between oxygen and transition metals, as well as the formation of oxygen-containing intermediates (*O, *OH, *OOH) during the OER process.^{152, 153} By using *operando* conditions, researchers can directly observe how oxygen species evolve (Figure 1-42), providing a deeper understanding of the catalytic mechanisms at the surface of the material.

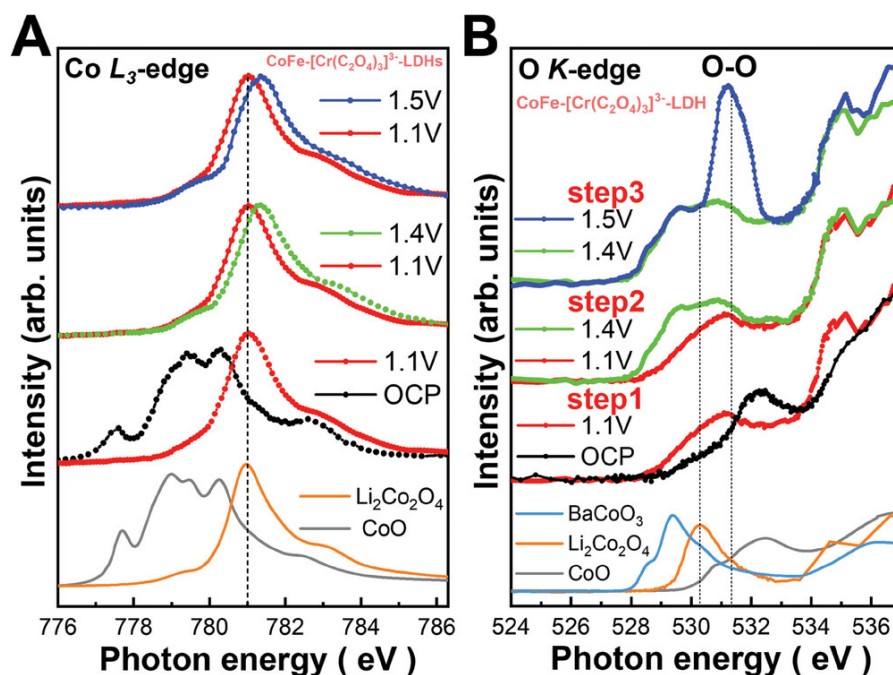


Figure 1-42. *Operando* soft-XAS characterization of high-valence Co as active site during OER. (A) Co L₃-edge and (B) O K-edge.¹⁵¹

1.7 Objective

The development and application of hydrogen energy are critical in the current transition to clean energy, with a primary focus on fuel cells and water electrolysis for hydrogen utilization and production, respectively. However, the number of high-performance catalysts that meet practical requirements remains limited and largely reliant on costly precious metals. This constraint primarily arises from kinetic limitations in the ORR and OER. Thus, developing new catalysts with high activity, durability, and reduced precious metal content is essential.

In recent years, significant progress has been made in ORR catalyst development, with researchers exploring strategies such as morphological control and alloying with transition metals to lower costs and enhance activity. For example, alloying Pt-based catalysts with transition metals like Ni and Co not only reduces Pt usage but also optimizes the catalyst's electronic structure, thereby improving performance. In the OER catalyst field, research has focused on reducing precious metal usage, enhancing stability, and managing impurities in electrolytes. Perovskite-structured catalysts, with their stability and activity under specific

potentials, are promising candidates for OER applications.

Beyond catalyst development, a comprehensive understanding of reaction mechanisms is critical to guide material design effectively. Advanced *operando* techniques that allow real-time observation of electronic structure and active site changes during catalysis are indispensable. Techniques such as *operando* X-ray, infrared, and ultraviolet laser methods have shown substantial benefits in revealing electronic states and structural evolution during reactions. Among these, *operando* XAS is a core technique for elucidating ORR and OER activities, with XANES and EXAFS analysis offering insights into electronic structure and coordination environment. Additionally, surface-sensitive soft XAS in total electron yield (TEY) mode allows for the detection of dynamic intermediate changes on catalyst surfaces, further deepening mechanistic understanding.

In this study, we report several advanced catalysts targeting ORR and OER reactions, including Pd@Pt core-shell nanowires, high-Ni-content PtNi nanowires, well-ordered PtCoNi nanowires, as well as perovskite-structured BaIrO₃ and SrIrO₃ for acidic conditions and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} for alkaline environments. Through TEM imaging and pair distribution function (PDF) analysis of crystal structure, we systematically examined how various structures impact catalytic activity. *operando* XAS was employed to monitor valence state and coordination environment changes during reactions, revealing the practical potential of these catalysts. Especially, surface-sensitive soft XAS in TEY mode allowed us to capture dynamic changes in intermediates during catalysis, which is crucial for understanding OER mechanisms. Overall, this study validates the application potential of these catalysts in ORR and OER processes and provides new perspectives for optimizing high-efficiency catalyst design.

1.8 Outline of the thesis

This thesis comprises eight chapters, presenting the applications and contributions of various novel catalysts in ORR and OER reactions. Through *operando* XAS, the reaction mechanisms are analyzed, providing guidelines for the design of next-generation catalysts.

Chapter 1 introduces the fundamental concepts and reaction principles of fuel cells and water electrolysis. It outlines current design principles and advancements for ORR and OER catalysts, emphasizing the importance of *operando/in situ* testing for understanding catalytic mechanisms.

Chapter 2 explores Pd@Pt core-shell nanowire catalysts for ORR, synthesized via a modified galvanic cell method, achieving uniform Pt coverage on Pd nanowires without complex control systems. Characterization reveals high ORR activity and stability, attributed to complete Pt monolayer shell, highlighting core-shell structure potential for fuel cell applications.

Chapter 3 focuses on PtNi nanowires as ORR catalysts. Post-annealing treatment forms a Pt-enriched surface layer on high-Ni-content PtNi nanowires, enhancing stability and activity. Techniques such as Pair Distribution Function (PDF) and *operando* XAS were used to study structural and electronic states, showing that the Pt-rich surface suppresses Pt oxidation and Ni dissolution at high potentials, significantly improving specific ORR activity.

Chapter 4 investigates PtCoNi intermetallic compound nanowires with an ordered L1₀ structure, which show superior ORR activity and stability. The electronic and structural changes during reactions confirm that the ordered L1₀ phase effectively suppresses Pt oxidation and stabilizes Co and Ni without further dissolution.

Chapter 5 examines the impact of structure and anionic environment on IrO_x catalysts in OER. *Operando* XAS and PDF analyses of amorphous SA3.5 and crystalline SA58 IrO_x under acidic conditions showed higher activity for SA3.5 but reduced stability due to anion poisoning. Crystalline SA58 demonstrated greater stability but lower activity. DFT calculations revealed that phosphate ions increase the oxidation state of Ir, reducing OER efficiency, offering insights into designing stable and efficient IrO_x-based catalysts.

Chapter 6 focuses on Ir-based perovskite oxides as OER catalysts, with *operando* XAS revealing the structure-activity relationship. Four distinct Ir-based perovskites (9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, and BCC-SrIrO₃) were synthesized and tested under PEMWE conditions.

Results indicate that 9R-BaIrO₃ shows optimal performance, attributed to its unique face-sharing [IrO₆] octahedral trimers and significant surface hydroxylation.

Chapter 7 investigates the OER activity of Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} catalysts, with a focus on how different Co and Fe doping levels influence catalytic performance. Using RDE and a novel forced-flow cell method, electrochemical testing of BSCF catalysts showed that appropriate Fe doping significantly enhances OER activity. *Operando* XAS revealed dynamic structural and electronic changes, demonstrating that Fe doping facilitates the formation of a high-spin Co²⁺(Td) to Co³⁺(Oh) transition, producing active CoOOH, which boosts catalytic activity.

Chapter 8 summarizes the findings and conclusions of this study and provides insights into the future development and design of fuel cell and water electrolysis catalysts.

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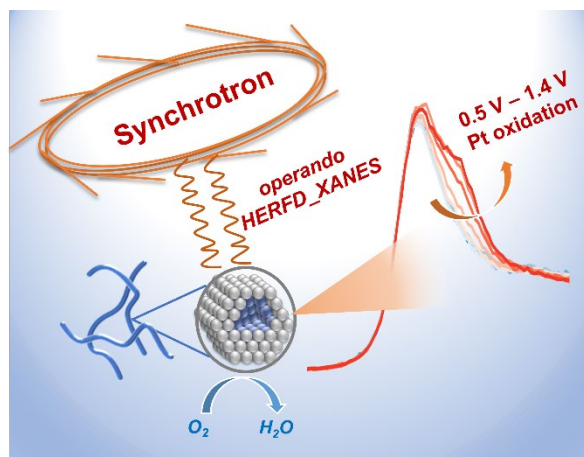
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Chapter 2. A Modified Galvanic Cell Synthesis of Pd@Pt Core-Shell Nanowire Catalysts: Structural Insights and Enhanced ORR Performance



One-dimensional nanostructures, specifically Pd@Pt core-shell nanowire catalysts, have garnered significant attention because of their potential to enhance the sluggish kinetics of the oxygen reduction reaction (ORR). However, fully realizing their potential depends on achieving consistent and uniform synthesis. In this study, we introduce

an improved galvanic synthesis method for Pd@Pt core-shell nanowire catalysts (Pd-NW@Pt/C) that eliminates the need for electrochemical control or reducing agents, making it more accessible and efficient than the traditional Cu underpotential deposition (Cu-UPD) method. Our approach ensures a uniform Pt shell, resulting in superior ORR activity, with a mass activity of $1.06 \text{ A mg}_{\text{Pt}}^{-1}$ and a specific activity of $0.80 \text{ mA cm}_{\text{Pt}}^{-2}$. Detailed *operando* X-ray absorption spectroscopy (XAS) measurements, including high-energy resolution fluorescence detection (HERFD-XAS), revealed that Pd-NW@Pt/C catalysts with a fully-covered Pt shell exhibit shorter Pt-Pt bond lengths and weaker oxygen binding energies compared to partially-covered Pt shell nanowire catalysts (Pd-NW@Pt/C-ref) and nanoparticle catalysts (Pd-NP@Pt/C), leading to significantly enhanced ORR activity. This study demonstrates the effectiveness of a modified galvanic cell method for producing high-performance Pd@Pt core-shell nanowire catalysts, offering insights into their structural and electronic properties.

2.1 Introduction

Reliance on non-renewable energy exacerbates global warming and pollution. Hydrogen

energy, with water as its only byproduct, offers an efficient, carbon-free alternative.^{1, 2} Proton-exchange membrane fuel cells (PEMFCs) efficiently convert chemical energy into electricity, but their application is hindered by the slow kinetics of the oxygen reduction reaction (ORR) and the limitations of conventional Pt/C catalysts in terms of cost, performance, and durability.³⁻⁵ Therefore, the development of novel catalysts is crucial for overcoming these challenges.

Fine-tuning the catalyst surface structure optimizes the relationship between molecular adsorption energy and lattice strain, thereby improving catalytic efficiency. Core-shell structures, such as Metal@Pt, effectively introduce strain due to lattice mismatches between the core and shell, which enhances atomic utilization and exposes more active sites.^{6, 7} Among various Metal@Pt structures, Pd@Pt stands out for its distinctive ORR activities due to optimized compressive strain.^{8, 9} The Pd core exerts a compressive force on the Pt layer, producing a "ligand effect" that shifts the Pt *d*-band center, weakening interactions with oxygen species and thereby boosting ORR activity.^{10, 11} Thus, the moderate compressive strain of the Pt surface layer can be enhanced by modulating the Pd core, such as by changing its morphology, which further improves ORR activity.

One-dimensional (1D) nanowires (NWs) exhibit a high surface-area-to-volume ratio, increasing the availability of active sites for catalytic reactions.^{12, 13} Unlike zero-dimensional nanoparticles (NPs) that suffer from aggregation and Ostwald ripening, NWs maintain their structural integrity and surface area during reactions, providing more stable catalytic activity.¹⁴⁻¹⁶ And structural defects like grain boundaries (GBs), surface atomic steps (exposing high-index facets), and a few amorphous regions form during NW growth, enhancing catalytic activity by disrupting the interface water network, destabilizing ORR intermediates, and promoting proton transfer.¹⁷ Additionally, their relatively long length reduces dependency on carbon supports for NP dispersion and electron conduction, potentially mitigating support corrosion issues common in Pt/C catalysts.¹⁸

Therefore, combining the advantages of 1D NWs with the tunable properties of core-shell structures results in a superior catalyst with enhanced performance and stability. Both

experimental¹⁹ and theoretical²⁰ evidence suggests that noble metal NWs, such as Pd NWs with 2–3 nm diameters, exhibit significant surface contraction, intensifying the strain on the Pt layer in the core-shell structure, thereby enhancing ORR activity. Adzic et al. pioneered a technique for carbon-supported Pd core Pt shell catalysts known as Pt@Pd/C.²¹ Their method involved the formation of a monolayer of Cu on the Pd core via Cu underpotential deposition (Cu-UPD), which was later replaced by a Pt monolayer shell. This approach was also adapted to produce Pd@Pt NWs, resulting in superior ORR performance.²² However, the highly precise potential control and limited yield of this method make it less suitable for widespread application. The characteristics of the metal core, such as particle size distribution, morphology, and surface structure, make potential control more challenging, easily resulting in an incomplete Pt shell layer.²³ This incomplete structure can lead to the clustering of surface Pt and dissolution of inner Pd, reducing ORR activity.^{24, 25} Yu et al. created Pd NWs using Te as a template, forming Pd@Pt core-shell NWs with specific thicknesses using bromide ions.²⁶ However, this intricate process still requires particular agents for reduction, stabilization, and temperature control.

Building on our previous research, the Cu-UPD/Pt displacement technique was improved to synthesize Pd@Pt core-shell nanoparticles.^{24, 27} In this method, carbon-supported Pd cores (Pd/C) were mixed in an acidic CuSO₄ solution with metallic Cu sheets. The interaction between Pd/C and metallic Cu establishes a Cu/Cu²⁺ equilibrium potential, initiating the Cu-UPD process, followed by Pt replacement. This efficient method eliminates the need for complex three-electrode systems and precise potential control, making the production of Pd@Pt catalysts with different morphologies and sizes more feasible, as well as increasing the yield.

In this study, a modified galvanic cell technique was used to produce Pd@Pt core-shell NW catalysts. Inductively coupled plasma atomic emission spectroscopy (ICP-AES), high-resolution transmission electron microscopy (HR-TEM), and energy-dispersive X-ray spectroscopy (EDS) mapping confirmed the fully-covered Pt shell in the galvanic cell-produced Pd-NW@Pt/C catalyst. This catalyst demonstrated enhanced catalytic performance compared to the partially-covered Pt shell layer in catalysts synthesized using the Cu-UPD

method (Pd-NW@Pt/C-ref). Additionally, the advantages of the NW structure are also highlighted when compared to core-shell nanoparticles (Pd-NP@Pt/C) synthesized by the galvanic method. Further investigations using a pair distribution function (PDF) and X-ray diffraction (XRD) indicated that the catalyst consisted of fcc and hcp phases with compact lattice structures. The *operando* high-energy resolution fluorescence detection-X-ray absorption spectroscopy (HEARD-XAS) and conventional XAS provided insight into the behavior of the catalyst, emphasizing the Pt-Pt bond lengths and surface electronic properties. These findings revealed that the Pd-NW@Pt/C catalyst with a uniform Pt shell exhibits weaker oxygen binding energy and shorter Pt-Pt bond lengths, which enhance ORR activity and durability.

2.2 Experimental Methods

2.2.1 Materials and reagents

Palladium nitrate ($\text{Pd}(\text{NO}_3)_2$, 97.0%), Dodecyltrimethylammonium bromide (DTAB, 96.0%), Toluene (99.0%), Ethanol (99.5%), Sulfuric acid (H_2SO_4 , 95.0%), Potassium tetrachloroplatinate (II) (K_2PtCl_4 , 44.0%), 2-propanol (99.7%), Chloroform (99.0%) and Copper (II) sulfate pentahydrate (CuSO_4 , 99.5%) were acquired from Fujifilm. Octadecylamine (ODA 99.0%) and Sodium borohydride (NaBH_4 , 98.0%) were purchased from Sigma-Aldrich. The electrolyte was prepared from ultra-pure water (Milli-Q, 18.2 M Ω) and perchloric acid (ultra-pure, Kanto Chemical Co. Inc.). The Vulcan XC-72 was purchased from Cabot Corporation. O_2 (99.995%), N_2 (99.999%), H_2 (5%, 95% N_2 balanced) gases were purchased from Kyoto Teisan Co., Ltd.

A Pt/C catalyst (29.1 wt. %; TEC10V30E) was purchased from Tanaka Kikinzoku Kogyo Co. Ltd., Japan.

2.2.2 Synthesis of Pd-NW/C and Pd-NP/C

Pd NWs were synthesized using an improved phase-transfer method based on Teng et al.²⁸

Initially, 13 mg of $\text{Pd}(\text{NO}_3)_2$, 60 mg of DTAB, and 400 mg of ODA were added to a three-necked flask containing 7 mL of toluene. The mixture was sonicated for 20 min under a nitrogen atmosphere to achieve proper dispersion. Subsequently, 13 mg NaBH_4 dissolved in 2 mL deoxygenated deionized water was added dropwise to the mixture, which was allowed to react for 1 h. The reaction product was extracted with 2 mL each of water and chloroform, and the organic phase was collected. After dilution with 10 mL of ethanol, the mixture was centrifuged at 8000 rpm for 10 min to obtain a black precipitate. The precipitate was washed three times with ethanol and dispersed in chloroform for storage. Vulcan carbon (6 mg) was then added to the solution, followed by sonication for 30 min. The Pd-NW/C (~13wt% Pd) was obtained by centrifugation. To immobilize the Pd NWs on the carbon support and remove the residual organic matter, the Pd-NW/C powder was dispersed in hexane, soaked for 12 h, filtered, and dried at room temperature.

The synthesis process of Pd nanoparticle (Pd-NP/C: ~15wt% Pd) is similar to that of Pd NWs but does not require a nitrogen atmosphere.

2.2.3 Synthesis of Pd-NW@Pt/C and Pd-NP@Pt/C by Galvanic Cell method

A solution containing 0.01 M CuSO_4 and 0.5 M H_2SO_4 was subjected to nitrogen bubbling for 1 h, and then the Pd-NW/C or Pd-NP/C powder was dispersed in the above solution under vigorous magnetic stirring. The copper sheet was submerged in the above solution and stirred for a certain time (30 min to 5 h). Upon completion of the reaction, the copper sheet was removed, and N_2 -saturated 10 mM K_2PtCl_4 solution was added to the suspension. The Pd-NW@Pt/C or Pd-NP@Pt/C catalyst was obtained after stirring for 10 min, followed by filtration and drying.

2.2.4 Synthesis of Pd-NW@Pt/C-ref by Cu-UPD method

Pd-NW@Pt/C-ref catalysts were synthesized using the Cu underpotential deposition (Cu-UPD) method in a standard three-electrode electrochemical cell. A reversible hydrogen electrode (RHE) with 5% H_2 was used as the reference electrode, a platinum mesh as the

counter electrode, and a glassy carbon rotating disk electrode (GC RDE, 0.196 cm²) as the working electrode. The GC RDE was polished with alumina and rinsed with ultrapure water prior to use.

A catalyst ink was prepared by dispersing 2 mg of Pd-NW/C catalysts in a mixture of ultrapure water and 2-propanol (1:1 ratio, 2 mL total) along with 40 μ L of Nafion® solution. The mixture was then sonicated for 30 min. Then, 10 μ L of the ink was deposited onto the GC RDE, which was rotated at 400 rpm to ensure even coating.

For the Cu-UPD, the RDE was immersed in a nitrogen-saturated solution of 10 mM CuSO₄ and 0.5 M H₂SO₄. The electrode underwent five cycles of cyclic voltammetry (CV) within the potential range of 0.27 V to 0.72 V vs. RHE at 50 mV/s. The optimal potential for Cu deposition was maintained for 10 min to form a Cu monolayer on the Pd NWs. Following Cu deposition, the electrode was transferred to a nitrogen-saturated solution of 10 mM K₂PtCl₄ and 0.5 M H₂SO₄. The Cu monolayer was replaced with Pt via a galvanic displacement reaction that proceeded for 10 min.

2.2.5 Characterization

The X-ray diffraction (XRD) of the prepared catalysts was conducted at a scanning rate of 2° min⁻¹ with a step at 0.02° to analyze the structure of the catalysts with Cu K α radiation (λ = 1.54056 Å) (Rigaku Ultima IV, Japan). Transmission electron microscopy (TEM) images were obtained using a JEM-2200FS microscope (JEOL, Ltd.) at 200 kV. A JEOL-JEM-ARM200F electron microscope was used for the high-resolution (HR) TEM analysis at 200 kV. EDX and EELS were performed using a JEOL-Dual SDD and Gatan-GIF Quantum-ER, respectively. Inductively coupled plasma (ICP) measurements were performed using an ICPE-9820 instrument (Shimadzu Corporation). X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantum 2000 system (ULVAC-PHI, Inc., Japan) using a monochromate Al K α X-ray source operating at 40 W and 1486.6 eV. X-ray total scattering data were collected on a Varex Imaging XRD1621 flat panel detector with a two-second exposure time and 150 integration time using synchrotron irradiation at BL22XU beamline of SPring-8. The optics,

including the beam center coordinates, the tilt of the detector, and the sample-to-detector distance (225.7759 mm), were calibrated using the PIXIA program²⁹ for the image data obtained for CeO₂ (NIST, 674B; lattice constant, $a = 5.41165 \text{ \AA}$). The wavelength ($\lambda = 0.181140 \text{ \AA}$) was calibrated through the PDF fitting for the CeO₂ data using the PDFfit2 program.³⁰ The ex-situ XAS measurements of Pt L_{III}-edge and Co K-edge were measured by synchrotron irradiation at beamlines BL36XU and BL14B2 of Spring-8. The *operando* XAS measurements of the Pt L_{III}-edge were carried out at beamlines BL36XU and BL37XU; the detailed information for the RDE test was similar to our previous report.^{31, 32} And the data analysis was carried out by ATHENA and ARTEMIS using the IFEFFIT program.³³ The *operando* HERFD-XAS spectra for the Pt L_{III}-edge were conducted at beamline BL39XU. The collected HERFD-XAS spectra were further fitted using an arrangement equation (eq 1) for the background and two pseudo-Voigt (Gaussian–Lorentzian, GL, product) equations (eq 2) for the peaks, as shown in the following:

$$\frac{A_{bg}}{\pi} \left[\tan^{-1} \left(\frac{E-E_{bg}}{\Delta E_{bg}} \right) + \frac{\pi}{2} \right] \quad (2-1)$$

$$\frac{A_n}{1+4m_n \frac{(E-E_n)^2}{\Delta E_n^2}} \exp \left[-4 \cdot \ln 2 \cdot (1-m_n) \cdot \frac{(E-E_n)^2}{\Delta E_n^2} \right] \quad (2-2)$$

Here, A_{bg} denotes the height for the arctan, which was adjusted to match the μ_E within the range of 11568-11570 eV. E_{bg} and E_n were determined as previous research.³⁴ m_n was set as 0.5.

2.2.6 Electrochemical testing

Preliminary cleaning involved 50 Cyclic voltammetry (CV) cycles from 0.02 to 1.20 V vs. RHE at 100 mV/s to remove residual organics. Final CV curves were recorded from 0.02 to 1.10 V vs. RHE at 50 mV/s in an N₂-saturated 0.1 M HClO₄ solution. Linear sweep voltammetry (LSV) was performed from 0.2 to 1.2 V vs. RHE at 10 mV/s with RDE rotation rates of 100, 400, 900, 1600, and 2500 rpm in an O₂-saturated 0.1 M HClO₄ solution. Specific activity (SA) at 0.9 V vs. RHE was calculated using the Koutecky-Levich equation. The oxygen

coverage tests were performed by LSV (0.50, 0.60, 0.70, 0.80, 0.90, 1.00, and 1.10 V *vs.* RHE), with each potential maintained for 5 min. The oxygen coverage charge was determined by dividing the reduction peak area of the Pt oxide species by the H_{upd} area. Accelerated durability testing (ADT) involved cycling between 0.65 and 1.00 V *vs.* RHE for 3 seconds each. After 10,000 cycles, the LSV was recorded to evaluate the catalyst stability. CO-stripping voltammetry was conducted by exposing the working electrode to CO-saturated 0.1 M HClO₄ at 0.12 V *vs.* RHE for 20 seconds, followed by N₂ bubbling for 40 min. Stripping voltammetry was then performed from 0.05 to 1.00 V *vs.* RHE.

2.3 Result and Discussion

2.3.1 Synthesis and characterization of Pd nanowires

The Pd-NW cores were synthesized using surfactant templates (ODA and DTAB). The growth mechanism of Pd NWs was investigated using TEM, HR-TEM, and HAADF-STEM. After adding an excess of the reducing agent NaBH₄, the Pd cation content rapidly decreased, as shown in Figure 2-1a. This results in the formation of thermodynamically unstable nanoparticles without complete NW structures. During the secondary growth of the particles, they preferred to grow along the equivalent and [111] direction due to the guiding effect of the long carbon chains of the surfactant.²⁸ Following the above process for 30 minutes, the generation of distinct NW structures could be more clearly observed (Figure 2-1b). After 1 h of reaction, a complete NWs network structure with an average diameter of 2.0 nm can be obtained and well-defined lattice plane with the *d*-spacing of the lattice fringes in the marked area was 0.23 nm and 0.19 nm in Figure 2-1c and Figure 2-2. As observed from Figure 2-1d and 2-2f, NWs formed by interconnecting small single-crystal particles or elongated primary nanostructures,^{12, 22, 35} resulting in a polycrystalline structure with amorphous regions, GBs, and surface steps, which induce structural micro-strain and regulate surface oxygen adsorption.^{17, 36}

Ensuring an inert gas reaction environment during secondary NW growth is crucial for

stacking and joining nanoparticles at different angles, which generates defects. These defects are susceptible to oxygen and tend to absorb oxygen molecules, leading to oxidative etching. Upon exposing the reaction mixture to air, a continuous NW structure was not observed; instead, particles with a diameter of about 2-5 nm and a regular lattice structure were formed (Figure 2-3). Adzic et al. prepared Pd-Ni NWs to minimize the use of precious metals, demonstrating excellent electrochemical properties.³⁵ The same synthesis method was used to incorporate transition metals into Pd NWs, forming the NW structure shown in Figures 2-4 to 2-6. However, increasing the transition metal content complicates NW formation due to oxygen adsorption and etching.

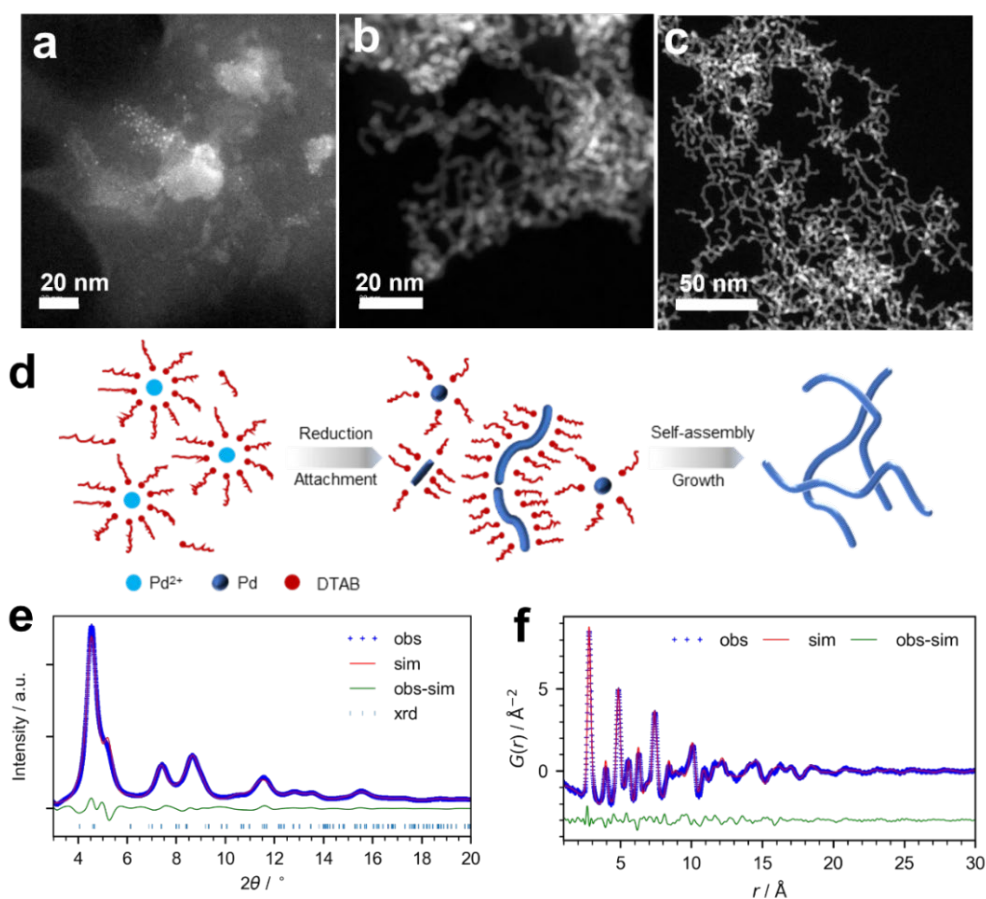


Figure 2-1. STEM images of Pd nanowires obtained after 10 min (a), 30 min(b), 1 h (c) reaction time in N_2 ; (d) Schematic illustration of Pd nanowire formation; (e) XRD and (f) PDF pattern of Pd nanowire.

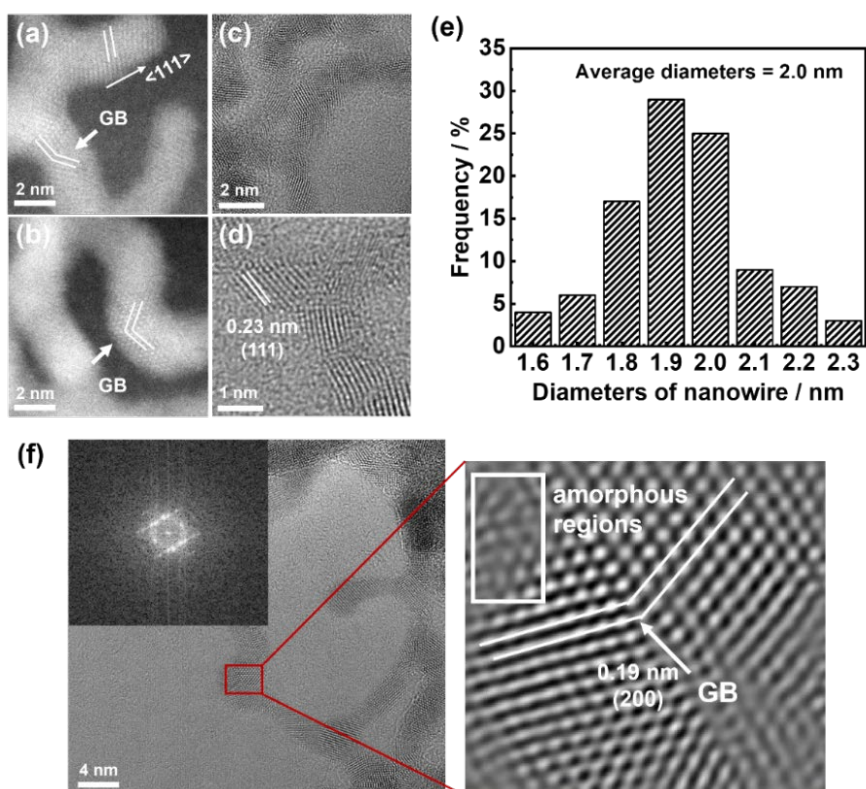


Figure 2-2. (a-d) TEM images, and (e) Pd nanowires diameter distribution. (f) HRTEM images and corresponding inverse FFT patterns of Pd nanowires.

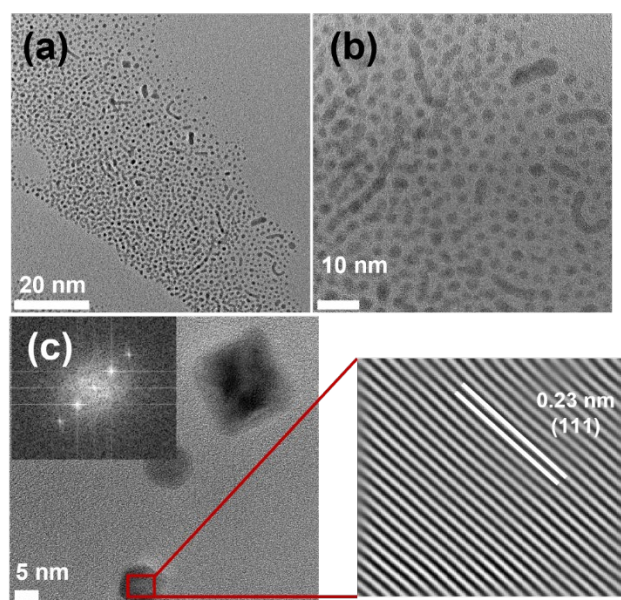


Figure 2-3. (a, b) TEM images of Pd nanowires obtained after 1 h in air. (c) HR-TEM images and corresponding inverse FFT patterns of Pd nanoparticles.

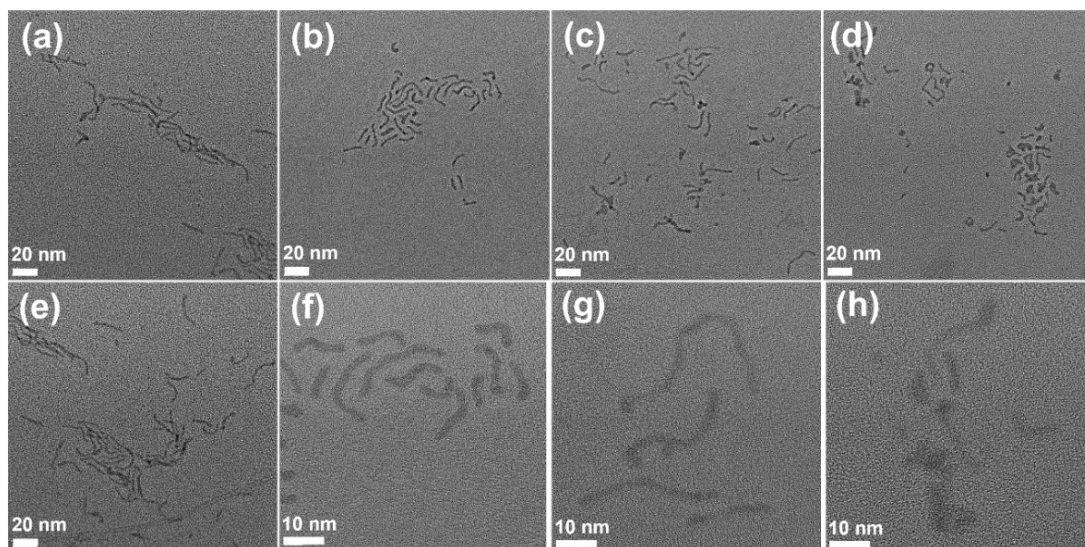


Figure 2-4. TEM of (a, e) $\text{Pd}_{0.9}\text{Ni}_{0.1}$; (b, f) $\text{Pd}_{0.8}\text{Ni}_{0.2}$; (c, g) $\text{Pd}_{0.7}\text{Ni}_{0.3}$; (d, h) $\text{Pd}_{0.6}\text{Ni}_{0.4}$ nanowires.

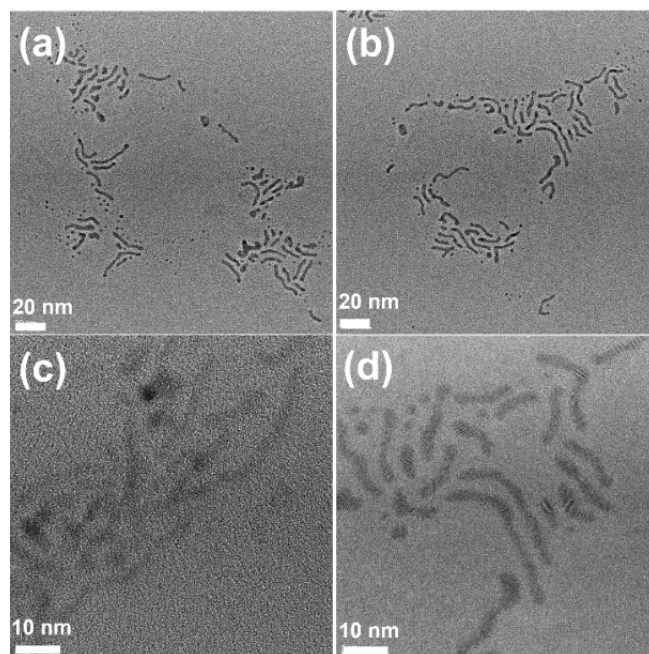


Figure 2-5. TEM of (a, c) $\text{Pd}_{0.9}\text{Co}_{0.1}$; (b, d) $\text{Pd}_{0.8}\text{Co}_{0.2}$ nanowires.

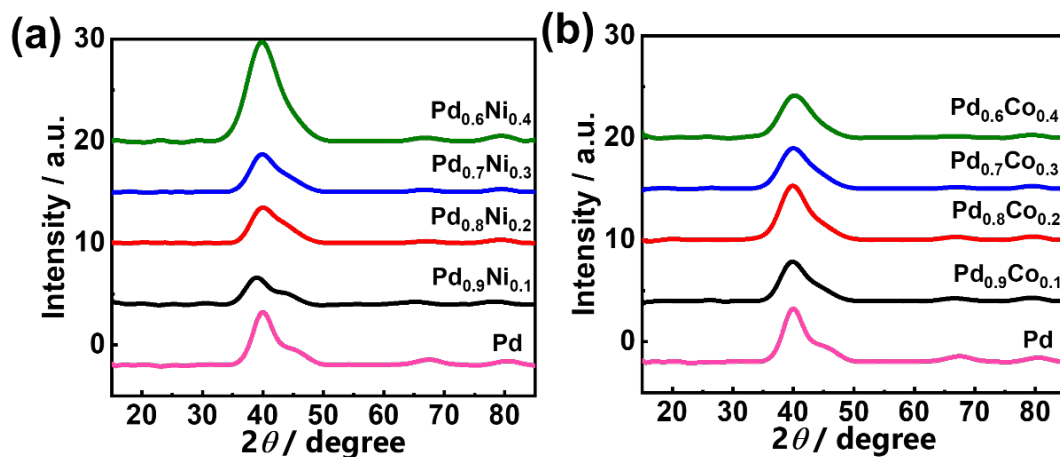


Figure 2-6. XRD pattern of (a) PdNi and (b) PdCo nanowire.

XRD results were used to probe the crystal structure, as shown in Figure 2-1e, with no impurity peaks observed. The observed data were fitted to the curves simulated using the fcc model (Figure 2-7), but the results were less impressive than those of the fcc+hcp model, which demonstrates the formation of hexagonal Pd domains (~10%). The total scattering pattern indicates a lattice constant of $a = 3.960 \text{ \AA}$ in the fcc phase and $a = 2.949 \text{ \AA} / c = 4.505 \text{ \AA}$ in the second hcp phase (Table 2-1). However, the Bragg reflections are relatively weak and broad in XRD, making it difficult to analyze the symmetry of the crystals and the analyzed results are less reliable.

The PDF technique, which provides the weighted probability of detecting any pair of atoms at a distance r , establishes the distribution of interatomic distances in real space and is a powerful tool for resolving material structures. According to the PDF analysis in Figure 2-1f, the observed data were also fitted with a curve simulated by an fcc+hcp Pd model with a shaped envelope for the NWs. The calculated lattice constants are $a = 3.958 \text{ \AA}$ in the fcc phase and $a = 2.870 \text{ \AA} / c = 4.641 \text{ \AA}$ in the second hcp phase (Table 2-1). This lattice constant in the fcc structures is larger than standard Pd crystals ($a = 3.89 \text{ \AA}$). This may be attributed to the potential effects of the organic matter residues on the surfaces during the synthesis or formation of the hydride phases.

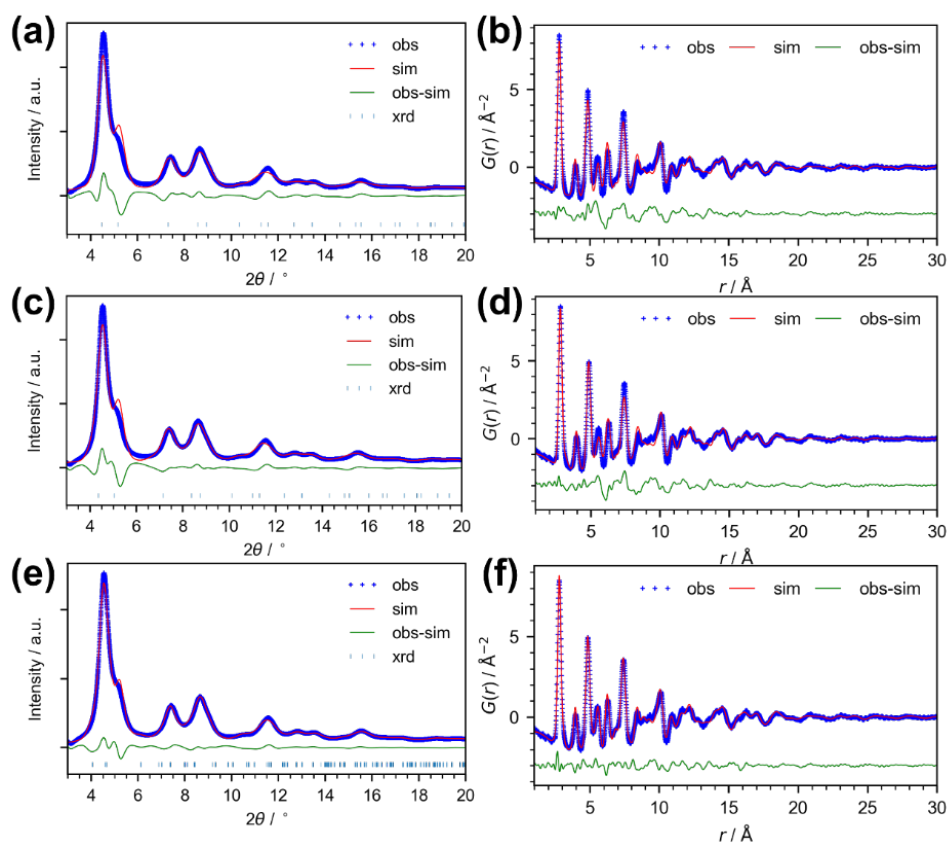


Figure 2-7. (a, c, e) Total scattering patterns and (b, d, f) Pair distribution functions of Pd nanowires. The observed curve was fitted with a curve simulated with (a, b) a fcc Pd model, (c, d) two fcc Pd models and (e, f) a fcc Pd model and a hcp Pd model.

Table 2-1. Lattice constants of Pd nanowires

Lattice constants in Å	XRD fcc	2 nd phase	PDF fcc	2 nd phase
Pd nanowires		<u>hcp</u>		<u>hcp</u>
(fcc + hcp model)	3.96008(1)	$a = 2.949(4)$ $c = 4.505(8)$	3.958(2)	$a = 2.870(15)$ $c = 4.64(4)$

Pd nanowires		<u>fcc</u>		<u>fcc</u>
(fcc + fcc	4.009(4)		3.961(3)	
model)		4.102(15)		4.33(6)
Pd nanowires				
(fcc model)	4.007(2)	None	3.963(3)	None

2.3.2 Synthesis and characterization of Pd-NW@Pt/C catalysts

A schematic representation of the synthesis of the core-shell structure catalysts using the galvanic cell method,²⁴ in accordance with our previous studies on Pd@Pt nanoparticles, is shown in Figure 2-8a and Figure 2-9. The process involved dispersing a certain amount of Pd-NW/C powder in a mixed solution of CuSO₄ and H₂SO₄, after which a Cu sheet was inserted and stirred continuously under a nitrogen atmosphere. This continuous stirring facilitated constant contact between the Pd particles and the Cu sheet, forming an electrochemical cell. Consequently, at the anode, the copper sheet dissolved to produce copper ions and generated a weak current (Cu to Cu²⁺), whereas, at the cathode, a layer of copper atoms was deposited on the surface of the Pd NWs to achieve electrochemical equilibrium (Cu²⁺ to Cu). The reaction was automatically stopped once a complete Cu monolayer structure formed on the metal surface. After a certain reaction time, the copper sheet was removed, and an N₂-saturated K₂PtCl₄ solution was introduced to obtain the Pd-NW@Pt/C catalysts. Compared to the conventional Cu-UPD approach (Figure 2-10), this method did not require any potential control throughout the synthesis process, and the amount of catalyst that could be synthesized was not limited. Moreover, owing to the generalization of Cu deposition and the characteristics of the replacement reactions, the galvanic cell method can be applied to synthesizing other Metal@Pt core-shell structures in addition to Pd metal, making large-scale generation possible.

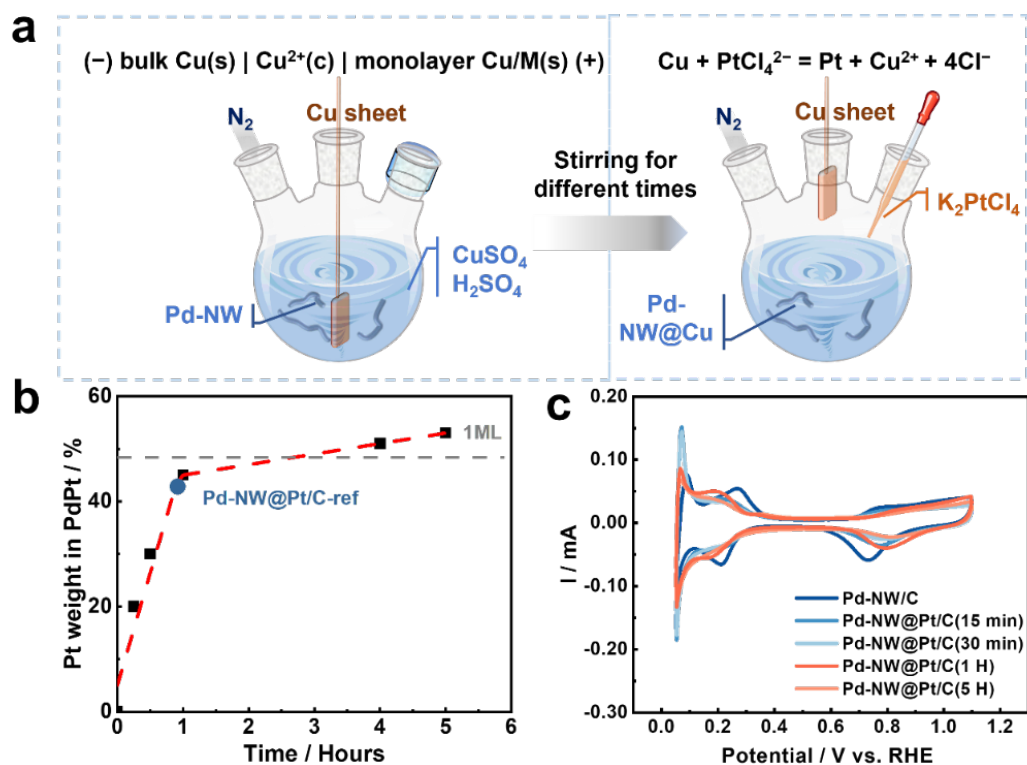


Figure 2-8. (a) Schematic diagram of the Galvanic Cell method (b) Pt weight percent in PtPd and (c) CVs of Pd-NW@Pt/C derived from Pd-NW@Cu/C with different stirring times.

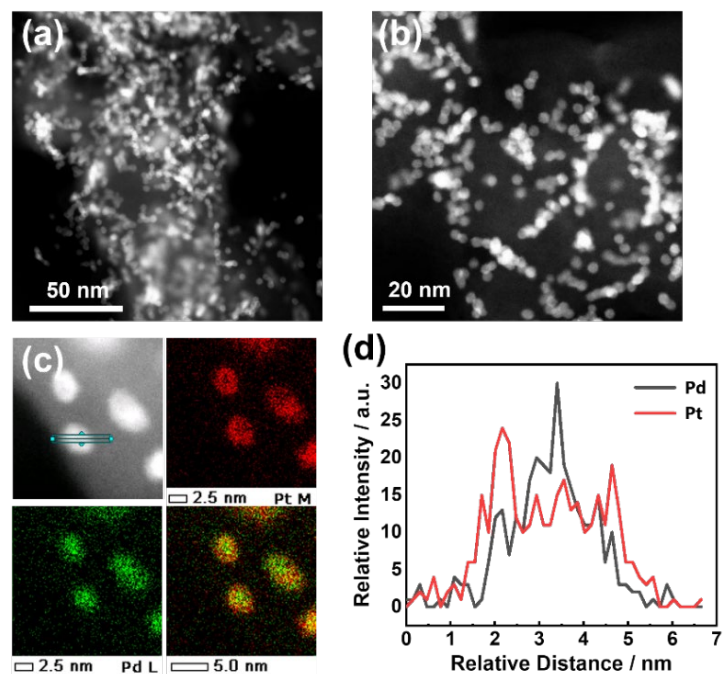


Figure 2-9. (a, b) STEM image of Pd@Pt/C nanoparticles obtained by galvanic cell method; (c) STEM-EDX element mapping spectrum and (d) line scanning profiles of Pd-NP@Pt/C.

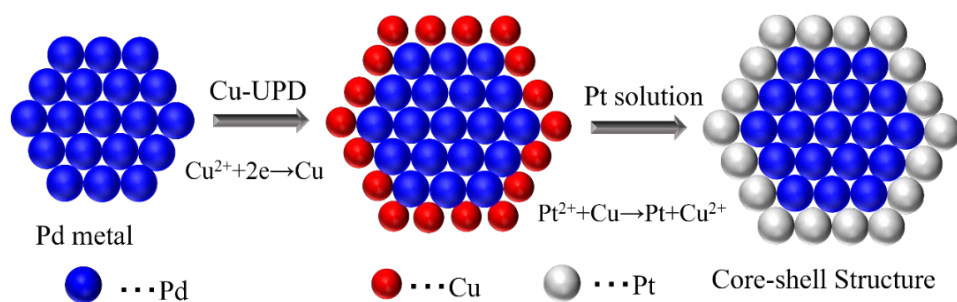


Figure 2-10. Schematic diagram of the Cu-UPD process.

The amount of Cu deposited on the Pd surface was controlled by regulating the stirring time, and after the PtCl_4^{2-} replacement, the Pt content in the obtained catalysts was determined by ICP measurements. As shown in Figure 2-8b, the Pt content increases linearly with increasing reaction time until reaching a stable monolayer structure after approximately 4-5 h of reaction, and a further increase in stirring time only leads to a slight increase in the Pt content. From this result, it can be concluded that once Cu forms a monolayer structure on the Pd surface, the subsequent deposition of the second layer is limited because of the lack of potential difference, preventing the formation of galvanic cells between the metals. Based on the theoretical calculations proposed by Abruña et al.,³⁷ approximating the nanowire structure as a column, it is inferred that the Pt content in PdPt is approximately 50 wt% when forming a monolayer Pt.

A similar trend can be seen in the CV curves in Figure 2-8c, where the Pd hydrogen adsorption peak located around $\sim 0.02\text{ V vs. RHE}$ decreases with increasing reaction time,³⁸ and a noticeable positive shift of the redox peak in the potential range of 0.6 to 0.8 V vs. RHE can be observed, representing a gradual shift of the redox potential from Pd ($\sim 0.7\text{ V vs. RHE}$) to Pt ($\sim 0.8\text{ V vs. RHE}$) after the generation of the core-shell structure. Comparing the ORR activities of Pt-NW@Pt/C catalysts at different reaction times (Figure 2-11) showed that catalysts with 4–5-hour reaction times had consistent and higher activity than those with shorter reaction times. This phenomenon also demonstrates the gradual formation of a complete Pt monolayer on the Pd surface.

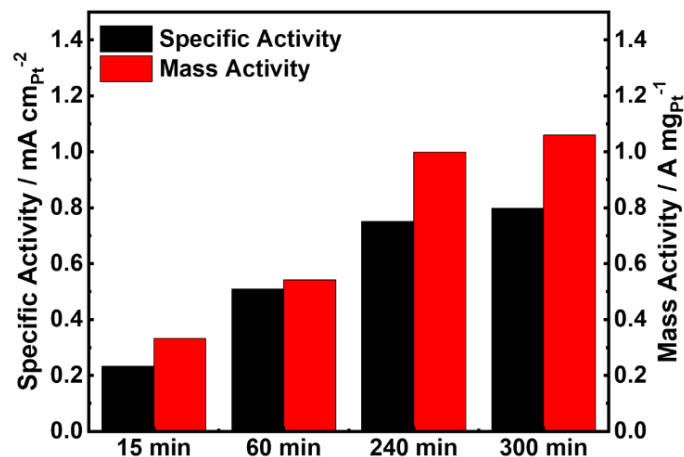


Figure 2-11. Comparison of specific activities and mass activities of the Pd-NW@Pt/C catalyst in different reaction time.

Similarly, core-shell NW catalysts (Pd-NW@Pt/C-ref) were also synthesized using the conventional Cu-UPD method. By comparing the CV curves before and after the replacement reaction, the shift in the redox peak demonstrates the formation of a core-shell structure (Figure 2-12). Moreover, the obvious Pd hydrogen adsorption peak proves that the synthesized catalysts can encapsulate a layer of Pt atoms on the Pd surface, but not uniformly or fully covered. The mass ratio of Pt shells, calculated from the charge (Q) during the chronoamperogram of the corresponding Cu underpotential,⁸ is around 41%, which does not reach the theoretically calculated value for the formation of a complete core-shell structure (Figure 2-13). STEM-EDX results (Figure 2-14) also confirm the incomplete core-shell formation. This finding demonstrates that more precise potential control is required when synthesizing core-shell structures via Cu-UPD for catalysts with irregular surfaces, making it more challenging to form complete core-shell structures.

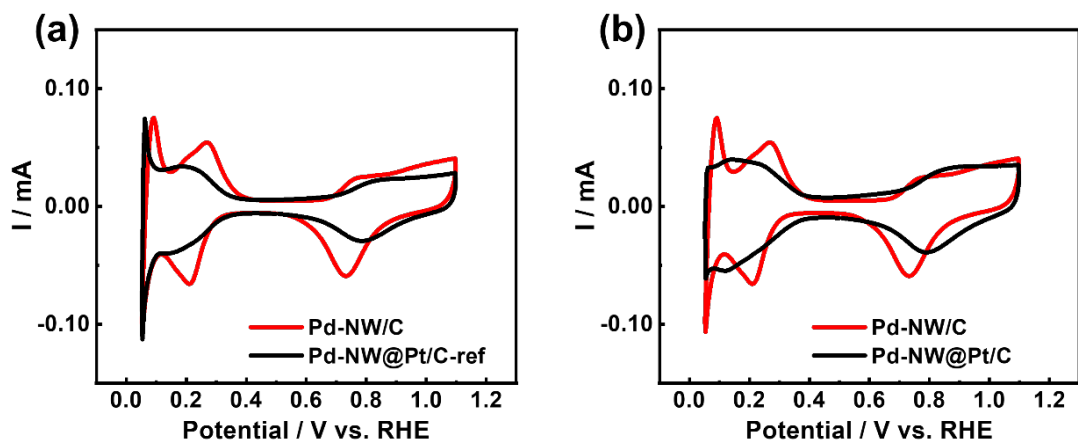


Figure 2-12. Cyclic voltammograms of Pd-NW/C and Pd-NW@Pt/C obtained from (a) Cu-UPD method and (b) galvanic cell method.

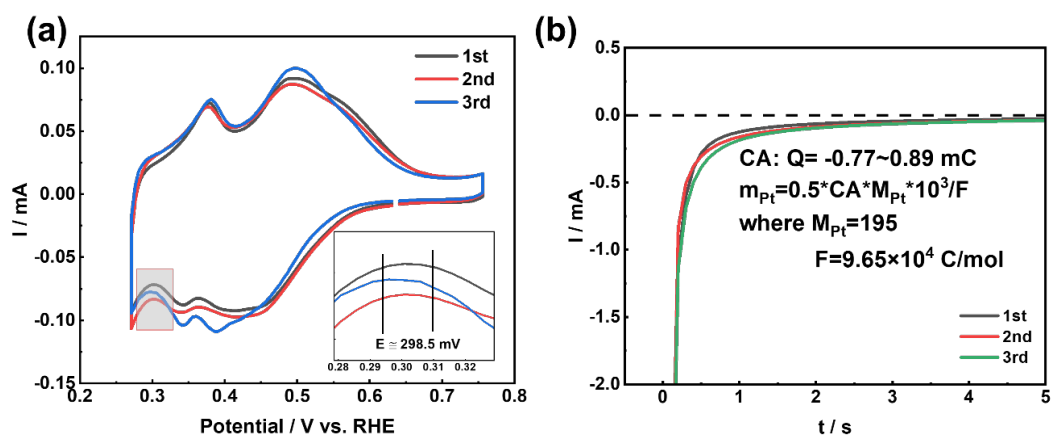


Figure 2-13. (a) Cyclic voltammograms of Cu underpotential deposition on different repeat experiments in N_2 -sat 0.1 M H_2SO_4 and 10 mM CuSO_4 . (b) Chronoamperogram for Pd-NW/C.

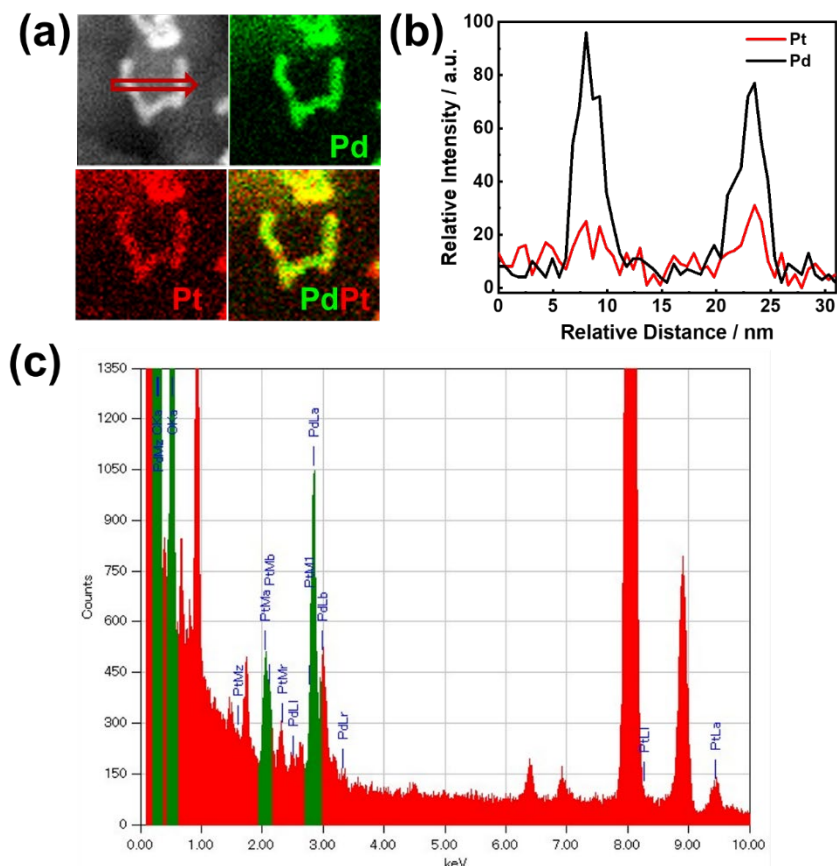


Figure 2-14. (a) STEM-EDX element mapping spectrum, (b) line scanning profiles and (c) elemental analysis of Pd-NW@Pt/C-ref.

Figure 2-15a-c showed TEM and HR-TEM images of Pd-NW@Pt/C after five hours of reaction. The NW structure with a diameter of approximately 2–4 nm is uniformly distributed on the carbon support, and both the apparent surface step and GBs can be clearly observed. The core-shell structure and elemental distribution of Pd-NW@Pt/C were examined using STEM-EDX line profiling (Figure 2-15d and e). The results show that after the substitution reaction, Pt atoms were introduced into the NW structure, forming a complete Pt shell on the surface.

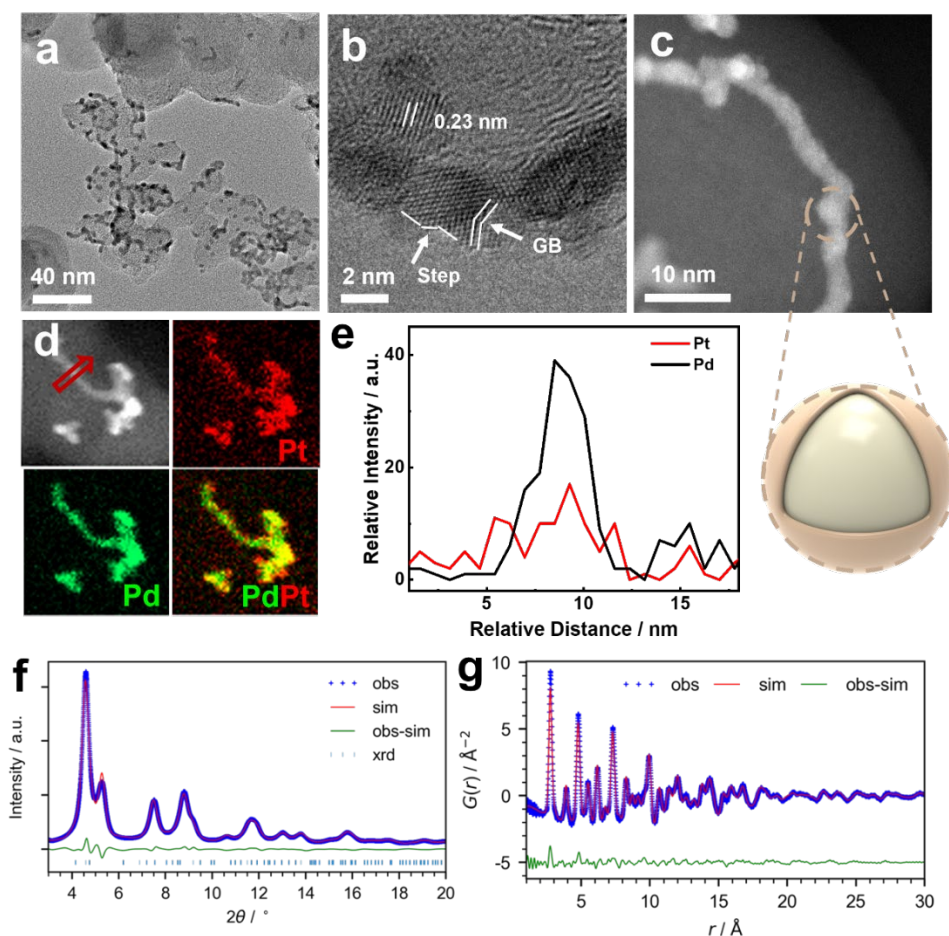


Figure 2-15. (a, b, c) TEM images, (d) STEM-EDX element mapping spectrum, and (e) line scanning profiles of Pd-NW@Pt/C obtained after 5 h reaction. (f) XRD and (g) PDF pattern of Pd-NW@Pt/C.

Figure 2-16a presents the Pd K-edge XANES of Pd-NW@Pt/C and Pd-NP@Pt/C. The absorption features were like those of the Pd foil, indicating the presence of metallic Pd. This observation agrees with the FT-EXAFS spectrum shown in Figure 2-16c. Two notable peaks between 2-3 Å are attributed to Pd-Pd/Pt bond pairs, while the radial peak near 1.3 Å is linked to the Pd-O signal.³⁹ Further fitting analysis shows that the Pd-Pd bond lengths of the Pd-NW@Pt/C and Pd-NP@Pt/C catalysts are 2.779 Å and 2.789 Å, respectively. The shorter bond lengths of NWs are attributed to their polycrystalline structure and structural defects, which produce local micro-strain that further tunes the adsorption of oxygen on the Pt surface.¹⁷

Figure 2-16b show the normalized Pt L_{III}-edge XANES of Pd-NW@Pt/C, Pd-NP@Pt/C and

Pt/C, respectively. The intensity of the white line revealed that all the catalysts were in the metallic state. Pt/C showed a higher white-line absorption peak, which was often linked to oxygen chemisorption on the surface. Furthermore, the significant difference between the two prominent peaks in the FT-EXAFS spectra can be attributed mainly to Pt-Pt/Pd bonds (Figure 2-16d).⁸ A comparison of Pt-Pt bond lengths shows that the Pd-NW@Pt/C and Pd-NP@Pt/C core-shell catalysts, with bond lengths of 2.726 Å and 2.732 Å respectively, are influenced by the ligand effect, leading to shorter distances than conventional Pt/C particles (2.750 Å). This bond contraction likely alters the d-band center, enhancing ORR activity and highlighting the advantages of the NW structure.⁴⁰

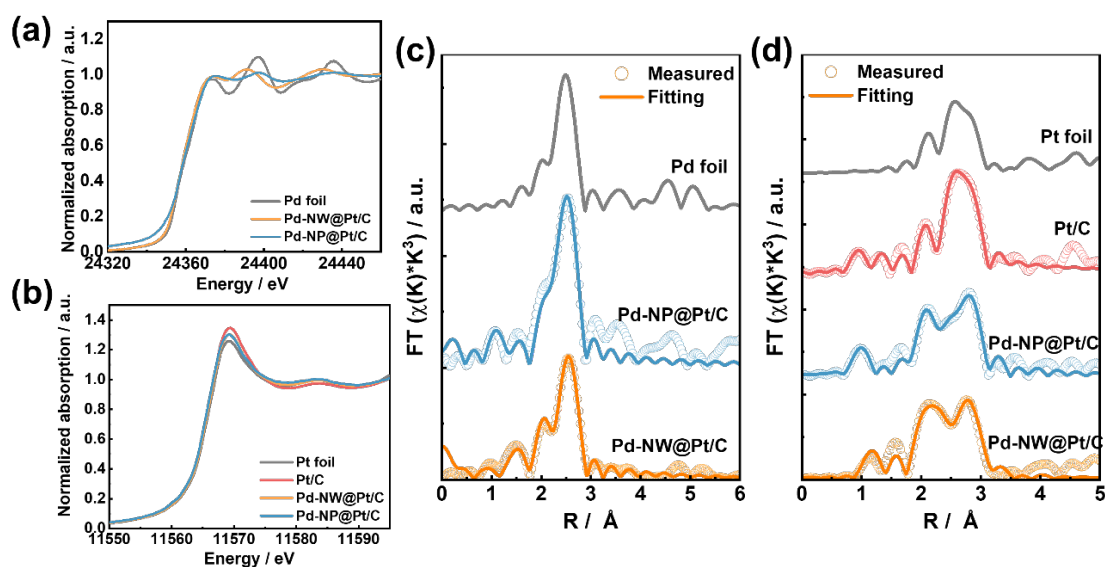


Figure 2-16. (a) Pd K-edge and (c) FT-EXAFS spectra of Pd-NW@Pt/C, Pd-NP@Pt/C and Pd foil, (b) Pt L_{III}-edge XANES spectra and (d) FT-EXAFS spectra of Pd-NW@Pt/C, Pd-NP@Pt/C, Pt/C and Pt foil.

In the Pt 4f XPS spectrum (Figure 2-17), the Pt 4f_{7/2} peak of the Pd-NW@Pt/C catalyst shows a negative shift of ~0.10 eV. This observation indicates a charge transfer from Pd to Pt due to their different electronegativities, further supporting the formation of the Pt@Pd core-shell structure and electronic interactions.^{41, 42}

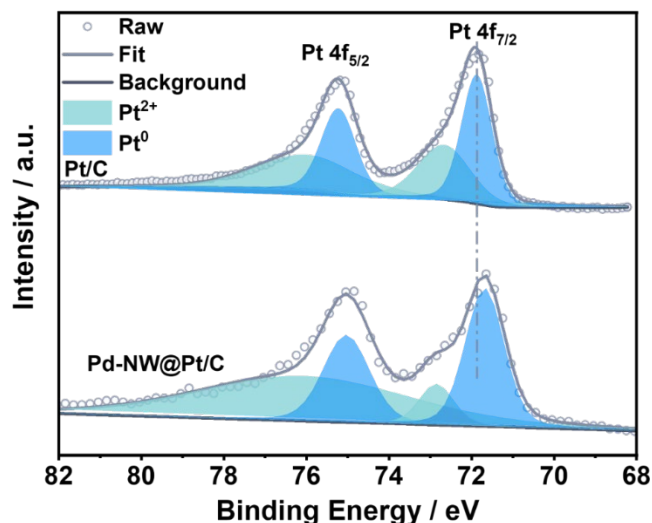


Figure 2-17. Pt 4f XPS spectra of Pt/C and Pd-NW@Pt/C.

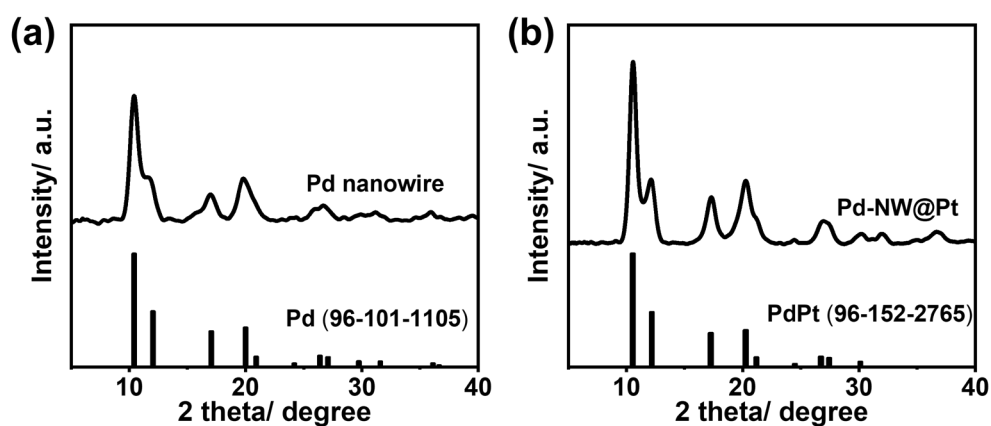


Figure 2-18. XRD pattern of Pd-NW and Pd-NW@Pt/C catalyst.

The XRD and PDF data of Pd-NW@Pt/C (Figure 2-18, Figure 2-19, Figure 2-15f and 2-15g) were also fitted with a curve simulated by fcc and hcp Pd mode. We calculated its lattice constant as $a=3.893$ Å by XRD and $a=3.900$ Å by PDF in the fcc phase from the total scattering patterns (Table 2-2). The core-shell structure exhibits a lattice similar to that of a standard Pd crystal ($a=3.89$ Å) and smaller than that of a Pt crystal ($a=3.92$ Å). The shrinkage of the lattice strain helps maintain a stable lattice structure, which can improve the stability and activity of the catalyst.³²

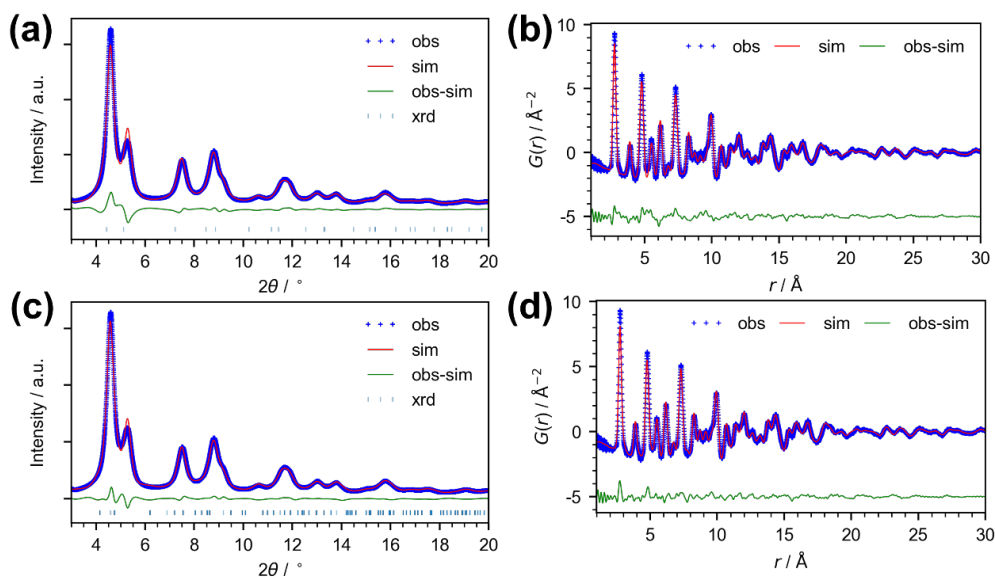


Figure 2-19. Total scattering patterns and Pair distribution functions of Pd-NW@Pt/C. The observed curve was fitted with a curve simulated with (a, b) a fcc Pd model and (c, d) a fcc Pd model and a hcp Pd model.

Table 2-2. Lattice constants of Pd-NW@Pt/C.

Lattice constants in Å	XRD fcc	2 nd phase	PDF fcc	2 nd phase
		<u>hcp</u>		<u>hcp</u>
Pd nanowires (fcc + hcp model)	3.96008(1)	$a = 2.949(4)$ $c = 4.505(8)$	3.958(2)	$a = 2.870(15)$ $c = 4.64(4)$
		<u>hcp</u>		<u>hcp</u>
Core/shell nanowires (fcc + hcp model)	3.8936(6)	$a = 2.879(4)$ $c = 4.556(8)$	3.9008(9)	$a = 2.88(2)$ $c = 4.64(5)$

Core/shell		<u>fcc</u>		
nanowires (fcc model)	3.9102(8)	4.05(1)	3.9032(13)	none

2.3.3 Electrochemical measurement

The electrocatalytic properties of the catalysts with core-shell NW structure were measured using the RDE method. Before the ORR measurements, the catalysts were subjected to 50 CV cycles to remove residual organic matter from the surface. Figure 2-20a shows the CV curves of the Pd-NW@Pt/C-ref, Pd-NW@Pt/C, and Pt/C catalysts obtained after cleaning; the redox peaks in the core-shell NW structured catalysts shifted to higher potentials compared to the Pt/C catalysts, indicating that they are less likely to oxidize and provide higher activity.⁸

To determine their ORR activity, LSVs were measured in oxygen-saturated 0.1 M HClO₄, as shown in Figure 2-20b and Figure 2-21 to 2-23. These results also indicate that the reaction follows a four-electron pathway, and there is a clear trend of a positive shift in the half-wave potential of the core-shell NW structured catalyst compared to Pt/C, confirming that this unique structure can significantly increase the ORR activity, which is further supported by its lower Tafel slope (Figure 2-24). Moreover, the core-shell structure can reduce Pt metal usage while improving the efficiency of Pt utilization. The results in Table 2-3 also show that the core-shell NW catalysts exhibited high electrochemically active surface areas of 132 and 113 m² g_{Pt}⁻¹ for the Pd-NW@Pt/C and Pd-NW@Pt/C-ref, respectively (ECSA normalized by Pt loading). The mass activity of Pd-NW@Pt/C is even as high as 1.06 A mg_{Pt}⁻¹.

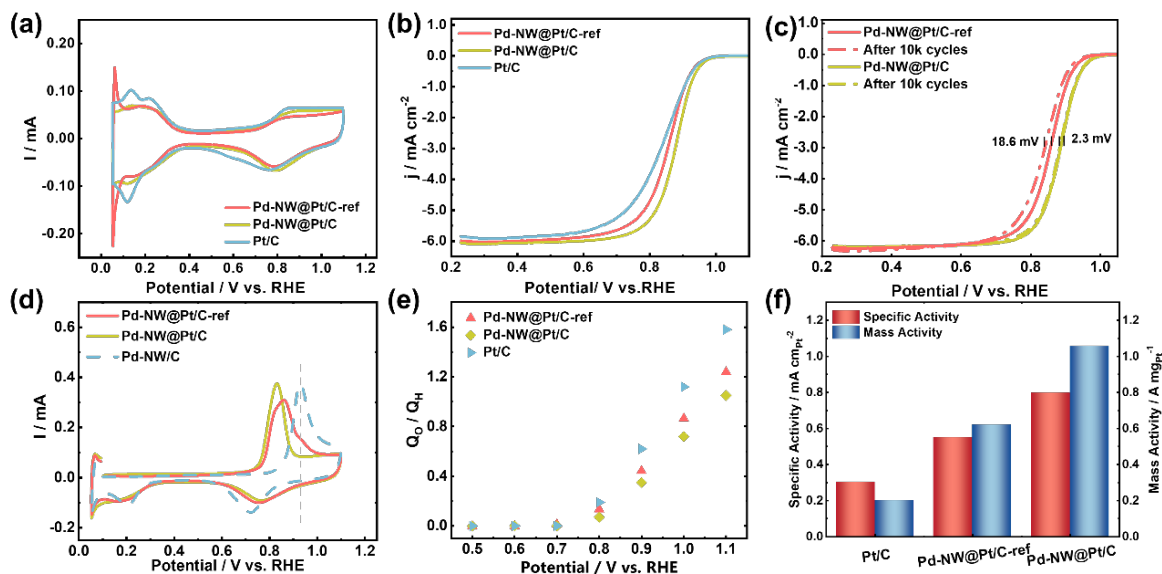


Figure 2-20. (a) CVs and (b) ORR polarization curves (1600 rpm) for the Pd-NW@Pt/C-ref, Pd-NW@Pt/C and Pt/C catalyst, respectively, in O₂-saturated 0.1M HClO₄. (c) ORR polarization curves before and after ADT. (d) The CO-stripping curves and (e) oxygen coverage of the Pd-NW@Pt/C-ref, Pd-NW@Pt/C and Pt/C catalyst. (f) Comparison of specific activities and mass activities.

Table 2-3. ECSA of Pd-NW@Pt/C. and Pd-NW@Pt/C-ref catalysts calculated by CO-stripping and H_{UPD}

ECSA (m ² /g _{Pt})	Pt/C	Pd-NW@Pt/C_Gal	Pd-NW@Pt/C_UPD
CO stripping	68	121	105
H _{UPD}	64	132	113

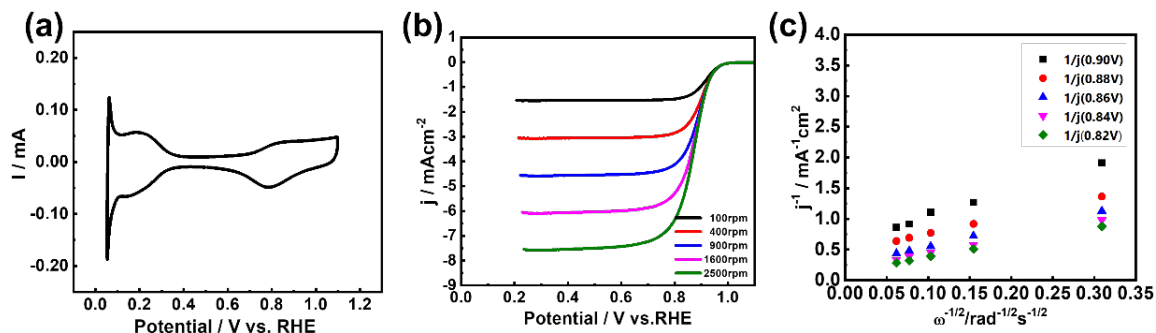


Figure 2-21. (a) Cyclic voltammograms of Pd-NW@Pt/C-ref obtained from Cu-UPD method. (b) linear sweep voltammogram and (c) Koutecky-Levich plot.

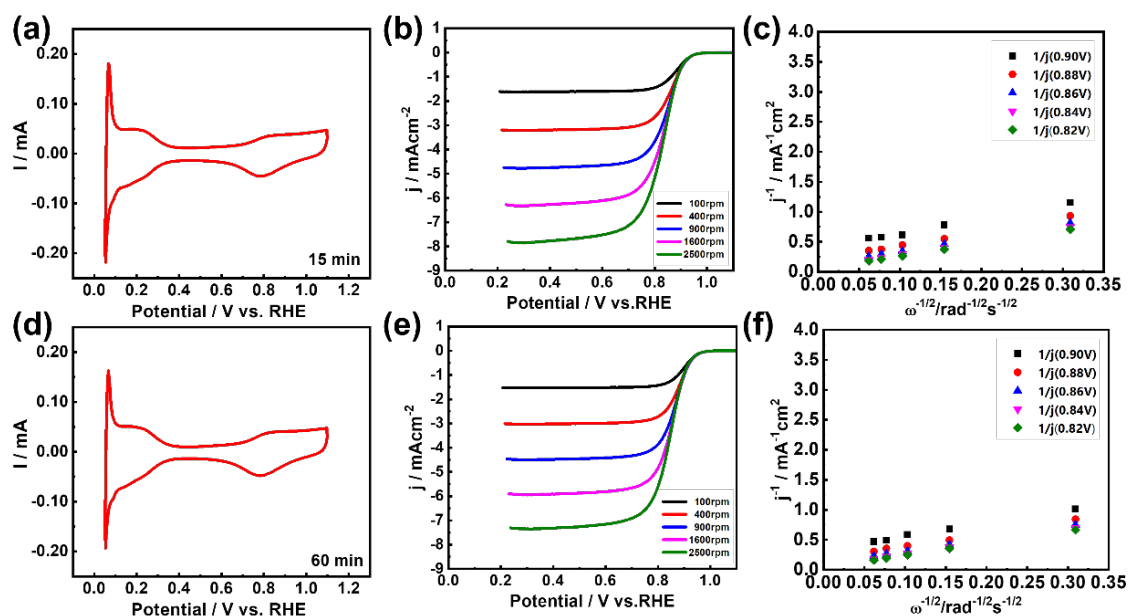


Figure 2-22. (a) Cyclic voltammograms, (b) linear sweep voltammogram (c) and Koutecky-Levich plot for Pd-NW@Pt/C catalyst obtained in 15 min and (d-f) in 30 min reaction.

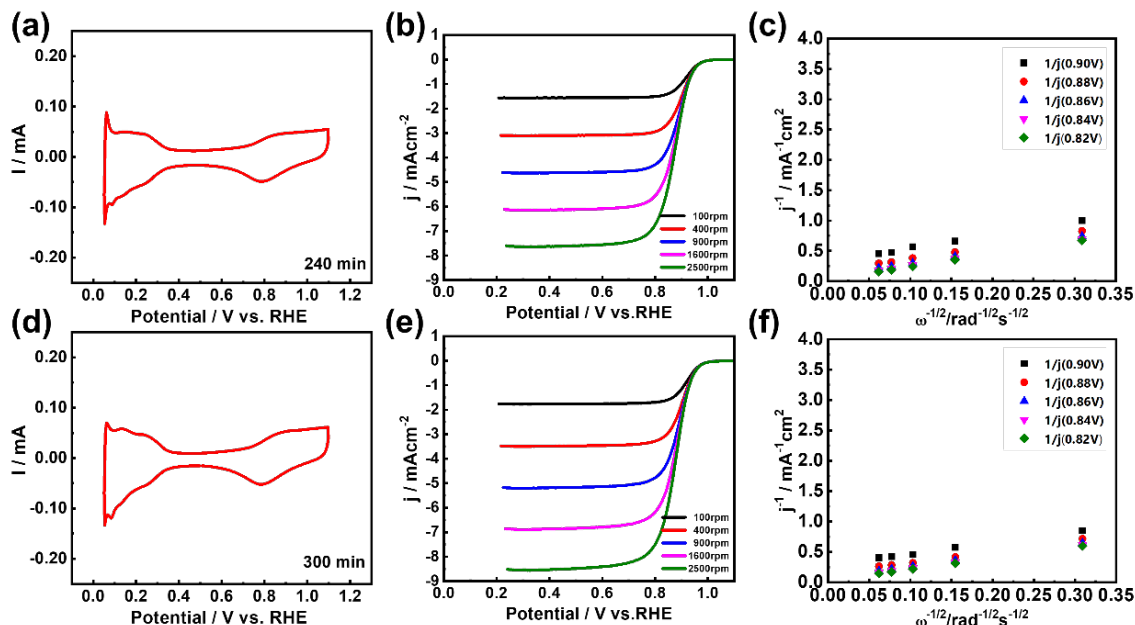


Figure 2-23. (a) Cyclic voltammograms, (b) linear sweep voltammogram (c) and Koutecky-Levich plot for Pd-NW@Pt/C catalyst obtained in 4 h and (d-f) in 5 h reaction.

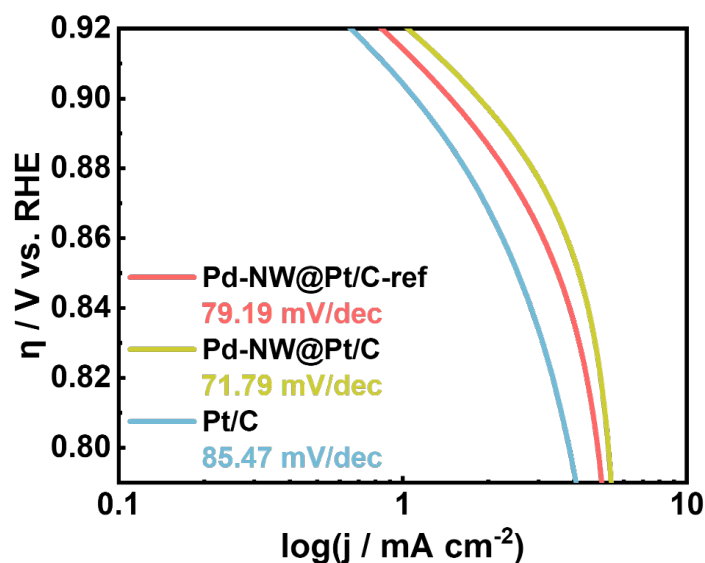


Figure 2-24. Tafel plot for the Pd-NW@Pt/C-ref, Pd-NW@Pt/C, and Pt/C catalyst, respectively.

To investigate the impact of surface Pt coverage on ORR activity, the catalysts synthesized by the two methods were fully compared. The Pd-NW@Pt/C synthesized by the galvanic cell method with a fully-covered Pt shell layer showed a higher specific activity ($0.80 \text{ mA cm}_{\text{Pt}}^{-2}$)

compared to the Pd-NW@Pt/C-ref with an incomplete shell layer ($0.55 \text{ mA cm}_{\text{Pt}}^{-2}$) (Figure 2-20f). This result indicates that the complete coating of Pt significantly increases catalytic activity. The long-term durability of the core-shell NWs catalysts was further investigated by ADT, as shown in Figure 2-20c. After 10 K cycles, the Pd-NW@Pt/C exhibits a small negative shift of $\sim 2.3 \text{ mV}$ in the half-wave potential. In contrast, under the same test conditions, Pd-NW@Pt/C-ref exhibited more severe degradation, with a significant half-wave potential decrease of 18.6 mV after ADT tests. This could be due to insufficient protection of exposed Pd, leading to accelerated dissolution and promoting the formation of Pt clusters and holes as reported previously.^{25, 43}

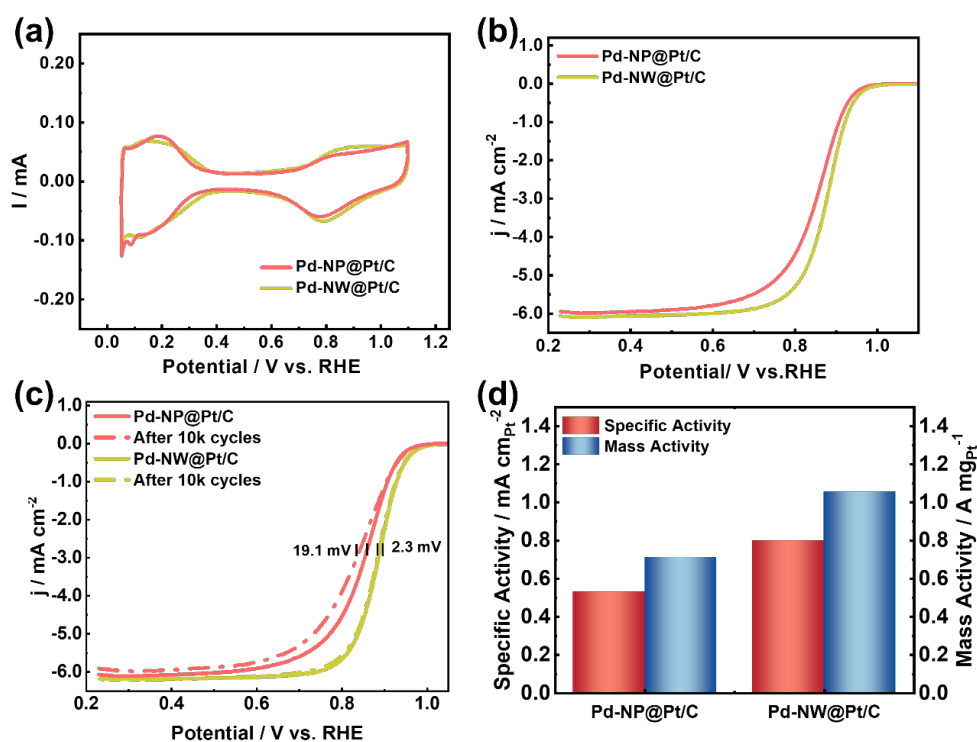


Figure 2-25. (a) CVs and (b) ORR polarization curves (1600 rpm) for the Pd-NW@Pt/C and Pd-NP@Pt/C catalyst. (c) ORR polarization curves before and after ADT. (d) Comparison of specific activities and mass activities.

Additionally, the developed Pd-NW@Pt/C catalyst demonstrated higher ORR activity and stability compared to the core-shell nanoparticle catalyst (Pd-NP@Pt/C) (Figure 2-25). The NW structure contains numerous GBs,⁴⁴ leading to more surface atomic deformation and strain, which exposes more high-index facets, effectively enhancing ORR activity.^{45, 46} Beside

nanoparticles tend to aggregate and undergo Ostwald ripening during ADT, whereas nanowires preserve their structural integrity, leading to more stable catalytic activity.⁴⁷

The CO-stripping results (Figure 2-20d) show that the peaks of the core-shell NW- structured catalysts are significantly shifted to the left compared to those of the Pd-NW/C catalysts, indicating the formation of the Pt layer. The Pd-NW@Pt/C-ref catalyst exhibits a broad CO-stripping peak with a small peak near ~ 0.92 V vs. RHE, the same position as the CO-stripping peak of Pd-NW/C, indicating an incomplete core-shell structure. In contrast, the Pd-NW@Pt/C catalyst shows a significant negative shift, suggesting weaker binding energy with oxygenated species, which favors ORR.⁴⁸

Oxygen coverage plays an important role in determining the extent of oxide binding on the catalyst surfaces.⁴⁹ Analysis from Figure 2-26 and Figure 2-20e reveals the reduction current profiles of the three catalysts. As the polarization potential increases from 0.50 to 1.10 V vs. RHE, oxygen coverage also increases. At 0.8 V vs. RHE, Q_O/Q_H surpasses 0.0, signifying the inception of Pt-OH oxide on the catalyst surface, which involves a single electron transfer.⁵⁰ At 1.1 V vs. RHE, Q_O/Q_H goes beyond 1.0, indicating a shift from Pt-OH to Pt-O oxide, necessitating two electron transfers for each platinum site.⁴⁹ Due to active site occupancy, Pt no longer engages in the ORR process in this state. Lower oxygen coverage of Pd-NW@Pt/C compared with the other catalysts suggests that fewer oxygen species are adsorbed on the surface at high potentials, and the Pt-O binding energy was weaker. The increased oxygen coverage observed in the Pd-NW@Pt/C-ref catalyst is attributed to the involvement of both Pt and Pd atoms in the oxidation process. The incomplete core-shell structure exposes Pd atoms with stronger oxygen binding energy, leading to secondary adsorption as oxygen molecules diffuse into the inner Pd layer.^{51, 52} This result demonstrates that the incomplete core-shell structure promotes further oxidation and solubilization of Pt and Pd, thereby decreasing ORR activity.

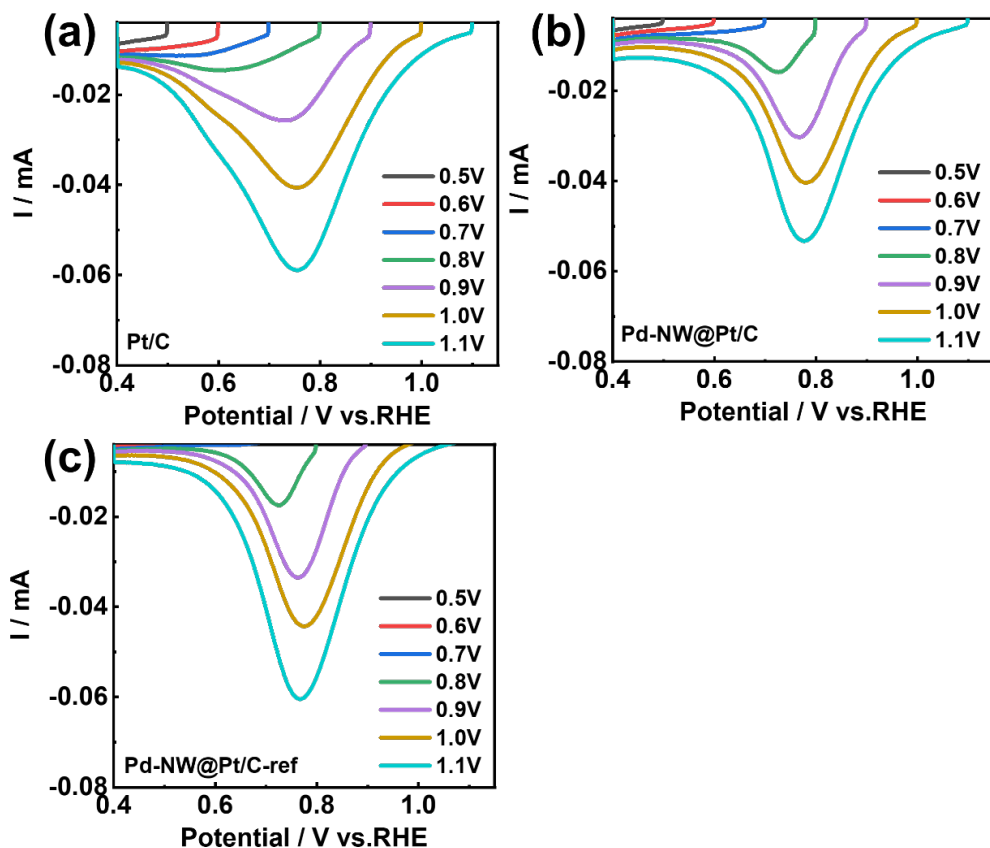


Figure 2-26. Reduction current profiles of oxide species on (a) Pt/C and (b) Pd-NW@Pt/C and (c) Pd-NW@Pt/C-ref catalyst.

2.3.4 Chemisorption observation from *operando* HERFD-XANES

To clarify the electronic states of Pt in the different catalysts during ORR, *operando* HERFD-XANES was employed. This approach outperforms traditional XAS in its ability to shorten the effective core-hole lifetime, particularly at the Pt L_{III} -edge. By stimulating $2p$ electrons towards either a single resonance tied to $5d$ holes or the s and d continuum states, HERFD-XAS achieves a sharper clarity than conventional XAS.^{34, 53-56}

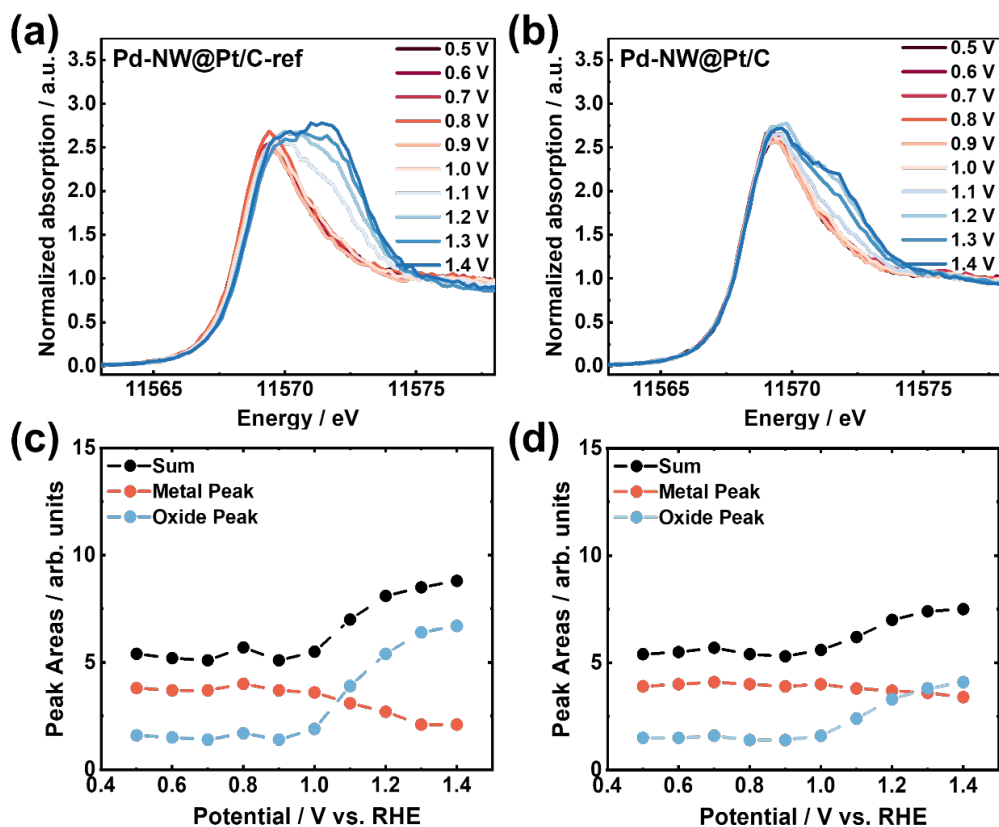


Figure 2-27. *operando* HERFD- Pt L_{III}-edge XAS analysis for (a) Pd-NW@Pt/C-ref and (b) Pd-NW@Pt/C catalyst at different polarization potential. Integrated peak areas of metal peak, oxides peak, and sum peak for (c) Pd-NW@Pt/C-ref and (d) Pd-NW@Pt/C.

A notable peak broadening and positive shift in the Pt L_{III}-edge white line intensity was observed with increasing polarization potential, especially in the Pt/C catalyst, due to Pt oxidation (Figure 2-27 and Figure 2-28). During 0.5 to 0.8 V vs. RHE, Pt showed hydroxyl (OH) adsorption,⁵⁷ as indicated by a slight shift in the peak and enhanced white line intensity. At potentials above 1.0 V vs. RHE, the Pt/C catalyst underwent a distinct oxidation process, eventually forming Pt-O bonds.⁵³ However, this change was not significant for Pd-NW@Pt/C, Pd-NW@Pt/C-ref, which suggests that the interaction between Pt and Pd in the core-shell structure reduces the binding energy of Pt with oxygen species, thereby inhibiting significant oxidation of Pt to PtO or PtO₂.

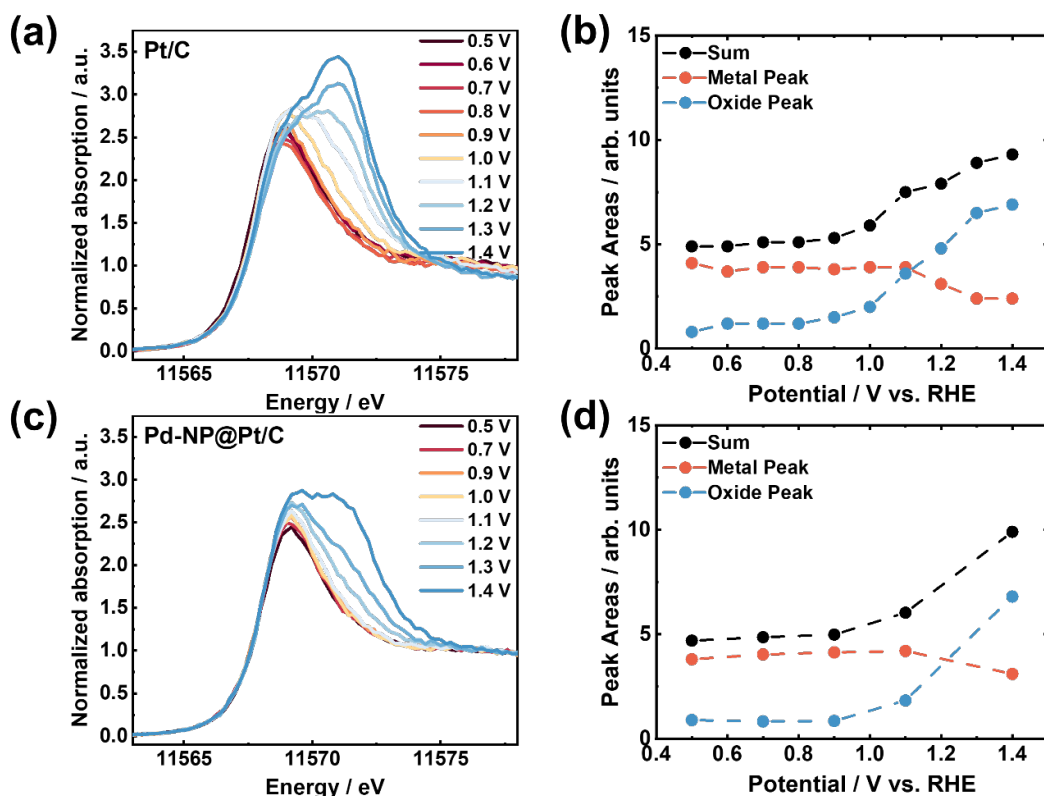


Figure 2-28. *operando* HERFD- Pt L_{III} -edge XANES analysis for (a) Pt/C and (c) Pd-NP@Pt/C catalyst varying different polarization potential. Integrated peak areas of metal peak, oxides peak and sum peak for (b) Pt/C and (d) Pd-NP@Pt/C catalyst.

In the spectral analysis, the arctangent function and two pseudo-Voigt peaks were used to map the two prominent peaks representing the metallic and oxidized forms of Pt.³⁴ As illustrated in Figures 2-28, 2-29, Figure 2-27c, and 2-27d, it is evident that the Pt oxide component is amplified with an increase in the polarization potential. In contrast to nanoparticle catalysts like Pt/C and Pd-NP@Pt/C, the core-shell NWs catalyst inhibits this oxidation because of its unique structural defects, which can weaken oxygen adsorption energy. It is worth noting that although the Pd-NW@Pt/C-ref can limit the production of PtO_x , the high polarization potential still leads to its conversion, which may cause Pt corrosion and reduce catalyst efficiency.⁵⁸ Differently, the oxidation of Pd-NW@Pt/C was significantly lower than that of Pd-NW@Pt/C-ref. The antioxidant property is attributed to the homogeneous Pt shell, which effectively protects the internal Pd, slows surface agglomeration and dissolution, and consequently reduces the binding energy to oxygen.

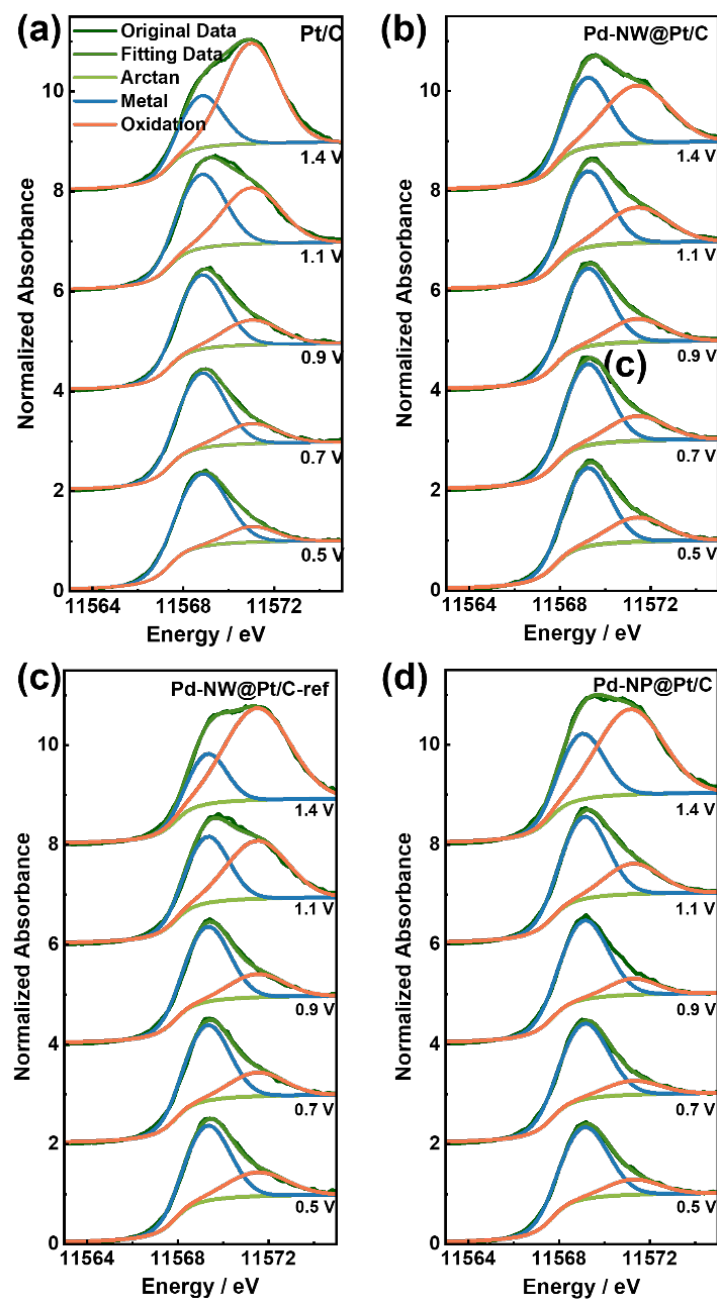


Figure 2-29. Least-square fits by two peaks (metal peak and oxides peak) for all HERFD-XAS spectra for (a) Pt/C, (b) Pd-NW@Pt/C, (c) Pd-NW@Pt/C-ref and (d) Pd-NP@Pt/C catalyst.

2.3.5 Conventional *operando* XAS measurements

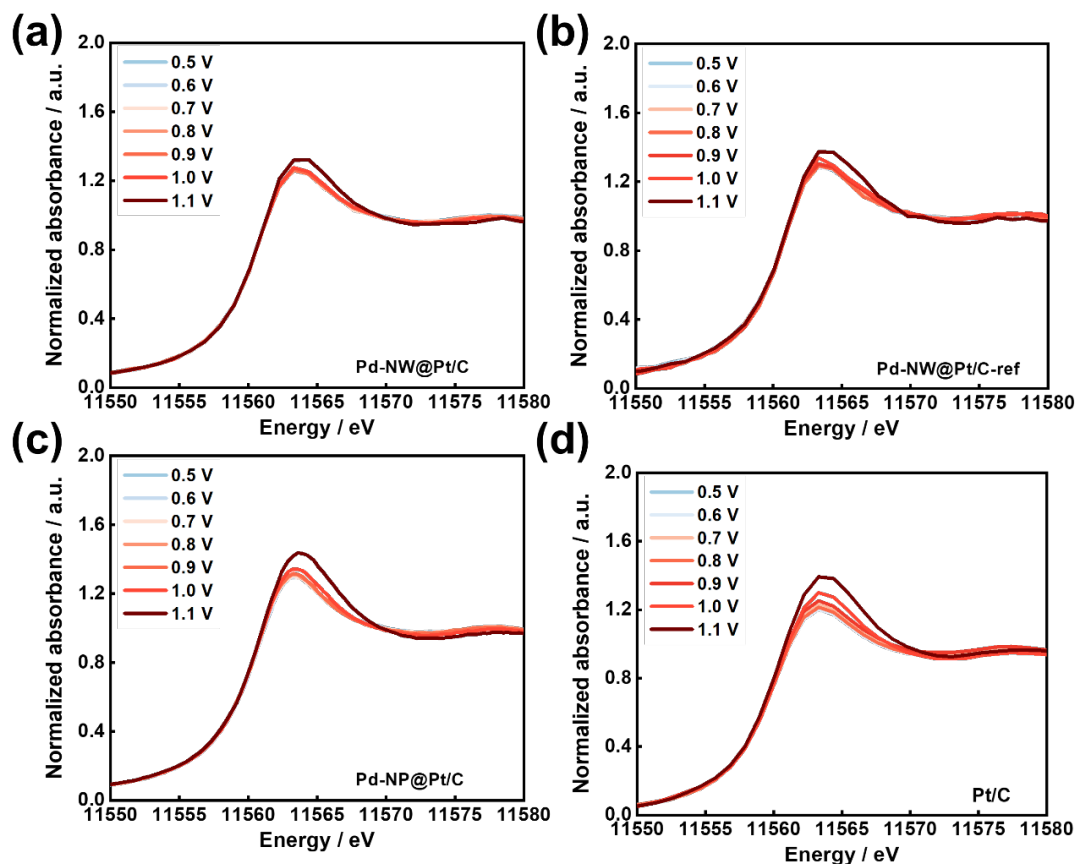


Figure 2-30. Normalized Pt L_{III}-edge XANES of (a) Pd-NW@Pt/C; (b) Pd-NW@Pt/C-ref; (c) Pd-NP@Pt/C and (d) Pt/C catalyst at different potential.

Figure 2-30 shows the normalized Pt L_{III}-edge XANES of the four catalysts at different potentials (0.5 to 1.1 V vs. RHE) to investigate the surface Pt oxidation state. Changes in the Pt oxidation state is detected by variations in the white line intensity (Δ XANES). As shown in Figure 2-31c, the Pt L_{III}-edge white line intensity peaks of both Pd-NW@Pt/C and Pd-NW@Pt/C-ref catalysts pronounced with increasing potential. The more complete Pt layer structure of Pd-NW@Pt/C exhibits a lower white line intensity, consistent with the HERFD-XANES results. This phenomenon was also observed in the results of Pt L_{II}-edge XANES spectra (Figure 2-32). FT-EXAFS and fitting results for Pd-NW@Pt/C, Pd-NW@Pt/C-ref, and Pd-NP@Pt/C are shown in Figure 2-33, Figure 2-31a and 2-31b, respectively. As higher polarization potential is applied, the Pt-O signal increases while the Pt-Pt signal decreases.

Additionally, the wavelet-transform EXAFS spectra (Figure 2-34) show the formation of Pt-O bonds at high potentials. However, Pd-NW@Pt/C showed smaller changes in the Pt-O regions than the other catalysts, suggesting lower binding energy with oxygenated species and less Pt-O bond formation on the Pt surface.

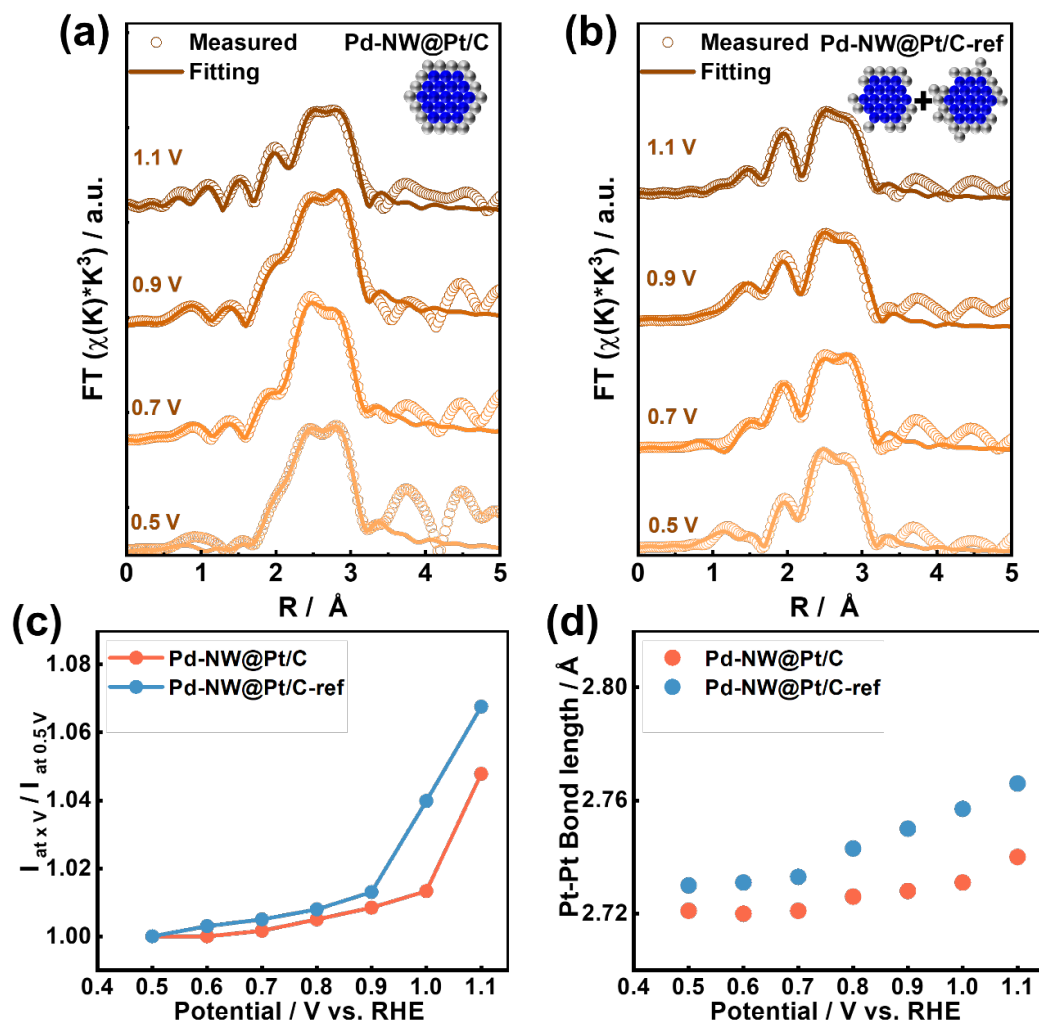


Figure 2-31. Pt L_{III}-edge FT-EXAFS spectra and corresponding fits for (a) Pd-NW@Pt/C and (b) Pd-NW@Pt/C-ref catalyst at different polarization potentials. (c) $\Delta\mu$ of the white line peak heights and (d) Pt-Pt bond length from the corresponding fitting results for Pd-NW@Pt/C and Pd-NW@Pt/C-ref catalyst.

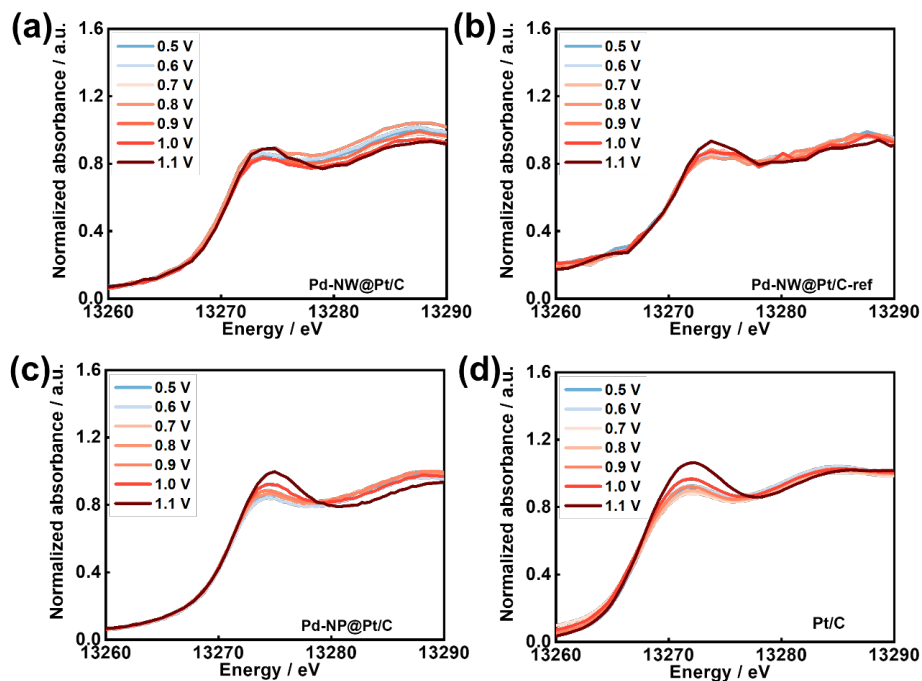


Figure 2-32. Normalized Pt L_{II}-edge XANES of (a) Pd-NW@Pt/C; (b) Pd-NW@Pt/C-ref; (c) Pd-NP@Pt/C and (d) Pt/C catalyst at different potential.

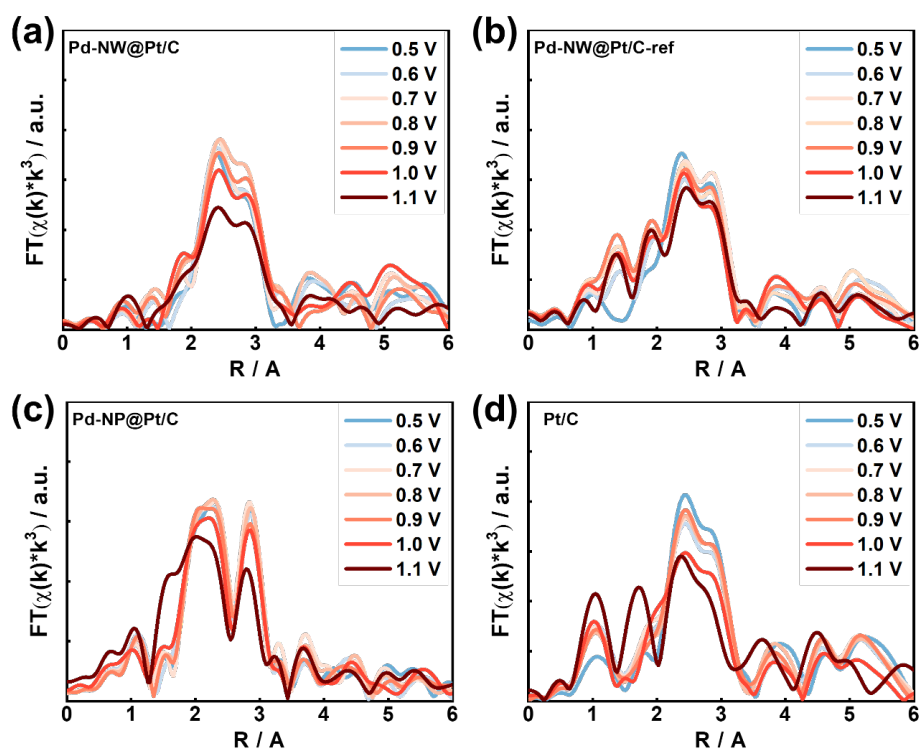


Figure 2-33. Pt L_{III}-edge FT-EXAFS spectra for (a) Pd-NW@Pt/C; (b) Pd-NW@Pt/C-ref; (c) Pd-NP@Pt/C and (d) Pt/C catalyst at different potential.

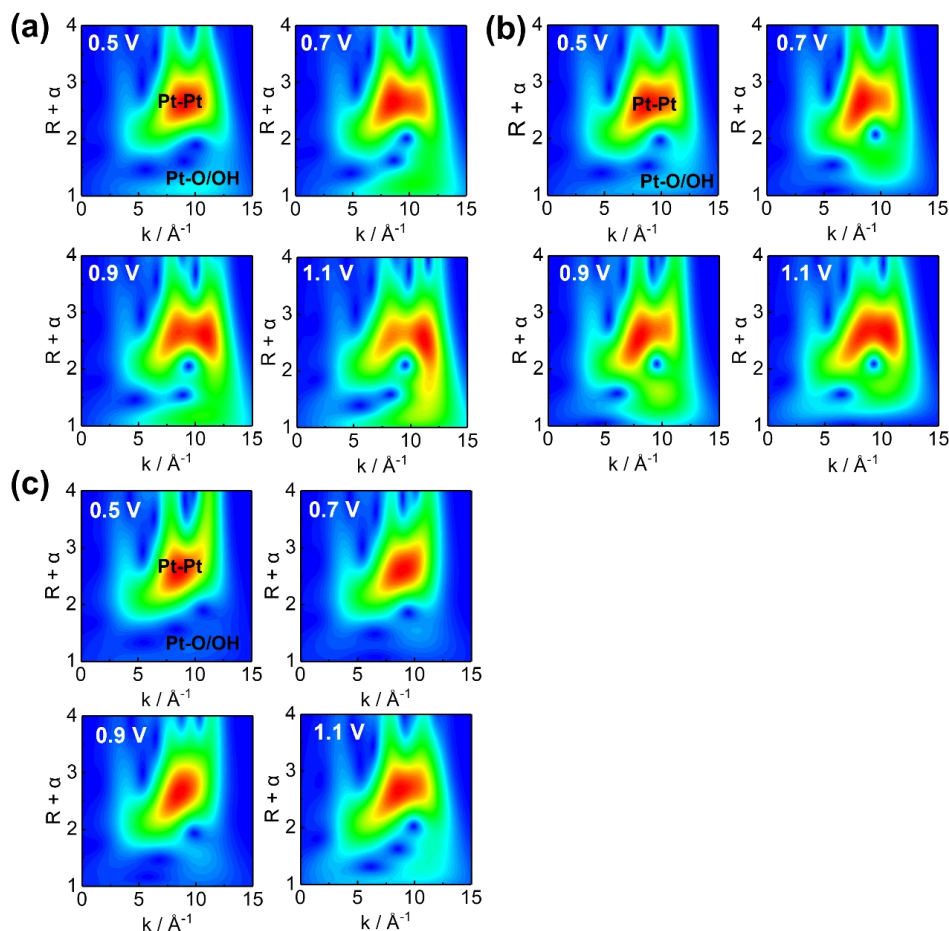


Figure 2-34. WT-EXAFS for (a) Pt/C, (b) Pd-NW@Pt/C-ref and (c) Pd-NW@Pt/C at different potentials.

Pt–Pt bond lengths were obtained from the FT-EXAFS results to understand the local structures, which is an important factor that can respond to the *d*-band center and thus affect the ORR activity.²⁵ Figure 2-31d, Figure 2-35, Table 2-4, 2-5 and 2-6 show the results of fitting and detailed fitting information. The Pt–Pt bond lengths of Pd-NW@Pt/C at 0.5 V vs. RHE is 2.721 Å, which is shorter compared to Pd-NW@Pt/C-ref (2.730 Å) and Pd-NP@Pt/C (2.735 Å). The difference in Pt-Pt bond lengths between the Pd-NW@Pt/C and Pd-NW@Pt/C-ref catalysts is attributed to variations in their Pt layer structures. Pd-NW@Pt/C has a uniform and dense Pt layer, while Pd-NW@Pt/C-ref exhibits heterogeneous Pt deposits due to the uneven nanowire surface and less precise control over the UPD potential. As a result, the average Pt-Pt bond length is shorter in Pd-NW@Pt/C due to its more consistent coverage. With increasing potential, the Pt-Pt bond length gradually becomes longer due to the decrease of Pt-Pt

coordination number and the formation of Pt-O,⁴⁹ which reaches 2.766 Å for Pd-NW@Pt/C-ref, 2.761 Å for Pd-NP@Pt/C and only 2.740 Å for Pd-NW@Pt/C at 1.1 V. The longer Pt-Pt bond length and increase in Pt-O coordination number indicate a rise in oxygenated species, which is detrimental to the ORR process.

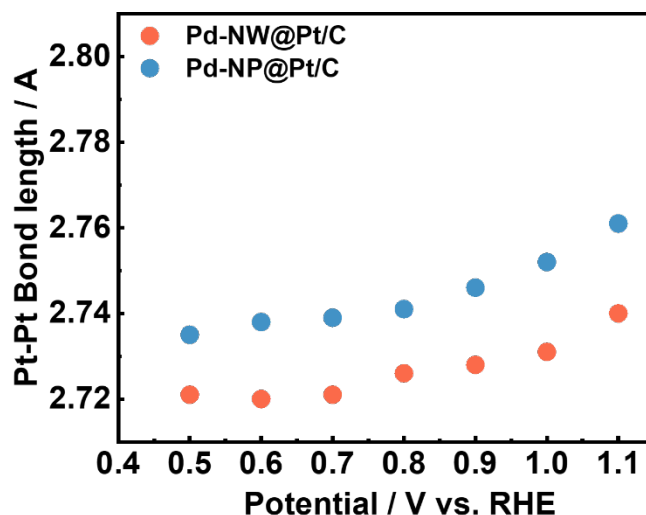


Figure 2-35. Pt-Pt bond length from the corresponding fitting results for Pd-NW@Pt/C and Pd-NP@Pt/C catalyst.

Moreover, at 1.1 V, the Pt-Pd bond length of Pd-NW@Pt/C-ref increases significantly to 2.760 Å, indicating a tendency for some Pt atoms to detach from Pd and form surface clusters.²⁵ In contrast, the change in Pd-NW@Pt/C is small, with the bond length at 2.741 Å and the Pt-Pd coordination number remaining almost constant. Some research showed that the Pt layer can reorganize to form Pt clusters and holes, exposing internal Pd atoms to the electrolyte. During the ORR process, these internal Pd atoms are gradually etched, with some Pd ions reducing and depositing on the carbon support. This results in a loss of core-shell structural dominance and a decrease in ORR activity, a phenomenon exacerbated by incomplete Pt shell layers.^{25, 43, 59, 60} Therefore, protecting the Pd core is crucial in developing Pd@Pt catalysts. The Pd-NW@Pt/C catalyst prepared using our proposed method, features a complete Pt layer, resulting in a shorter Pt-Pt bond length, better protection for the internal Pd core, and reduced binding energy between Pt and oxygen-containing species, thus enhancing catalytic activity.

Table 2-4. The corresponding R space curve fitting results of Pt L_{III}-edge for the Pd-NW@Pt/C catalysts varying different potential. Fitting details: S_0^2 was fixed at 0.90, which was obtained by fitting the reference foils. Fits were undergone in R-space for $1.2 \leq R \leq 3.2$ Å, and the k_{1,2,3} weighting for $\Delta k = 3 - 12$ Å⁻¹.

	Bond	Length/Å	CN	$\Delta E/eV$	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.721(3)	7.0(4)	7.816	0.008(5)	0.1%
	Pt-Pd	2.721(4)	1.8(2)	8.170	0.008(4)	
	Pt-O	2.050(2)	0.1(1)	-12.76	0.002(1)	
0.6 V	Pt-Pt	2.720(5)	6.8(6)	6.589	0.006(1)	0.8%
	Pt-Pd	2.700(7)	1.5(3)	8.052	0.005(3)	
	Pt-O	1.970(3)	0.1(3)	-15.80	0.005(2)	
0.7 V	Pt-Pt	2.720(7)	6.5(7)	7.166	0.006(3)	0.2%
	Pt-Pd	2.721(2)	1.5(5)	8.493	0.006(2)	
	Pt-O	2.050(3)	0.1(2)	-21.01	0.005(1)	
0.8 V	Pt-Pt	2.728(8)	6.3(4)	7.802	0.009(4)	0.8%
	Pt-Pd	2.710(2)	1.2(4)	8.156	0.004(3)	
	Pt-O	2.044(3)	0.2(1)	8.980	0.009(6)	
0.9 V	Pt-Pt	2.726(9)	7.5(7)	7.835	0.008(3)	0.2%
	Pt-Pd	2.710(3)	1.4(5)	7.460	0.006(2)	
	Pt-O	2.031(4)	0.2(7)	-10.20	0.008(4)	
1.0 V	Pt-Pt	2.731(7)	7.1(9)	9.062	0.008(2)	0.2%

	Pt-Pd	2.721(3)	1.9(8)	7.532	0.009(5)	
	Pt-O	2.022(9)	0.5(5)	7.413	0.014(6)	
1.1 V	Pt-Pt	2.740(8)	4.8(8)	10.78	0.009(3)	1.1%
	Pt-Pd	2.741(8)	1.1(7)	7.807	0.007(2)	
	Pt-O	2.022(7)	1.1(9)	15.84	0.006(5)	

Table 2-5. The corresponding R space curve fitting results of Pt L_{III}-edge for the Pd-NW@Pt/C_ref catalysts varying different potential.

	Bond	Length/Å	CN	ΔE/eV	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.730(7)	7.1(5)	5.075	0.005(4)	0.8%
	Pt-Pd	2.721(2)	0.5(3)	10.77	0.008(2)	
	Pt-O	2.099(2)	0.1(1)	4.115	0.007(4)	
0.6 V	Pt-Pt	2.731(5)	8.9(2)	4.607	0.003(1)	0.3%
	Pt-Pd	2.735(8)	0.5(2)	15.72	0.004(2)	
	Pt-O	2.045(2)	0.1(5)	18.17	0.005(2)	
0.7 V	Pt-Pt	2.733(3)	9.0(6)	3.948	0.007(3)	0.5%
	Pt-Pd	2.740(6)	0.5(3)	14.95	0.007(5)	
	Pt-O	2.050(3)	0.1(2)	26.75	0.006(4)	
0.8 V	Pt-Pt	2.743(9)	6.9(5)	8.036	0.005(4)	0.6%
	Pt-Pd	2.741(3)	0.6(3)	13.90	0.002(1)	

	Pt-O	2.044(3)	0.4(2)	-24.92	0.001(1)	
0.9 V	Pt-Pt	2.750(6)	8.0(10)	7.711	0.009(7)	0.5%
	Pt-Pd	2.740(7)	0.5(7)	4.351	0.008(3)	
	Pt-O	2.040(4)	0.5(5)	12.77	0.037(9)	
1.0 V	Pt-Pt	2.757(6)	8.0(4)	10.35	0.006(2)	0.5%
	Pt-Pd	2.742(2)	0.5(3)	-0.007	0.007(4)	
	Pt-O	2.001(3)	0.6(2)	18.61	0.006(4)	
1.1 V	Pt-Pt	2.766(4)	4.4(8)	11.92	0.005(1)	1.9%
	Pt-Pd	2.760(5)	1.0(5)	6.082	0.008(7)	
	Pt-O	1.990(4)	1.6(9)	19.06	0.016(4)	

Table 2-6. The corresponding R space curve fitting results of Pt L_{III}-edge for the Pd-NP@Pt/C catalysts varying different potential.

	Bond	Length/Å	CN	$\Delta E/eV$	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.735(8)	7.0(3)	7.816	0.007(3)	0.1%
	Pt-Pd	2.711(2)	1.8(2)	8.170	0.008(4)	
	Pt-O	2.050(1)	0.1(1)	12.74	0.007(2)	
0.6 V	Pt-Pt	2.738(8)	6.7(7)	6.589	0.006(4)	0.7%
	Pt-Pd	2.715(8)	1.5(4)	8.052	0.005(3)	
	Pt-O	2.050(1)	0.1(5)	-15.80	0.005(2)	

0.7 V	Pt-Pt	2.739(2)	6.5(5)	7.166	0.006(4)	0.2%
	Pt-Pd	2.710(1)	1.6(4)	8.493	0.006(4)	
	Pt-O	2.050(1)	0.1(2)	21.10	0.009(7)	
0.8 V	Pt-Pt	2.741(7)	6.9(5)	8.036	0.005(4)	0.5%
	Pt-Pd	2.710(4)	1.1(3)	8.156	0.004(2)	
	Pt-O	2.045(3)	0.2(3)	8.980	0.004(3)	
0.9 V	Pt-Pt	2.746(9)	7.5(10)	7.832	0.008(7)	0.2%
	Pt-Pd	2.710(7)	1.4(5)	7.460	0.006(5)	
	Pt-O	2.024(4)	0.6(6)	10.20	0.004(3)	
1.0 V	Pt-Pt	2.752(7)	6.7(4)	9.062	0.008(2)	0.2%
	Pt-Pd	2.720(4)	1.9(4)	7.533	0.009(6)	
	Pt-O	2.022(10)	0.9(8)	7.413	0.015(7)	
1.1 V	Pt-Pt	2.761(3)	4.8(4)	10.78	0.009(4)	1.0%
	Pt-Pd	2.740(4)	1.6(6)	7.807	0.008(5)	
	Pt-O	2.009(4)	2.0(7)	15.84	0.006(3)	

2.4 Conclusion

In conclusion, the Pd NWs core with Pt shell catalysts was synthesized using the galvanic cell method without any precise potential control and reducing agents. This method enables large-scale synthesis of core-shell NW catalysts and facilitates obtaining uniform platinum shells, as confirmed by ICP, CO stripping, and STEM analysis. Structural analysis by XRD and PDF showed that Pd-NW@Pt/C had a mixed fcc and hcp phase with shorter lattice constants

than those of standard Pt crystals, reflecting the stability of the structure. As a result, the ORR activity was improved with the high ECSA of $132 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ and superior mass activity of $1.06 \text{ A mg}_{\text{Pt}}^{-1}$, which is 5.1 times than Pt/C. Both *operando* HERFD and conventional XAS analyses revealed that the Pd-NW@Pt/C catalysts have shorter Pt-Pt bond lengths and weaker oxygen binding energies compared to partially-covered Pt shell layer catalysts (Pd-NW@Pt/C-ref) and nanoparticles (Pd-NP@Pt/C), thereby effectively enhancing catalytic activity.

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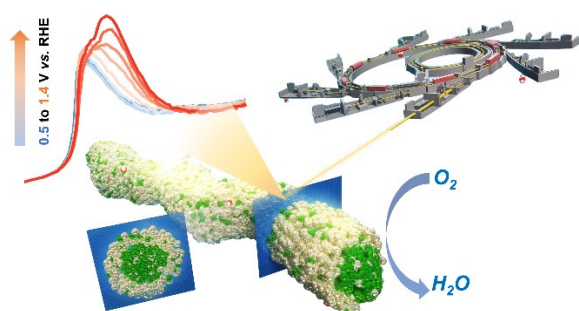
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Chapter 3. Structural Insights and Electronic State Analysis of PtNi Nanowire Catalysts by *operando* High-Energy Resolution Fluorescence Detection X-ray Absorption Spectroscopy



Low-platinum alloy nanowire (NW) catalysts improve the performance of polymer electrolyte membrane fuel cells, but ultrafine PtNi-NW catalysts, particularly those with high Ni content, often experience significant Ni leaching

during electrochemical processes. In this study, a Pt-rich surface layer was successfully formed on PtNi NWs through a simple post-annealing process. Pair distribution function (PDF) analysis revealed a Pt surface layer with a face-centered cubic (fcc) structure, along with internal body-centered cubic (bcc) PtNi and fcc Ni phases. *Operando* X-ray absorption spectroscopy (XAS), including conventional and high-energy resolution fluorescence detection (HERFD) XAS, was used to investigate the catalysts' electronic states and structural changes under oxygen reduction reaction (ORR) conditions. The results showed that the Pt-rich surface layer of PtNi-NW/C catalysts, with its short Pt-Pt bond lengths, effectively suppresses Pt oxidation at high polarization potentials and restricts Ni leaching, leading to a significant increase in ORR-specific activity of $2.07 \text{ mA cm}_{\text{Pt}}^{-2}$, which is a 2.5- and 7-fold activity enhancement compare to Pt-NW/C and commercial Pt/C catalysts.

3.1 Introduction

Polymer electrolyte fuel cells (PEFCs) efficiently convert chemical energy into electrical energy, offering high efficiency, low noise, and clean operation.¹⁻³ Due to their potential as a reliable energy source, they have gained significant attention for

applications in vehicles and portable electronics, addressing the energy crisis.⁴ Carbon-supported Pt nanoparticles (Pt/C) have been widely used as oxygen reduction reaction (ORR) electrocatalysts due to their excellent properties.⁵ However, the high cost and limited utilization of commercial Pt/C catalysts, where approximately 60% of Pt remains inaccessible, pose substantial challenges.^{6, 7} As a result, developing low-platinum catalysts with enhanced activity has become a key area of research to improve PEFC efficiency while reducing costs.

Recent efforts have focused on developing cost-effective electrocatalysts by alloying Pt with transition metals like Fe, Co, and Ni,^{8, 9} which reduces Pt content while enhancing the intrinsic activity of the electrocatalysts.¹⁰ Among these alternatives, PtNi alloys have attracted considerable attention due to the beneficial effects of Ni atoms on the Pt structure, leading to superior catalytic performance.¹¹ Additionally, strategies such as size control,^{12, 13} metal doping,¹⁴ structural modifications,¹⁵ and the creation of specific morphologies such as nanowires (NWs) have been employed to further refine the properties of these alloy catalysts.¹⁶

One-dimensional NWs with active crystalline surfaces, anisotropic structures, minimal aggregation, and efficient conduction have emerged as promising ORR catalysts.¹⁷ For instance, jagged Pt-NWs demonstrate outstanding ORR activity with specific surface structural feature.¹⁸ However, the stability and durability of bimetallic catalysts remain a challenge due to the dealloying of transition metals during fuel cell operation.¹⁵ Intentional dealloying has been explored to exploit defects as a catalytic advantage,¹⁹ but this often leads to the loss of beneficial alloy properties and issues like membrane and ionomer contamination.²⁰ Takahashi et al. observed that the Co content in Pt₁Co₂ nanoparticle catalysts dropped to 20% after undergoing 300 cyclic voltammetry (CV) cycles,²¹ and Ahluwalia et al. reveal a Ni loss from the Pt₁Ni₃ catalyst ranging between 55% to 90% during potential cycling.²² This dealloying effect was even more pronounced in ultrafine NWs. Kato et al. found that, after 100 cycles of electrochemical cleaning, the atomic ratio of platinum to nickel in PtNi-NW catalysts

decreased from 52:48 to 94:6.²³ Additionally, Pt oxides formed on Pt and Pt alloy NWs with 1D anisotropy exhibit structural and electronic properties that differ from conventional nanoparticle catalysts.²⁴ Retaining high Ni content in catalysts, especially in ultrafine NWs, and thoroughly examining their structural and electronic changes under *operando* conditions remain critical challenges.

Operando X-ray absorption spectroscopy (XAS), including high-energy resolution fluorescence detection (HERFD) XAS, has been essential for investigating the structure and electronic states of Pt catalysts under reaction conditions.^{15, 25} HERFD-XAS enhances the resolution of spectral features compared to conventional XAS,²⁶ making it particularly effective for identifying changes in the near-edge absorption maximum, or "white line".²⁷ This improved resolution allows for clearer differentiation between Pt metal and Pt oxides, providing valuable insights into the electronic states of PtNi alloy catalysts under *operando* conditions. Additionally, X-ray powder diffraction (PXRD) combined with pair distribution function (PDF) analysis is useful for the structural analysis of nanomaterials with low crystallinity and multiple phases.²⁸

In this study, Pt₂₅Ni₇₅ nanowires (PtNi-NW/C) with high Ni content were synthesized through an H₂/N₂ post-annealing treatment, resulting in a Pt-rich surface and PtNi alloy core, demonstrating enhanced ORR activity compared to commercial Pt/C and Pt-NW/C catalysts. PDF analysis revealed a structure comprising pure Ni face-centered cubic (fcc) and PtNi body-centered tetragonal (bct) phases in the bulk, with a Pt fcc phase on the surface characterized by compressed lattice parameters compared to standard Pt crystals. *Operando* conventional and HERFD-XAS analyses confirmed that the PtNi-NW/C catalyst exhibits lower oxygen bonding energy and a shorter Pt-Pt bond length, further enhancing ORR activity and stability. These findings underscore the key structural features of the PtNi alloy NWs and provide valuable insights for future catalyst design.

3.2 Experimental Methods

3.2.1 Materials

Pt (II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 98%), Ni (II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%), tungsten hexacarbonyl ($\text{W}(\text{CO})_6$, 99%) were purchased from Sigma-Aldrich. Ethanol (99.5%), 2-Propanol (99.7%), oleylamine (OAm, 85%), cyclohexane (99.5%) glucose, and hexadecyltrimethylammonium chloride (CTAC, 99%) were purchased from Fujifilm. The electrolyte was prepared from ultra-pure water (Milli-Q, 18.2 M Ω) and perchloric acid (ultra-pure, Kanto Chemical Co. Inc.). The Vulcan XC-72 was purchased from Cabot Corporation. O₂ (99.995%), N₂ (99.999%), H₂ (5%, 95% N₂ balance) gases were purchased from Kyoto Teisan Co., Ltd.

The Pt/C catalyst (29.1 wt%; TEC10V30E) was purchased from Tanaka Kikinzoku Kogyo Co. Ltd., Japan.

3.2.2 Synthesis of the Pt nanowire catalyst

Synthesis of the Pt-NW catalyst involved dissolving 10 mg $\text{Pt}(\text{acac})_2$, 6.4 mg $\text{Ni}(\text{acac})_2$, 5 mg $\text{W}(\text{CO})_6$, and 40 mg CTAC in 5 mL of OAm. The mixture was sealed in a 30 mL glass vial and sonicated at room temperature for 1 hour to form a homogeneous suspension. It was then heated at 160 °C for 2 hours to produce NW-structured catalysts. Residual organic impurities were removed by washing with a cyclohexane/ethanol mixture, followed by drying at room temperature to obtain a black powder. Subsequently, the product was dispersed in 15 mL of cyclohexane/ethanol, and 30 mg of carbon black (Vulcan XC-72) was added. The mixture was sonicated in an ice-water bath for 2 hours and centrifuged to obtain Pt-NW/C (12.3 wt% Pt). The catalyst was then dispersed in 0.1 M HClO_4 solution and heated to 80 °C for 2 hours to remove excess Ni. After etching, the sample was filtered, washed with water, and dried in an oven at 60 °C.

3.2.3 Synthesis of the PtNi nanowire catalyst

The Pt₂₅Ni₇₅ NW catalyst (PtNi-NW/C) (11.9 wt% Pt) was synthesized using a process similar to that of Pt NWs, without acid leaching. In this method, 70 mg of glucose and 20 mg of Ni(acac)₂ were added to the reactants. For the synthesis of the Pt₄₀Ni₆₀ NW catalyst, the amount of Ni(acac)₂ was reduced to 10 mg. The resulting NW samples were calcined at temperatures between 250 and 450 °C for 1 hour under a 5% H₂ and 95% N₂ atmosphere to achieve the Pt-rich surface layer structure.

3.2.3 Characterization

Synchrotron XRD patterns were collected in BL02B2 at SPring-8, Japan, and the background was subtracted using Match! 3 software. The wavelength was calibrated with CeO₂ (SPring-8) as 0.61950 Å. X-ray photoelectron spectroscopy (XPS) data were collected at the BL7U Aichi Synchrotron Radiation Center. The incident X-rays source was Monochromated Al-K α (1486.6 eV) and photoelectron extraction angle was 45°. The carbon 1s peak was set at 284.60 eV for charge correction. The background was subtracted using the Shirley method. The morphologies of the NW samples were observed using a JEM-2200FS transmission electron microscope (JEOL, Ltd.) at an acceleration voltage of 200 kV. For High-resolution transmission electron microscopy (HR-TEM) imaging and energy-dispersive X-ray spectroscopy (EDS) mapping, the JEOL-JEM-ARM200F was used.

3.2.4 X-Ray Total scattering measurements

X-ray total scattering data for pair distribution function (PDF) analysis were collected using synchrotron radiation at the BL22XU beamline of SPring-8, Japan. A Varex Imaging XRD1621 flat panel detector captured the data, with a 2-second exposure and a 150-second integration time. Calibration of the beam center coordinates, detector tilt, and sample-to-detector distance (225.7759 mm) was performed using the PIXIA program, based on image data from CeO₂ (NIST, 674B; lattice constant, $a = 5.41165$ Å).

²⁹ The wavelength ($\lambda = 0.180420 \text{ \AA}$) was calibrated through PDF fitting of the CeO_2 data using PDFfit2.³⁰

The data were normalized with the form factor using the Faber-Ziman formalism and the MaterialsPDF program.²⁹ The structure function, $S(Q)$, was converted into reduced PDFs, $G(r)$, through Fourier transformation within the Q range of $1.3\text{--}29.0 \text{ \AA}^{-1}$. Simultaneous joint curve fitting and simulation of the PDF data and XRD patterns were performed using the TOPAS program with a common structural model,³¹ assuming individual lattice constants for PDF and XRD analyses.

3.2.5 Electrochemical measurement

All electrochemical experiments were performed in a three-electrode cell at room temperature. A reversible hydrogen electrode (RHE) with 5% H_2 was used as the reference electrode, Pt mesh as the counter electrode, and a glassy carbon rotating disk electrode (RDE) ($\Phi=5 \text{ mm}$) with a drop-coated catalyst served as the working electrode (WE). Prior to measurements, the glassy carbon RDE was polished with alumina micropolish and rinsed three times with water to remove any residual particles.

The catalyst ink was prepared by dispersing 2 mg of catalyst in a 2 ml mixture of ultrapure water and 2-propanol (0.3:1.7), along with 40 μL of 5 wt% Nafion® solution as a binder. The mixture was sonicated for 30 minutes and then deposited onto the glassy carbon RDE with a Pt loading of $6.5 \mu\text{g cm}^{-2}$. Before testing the oxygen reduction reaction (ORR), 50 cycles of cyclic voltammetry (CV) were carried out in N_2 -saturated 0.1 M HClO_4 , scanning between 0.02 and 1.2 V (vs. RHE) at 100 mV s^{-1} to remove residual surfactants. After activation, a stable CV was recorded at a scan rate of 50 mV s^{-1} .

ORR linear sweep voltammograms (LSVs) were recorded in O_2 -saturated 0.1 M HClO_4 , scanning from 0.2 to 1.2 V vs. RHE at 10 mV s^{-1} . LSVs under different mass transport conditions were measured using a rotating disk electrode (RDE) system with rotational speeds ranging from 100 to 2500 rpm. The ORR data were corrected using an

N₂ background and analyzed with the Koutechy-Levich (K-L) equation at 0.9 V vs. RHE. The electrochemical active surface area (ECSA) was determined by integrating the hydrogen adsorption charge over the CV curve, assuming a hydrogen monolayer adsorption value of 210 $\mu\text{C}/\text{cm}^2$.

The accelerated degradation test (ADT) was conducted by applying constant potential polarization at 0.60 V and 1.00 V, each held for 3 s, and repeated for 10,000 cycles. After the ADT cycles, LSV was performed to evaluate the stability of the catalysts.

Oxygen coverage was determined by calculating the ratio of charges associated with reducing surface oxides (Q_O) to those from hydrogen underpotential deposition (Q_H). The Q_O values were measured by stepping the electrode potential from 0.4 V vs. RHE to specific potentials ranging from 0.5 to 1.1 V vs. RHE in N₂-saturated 0.1 M HClO₄, holding for 5 minutes, and then scanning back to 0.4 V at 50 mV s⁻¹.

$$\text{Oxygen coverage} = \frac{Q_O}{Q_H} \quad (3-1)$$

CO stripping voltammograms were obtained by immersing the working electrode in CO-saturated 0.1 M HClO₄ at 0.12 V vs. RHE for 20 minutes, allowing full CO adsorption on the catalyst. The electrolyte was then purged with N₂ gas for 40 minutes to remove any remaining CO. The adsorbed CO was stripped from the catalyst surface by scanning from 0.02 to 1.0 V vs. RHE at a rate of 10 mV s⁻¹.

3.2.6 *operando* Conventional XAS measurement

XAS measurements were carried out at the BL37XU beamline in SPring-8, Japan. Monochromatic X-rays were generated using a Si (111) monochromator and a total reflection Ru mirror (4 mrad). The *operando* cell setup, as described in previous studies,³² were made from polyether ether ketone (PEEK). An Ag/AgCl electrode (Saturated KCl, RE-8, EC Frontier CO., LTD., Japan) and a platinum mesh served as the reference and counter electrodes, while the working electrode was a glass-carbon RDE coated with the catalyst. Gas was introduced into the electrolyte through a PTFE tube at the

bottom of the cell, with a check valve (MFTD-6V, AS ONE Corporation, Japan) at the top to maintain stable pressure during gas bubbling. X-ray measurements were conducted through a 25 μm Kapton® film window. Data analysis was performed using ATHENA and ARTEMIS from the IFEFFIT software suite.³³

3.2.7 *operando* High-Energy Resolution Fluorescence Detection-XAS

Operando HERFD-XAS spectra of the Pt L₃-edge were acquired at the BL39XU beamline at SPring-8, Japan, in a 0.1 M HClO₄ electrolyte under O₂-saturated conditions, with the potential referenced to the reversible hydrogen electrode (RHE). X-ray emission spectroscopy (XES) was employed to monochromatize the fluorescent X-rays before collecting the XAS signals. During the test, collimated and monochromatic X-rays were generated using Si (220) monochromators and a total-reflection Rh mirror (4.5 mrad). The HERFD-XAS spectra were fitted using an arrangement equation for the background and two pseudo-Voigt (Gaussian-Lorentzian) equations for the peaks.

$$\frac{A_{bg}}{\pi} \left[\tan^{-1} \left(\frac{E-E_{bg}}{\Delta E_{bg}} \right) + \frac{\pi}{2} \right] \quad (3-2)$$

$$\frac{A_n}{1+4m_n \frac{(E-E_n)^2}{\Delta E_n^2}} \exp \left[-4 \cdot \ln 2 \cdot (1-m_n) \cdot \frac{(E-E_n)^2}{\Delta E_n^2} \right] \quad (3-3)$$

Here, A_{bg} denotes the height for the arctan, which was adjusted to match the μ_E within the range of 11568-11570 eV. E_{bg} and E_n were determined as previous research.³⁴ m_n was set as 0.5.

3.3 Results and Discussion

3.3.1 Identification of the Pt nanowire structure

In the typical synthesis of Pt-NWs, OAm functions as both the solvent and surfactant, CTAC acts as a capping agent, and Ni(acac)₂ is introduced to facilitate NW formation, as outlined in the experimental section. The presence of a small amount of Ni²⁺ is crucial

for the anisotropic growth of Pt NWs (Figure 3-1), as previous studies have shown that transition metal cations can slow Pt^{2+} reduction and promote the formation of one-dimensional structures.³⁵ Due to the limited reducing capability of OAm, the $\text{Ni}(\text{acac})_2$ in the system was not fully reduced, preventing the formation of a PtNi-NW catalyst.³⁶ After acid treatment, ICP analysis revealed that only 3 at% of Ni remained in the alloy ($\text{Pt}_{97}\text{Ni}_3\text{-NW/C}$), with no significant Ni signal observed in STEM-EDS mapping (Figure 3-2). Considering the further dissolution of Ni during electrochemical testing (e.g., cleaning CV process) and for comparison with PtNi-NW, this catalyst was named Pt-NW/C, as the remaining Ni content does not significantly affect its Pt-rich properties.

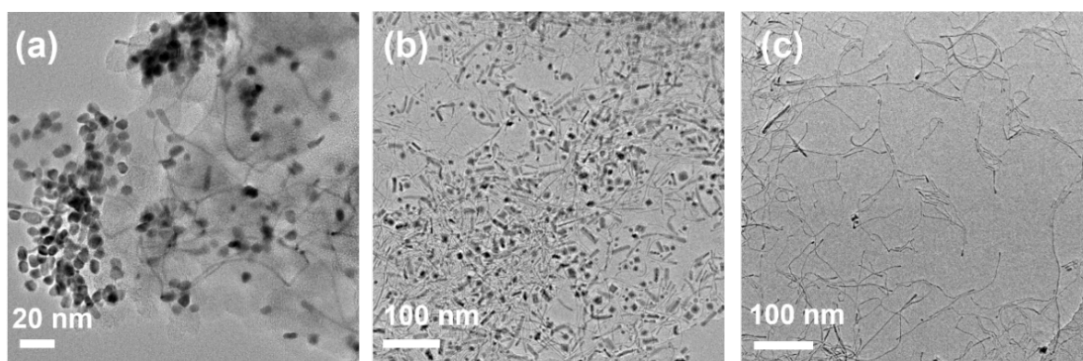


Figure 3-1. TEM image of Pt-NW catalyst synthesized using (a) 0 mg, (b) 2.5 mg and (c) 6.4 mg $\text{Ni}(\text{acac})_2$.

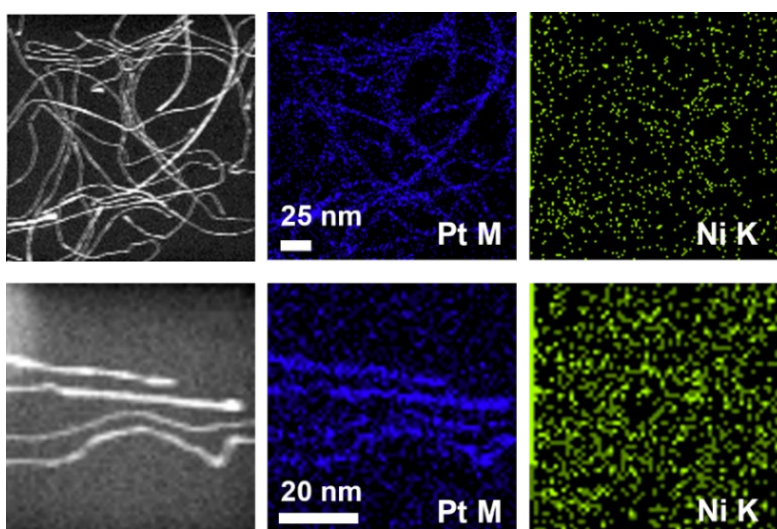


Figure 3-2. STEM-EDS element mapping spectrum of Pt-NW/C.

The morphological characteristics of the synthesized Pt-NWs were analyzed using TEM, HR-TEM, and HAADF-STEM. As shown in Figure 3-3 and Figure 3-4, the NWs are uniformly dispersed on the carbon support without noticeable agglomeration, with an average length of 11.3 ± 6.6 nm and a diameter of 2.5 ± 1.2 nm. The selected area electron diffraction (SAED) image (inset in Fig. 1a) shows distinct polycrystalline diffraction rings, where the first ring corresponds to carbon and rings 2 through 5 align with the (111), (200), (220), and (311) facets of Pt with $Fm-3m$ symmetry, confirming the high crystallinity of the NWs.

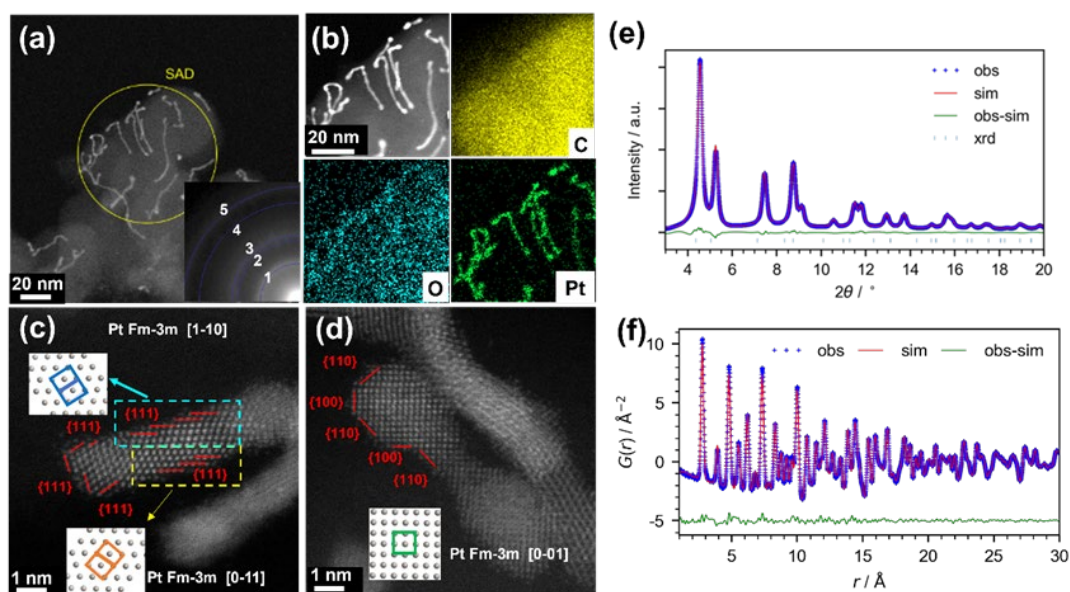


Figure 3-3. (a, c, d) HAADF-STEM image, (b) STEM-EDS element mapping spectrum, (e) Powder XRD patterns, and (f) PDF patterns of Pt-NW/C (obs: observed data, sim: fitted data, obs-sim: residual value). The inset in (a) is SAED image from the yellow area.

Figure 3-3c shows that most of the NWs have a lattice spacing of 0.227 nm, corresponding to the (111) facets of a typical fcc Pt nanocrystal. Atomic-level observations revealed a polycrystalline nature, suggesting a stepped structure. Surface defects within the NWs, including grain boundaries (GBs), kinks, and steps, disrupt the interfacial water network and destabilize ORR intermediates, significantly enhancing catalytic activity.^{24, 37}

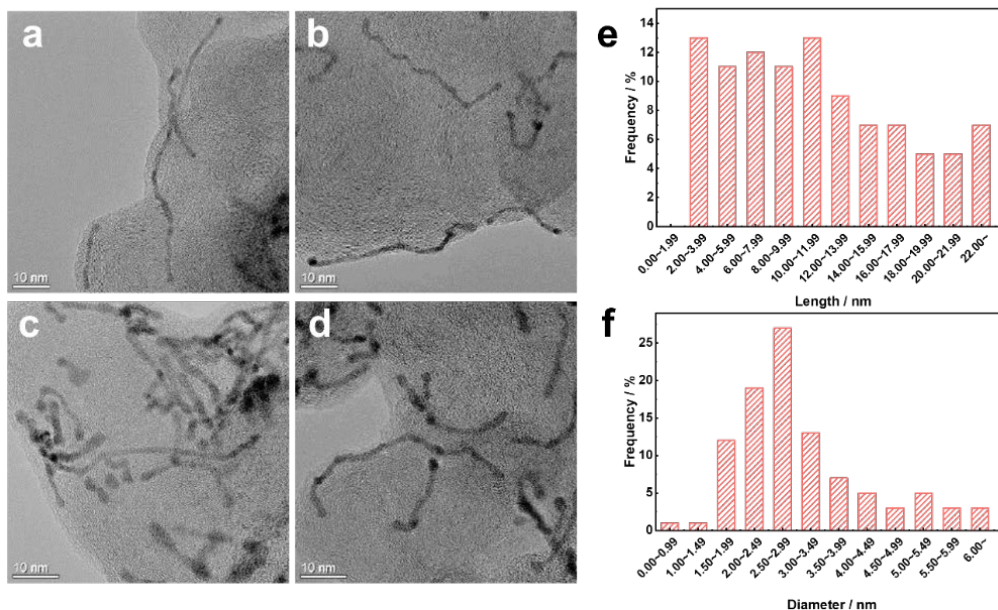
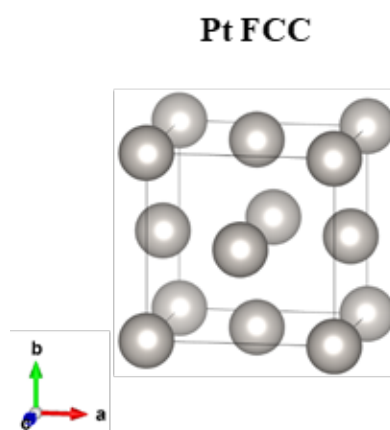


Figure 3-4. (a-d) TEM images, (e) length distribution and (f) diameter distribution of Pt-NW/C.

Lattice constants in / Å	XRD main	XRD sub	PDF main	PDF sub
Pt -NW/C	3.91834(13)	4.109(3)	3.92152(19)	none

Table 3-1. Fitting model and the extracted parameters of Pt nanowire



PXRD patterns, recorded with a wavelength (λ) of 0.61950 Å, were used to analyze the Pt-NW crystal structure (Figure 3-3e). By simulation with fcc Pt models, the total scattering patterns indicated a lattice constant of 3.918 Å (Table 3-1). However, the

weak and broad Bragg reflections made precise determination of crystal symmetry challenging, highlighting the need for alternative methods to enhance precision. The PDF technique, which provides the weighted probability of detecting any pair of atoms at a distance r , establishes the distribution of interatomic distances in real space and is a powerful tool for resolving material structures. PDF results indicated a slightly larger lattice constant of 3.921 Å compared to the PXRD measurement (Figure 3-3f), while the synthesized NWs exhibited a more compact lattice structure than standard Pt crystals (3.925 Å).³⁸

3.3.2 Identification of the PtNi alloy nanowire structure

To address the issue of weak reduction by OAm in the synthesis of PtNi-NW/C, glucose was used as a stronger reducing agent, ensuring the complete reduction of Ni during the formation of PtNi NWs.³⁶ The TEM and STEM-EDS spectra of the PtNi-NW/C before H₂/N₂ annealing (Figure 3-5) revealed that the NWs had diameters ranging from 2 to 3 nm, and the distribution of Ni in the structure was non-uniform. Given the more positive reduction potential of Pt²⁺/Pt compared to Ni²⁺/Ni, the structural features of the Pt core and Pt-Ni shell formation can be deduced, which is further confirmed by the HR-TEM images (Figure 3-6).^{18, 39} Due to the sensitivity of metallic nanostructures with highly segregated compositions to exposure atmospheres,^{40, 41} efforts were focused on engineering Pt-rich layer PtNi-NWs through thermal annealing under an H₂/N₂ atmosphere.

To prevent agglomeration, PtNi-NW/C was annealed at various temperatures (Figure 3-7), resulting in different morphological changes. The experimental results show that annealing at 400 °C produces NWs with an average length of 8.5 ± 8.1 nm and a diameter of 2.6 ± 1.5 nm (Figure 3-8). At temperatures above 400 °C, large particles were observed, indicating the disruption of the NW structure and the onset of agglomeration.

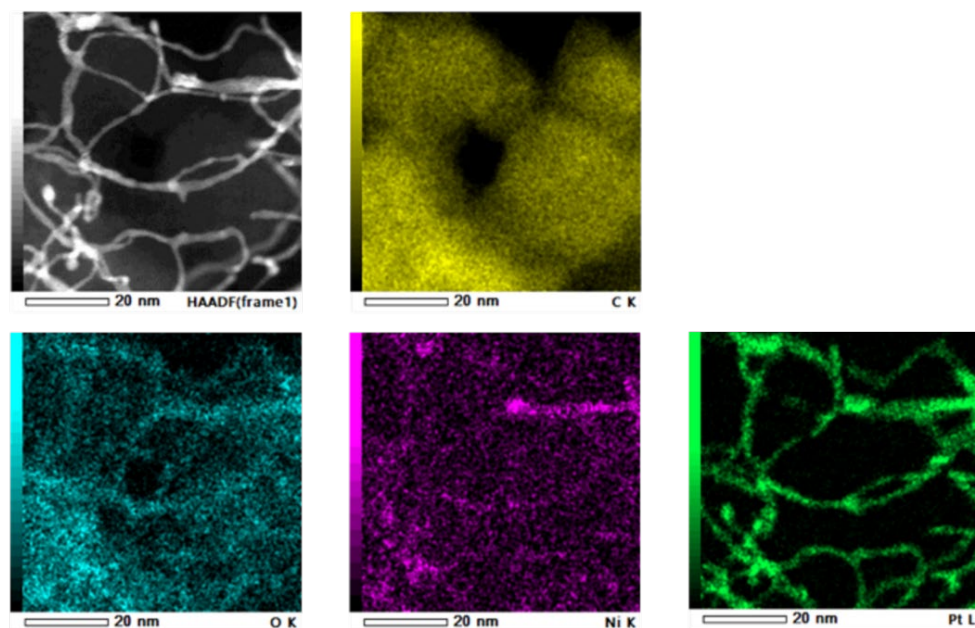


Figure 3-5. STEM image and EDS element mapping for PtNi-NW/C before H₂/N₂ annealing treatment.

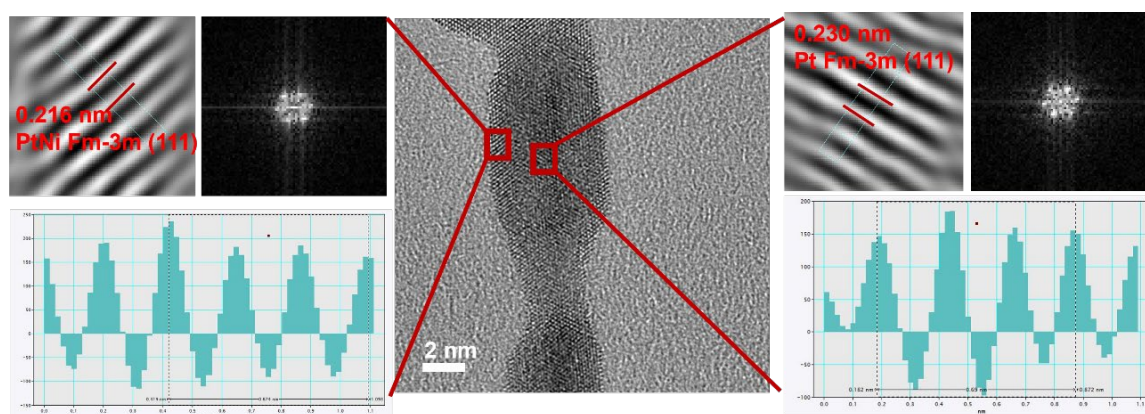


Figure 3-6. HRTEM and FFT patterns of PtNi-NW/C without annealing treatment.

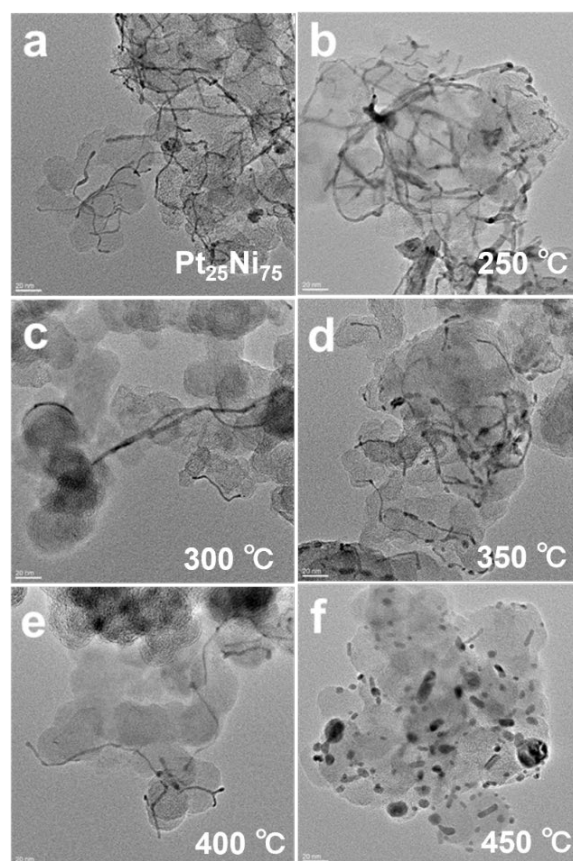


Figure 3-7. TEM image of PtNi-NW/C (a) before and after (b) 250 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C and (f) 450 °C H₂/N₂ annealing treatment.

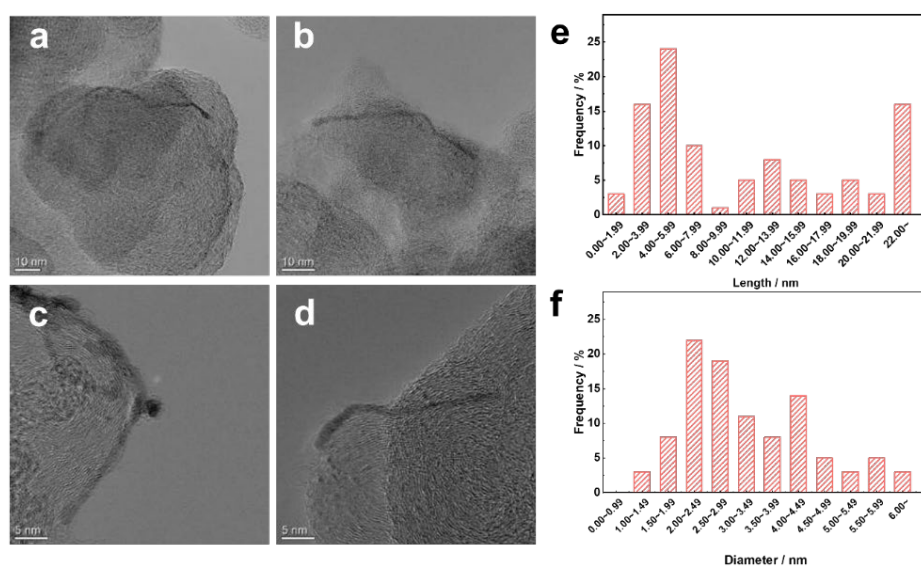


Figure 3-8. (a-d) TEM images, (e) length distribution and (f) diameter distribution of PtNi-NW/C.

To further demonstrate the effect of annealing temperature on the formation of a Pt-rich surface, STEM-Electron Energy Loss Spectroscopy (EELS) characterization was performed on PtNi-NW/C annealed at 300 °C. As shown in Figure 3-9, the distribution of Pt and Ni within the NW structure was uniform, with no significant element segregation. This is attributed to the slow atomic diffusion and surface relaxation at lower temperatures (~ 300 °C).⁴² In contrast, the sample annealed at 400 °C showed a decreased Ni concentration from the core to the surface, revealing a PtNi alloy core and a Pt shell structure, highlighting the formation of a Pt-rich surface layer (Figure 3-10). Further STEM-EDS mapping and HR-TEM analysis (Figure 3-11 and Figure 3-12) confirmed the development of the core-shell structure. Studies indicate that annealing at around 400 °C accelerates bulk atom diffusion and element segregation, leading to a concentration gradient that forms a Pt-rich surface.⁴³ This arrangement contributes to the specific catalytic properties of PtNi NW/C catalysts by balancing the strain effects of Ni in the core with a stable, highly active Pt-rich shell. Therefore, 400 °C was selected as the optimal annealing temperature. Subsequent PXRD results (Figure 3-13) indicate improved crystallinity of PtNi-NW/C after annealing.

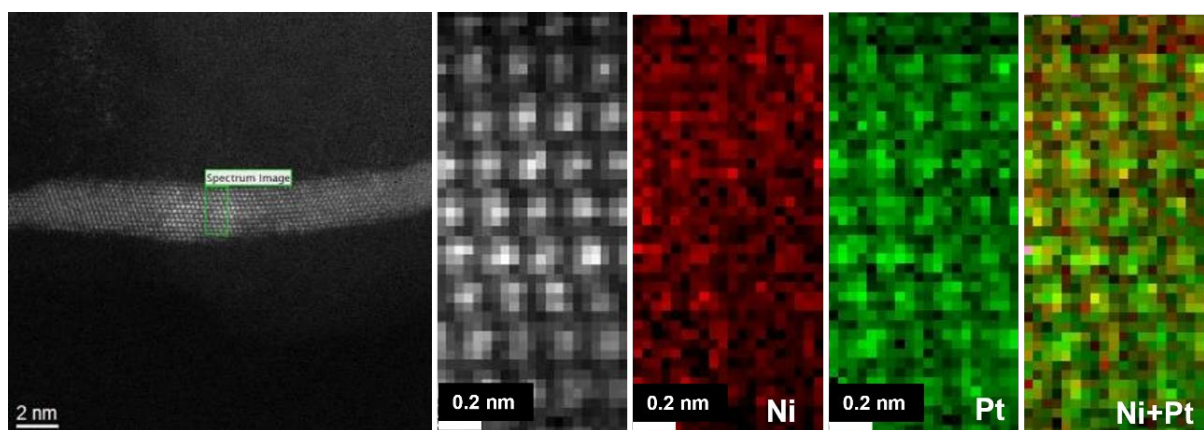


Figure 3-9. STEM-EELS mappings for PtNi-NW/C after 300°C annealing treatment.

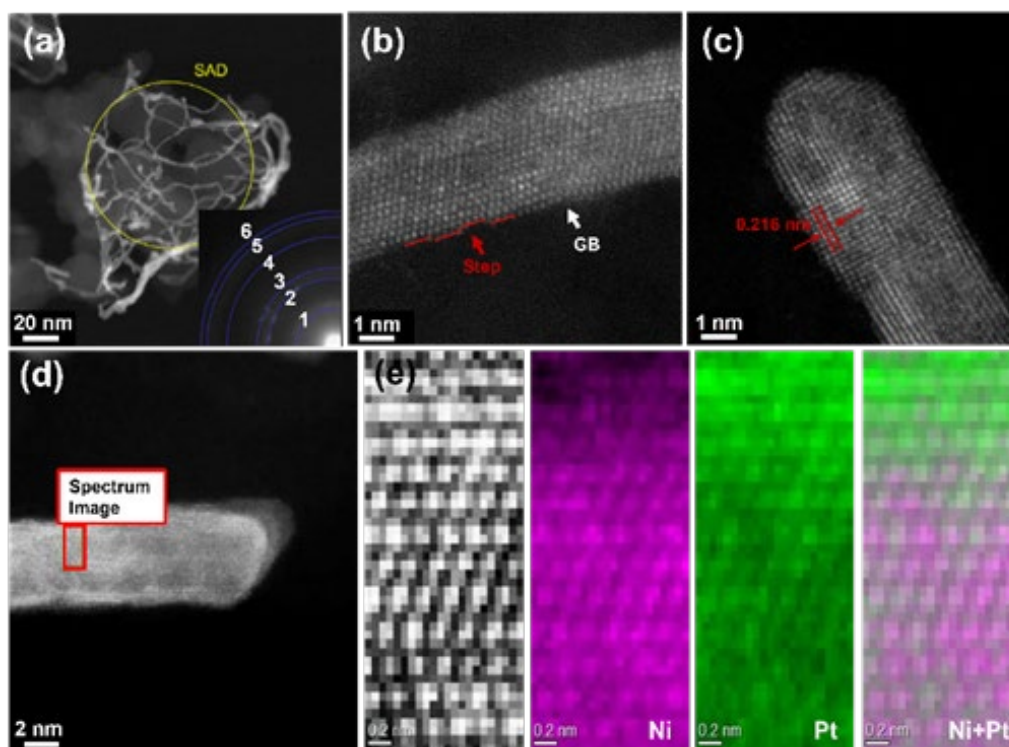


Figure 3-10. (a, b, c, d) HAADF-STEM image and (e) STEM-EELS mappings for PtNi-NW/C.

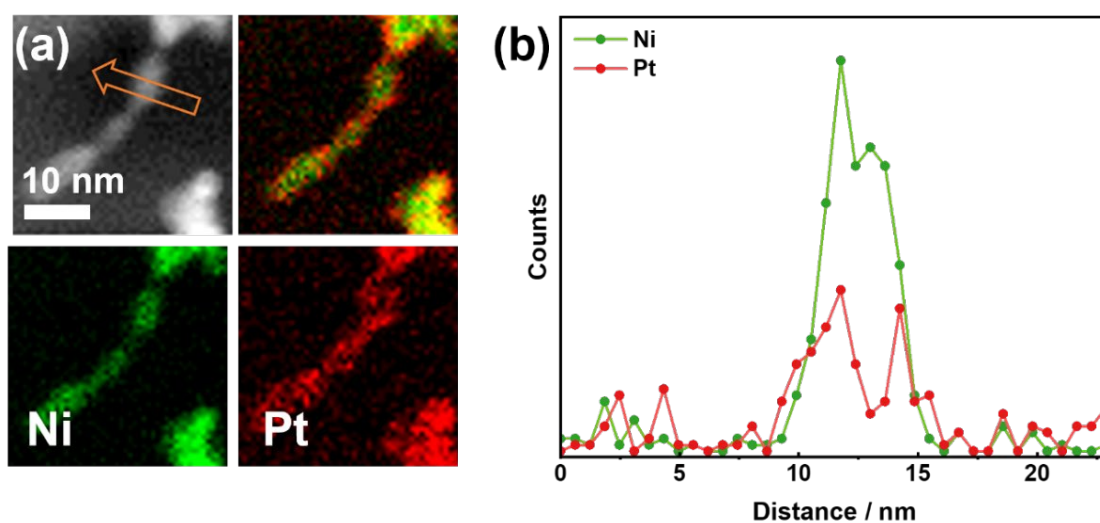


Figure 3-11. (a) STEM-EDS element mapping spectrum, and (b) line scanning profiles of PtNi-NW/C.

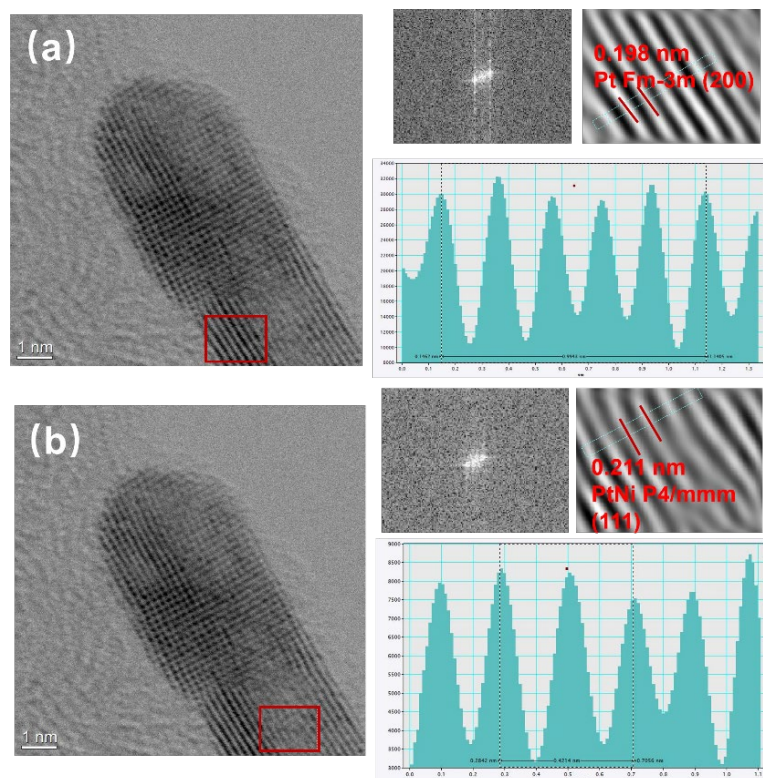


Figure 3-12. HRTEM and FFT patterns of PtNi-NW/C in (a) Pt-rich layer and (b) PtNi alloy core.

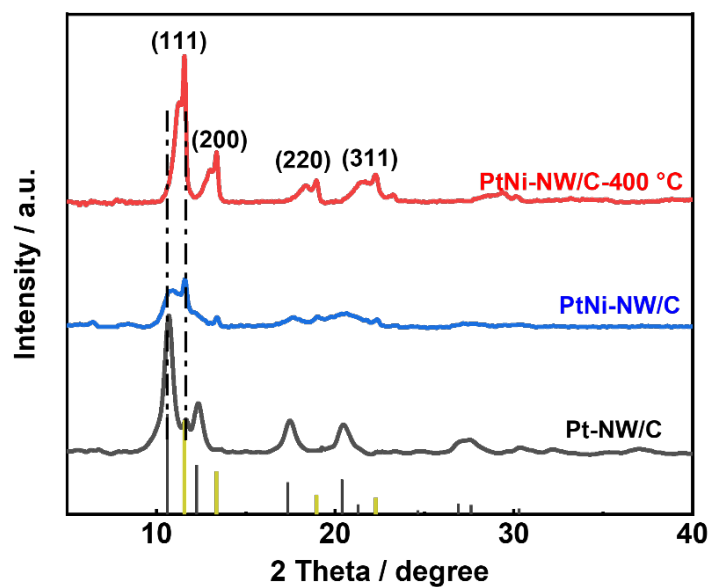


Figure 3-13. XRD pattern for Pt-NW/C, PtNi-NW/C before and after 400°C annealing treatments. The yellow bar is standard Ni and the gray bar is standard Pt.

Figure 3-10a presents HAADF-STEM and SAED images of the PtNi-NW/C catalysts, providing further insight into the synthesized structure. Diffraction rings 2, 3, and 4 correspond to the (111), (200), and (220) facets of Pt₇₅Ni₂₅ with *Fm-3m* symmetry, along with the (101), (110), and (002) facets of PtNi with *P4/mmm* symmetry, indicating the presence of the bct alloy phase in the NWs. Figure 3-10b and c highlight the steps and grain boundaries in PtNi-NW/C.²⁴

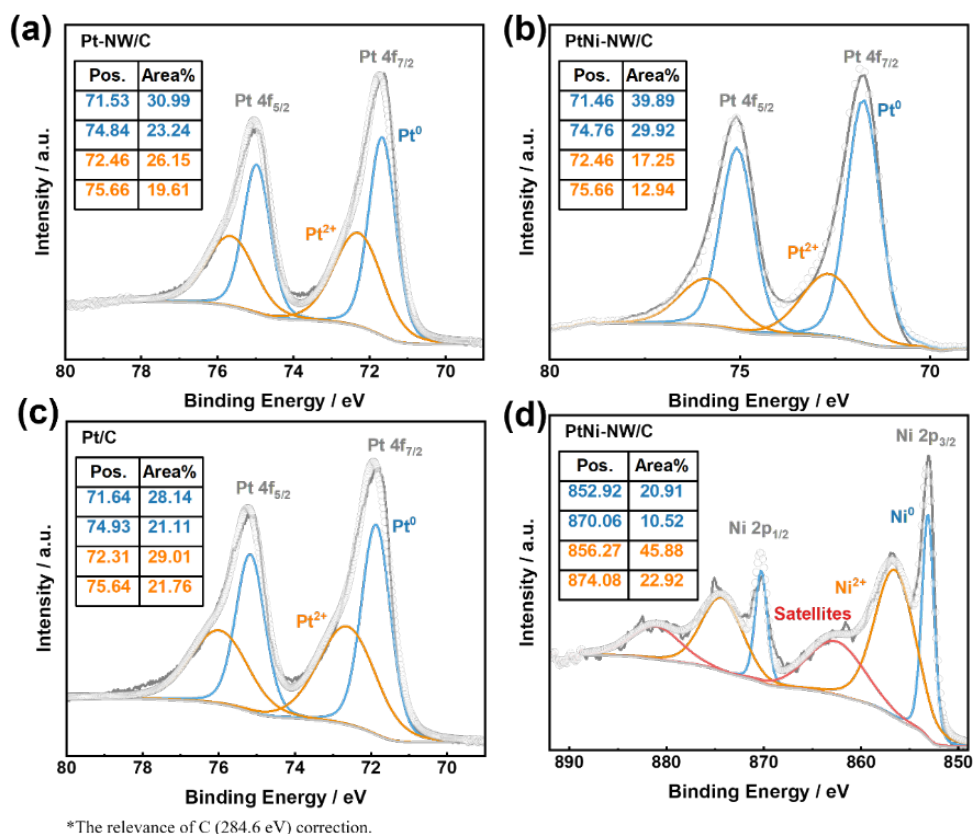


Figure 3-14. XPS spectra for the (a) Pt-NW/C, (b) PtNi-NW/C and (c) Pt/C of Pt 4f and (d) Ni 2p.

XPS was used to analyze the elemental composition and valence states in catalysts (Figure 3-14 and Table 3-2). The Pt 4f binding energy in PtNi-NW/C (71.46 eV) showed a slight negative shift compared to Pt-NW/C (71.53 eV), attributed to the interaction between Pt and Ni, where Pt exhibits an electron-withdrawing effect.^{44, 45} This electron transfer also leads to a partial oxidation state of Ni, with Ni²⁺ accounting

for approximately 69%. The Pt/Ni atomic ratio in PtNi-NW/C, determined from the XPS survey spectra (Fig. S13†), was 1/3, consistent with the ICP-MS results (26.9/73.1).

Table 3-2. XPS analysis result of PtNi-NW/C and Pt-NW/C.

PtNi-NW/C	C1s	O1s	Pt4f	Ni2p
Mole ratio (Normalize to C)	1.00	0.02	0.004	0.01
Elemental content ratio (mole%)	96.7	1.6	0.4	1.3
Binding Energy / eV	284.6	532.2	4f _{7/2} 71.5	2p _{3/2} 852.9
Pt-NW/C	C1s	O1s	Pt4f	
Mole ratio (Normalize to C)	1.00	0.02	0.01	
Elemental content ratio (mole%)	96.7	1.6	1.8	
Binding Energy / eV	284.6	532.2	4f _{7/2} 71.5	

Ex-situ XAS analysis was conducted to further evaluate the valence states and coordination environments of Pt and Ni. The X-ray absorption near edge structure (XANES) spectra for the Pt L₃-edge (Figure 3-15a) indicate a metallic state in both Pt-NW/C and PtNi-NW/C.⁴⁶ Additionally, the reduced white line intensity for Pt in PtNi-NW/C compared to Pt-NW/C suggests electron transfer from Ni to Pt in the PtNi alloy, consistent with XPS results. Ni K-edge XANES spectra (Figure 3-15d) show that the white line intensity of PtNi-NW/C falls between that of Ni foil and NiO, indicating a Ni valence state between 0 and +2. Fourier-transformed Extended X-ray absorption fine structure (FT-EXAFS) analyses for the Pt L₃-edge and Ni K-edge (Figure 3-15b and e) provide insights into the local atomic structure, with PtNi-NW/C exhibiting a positive

shift in the Ni-Ni signal and a negative shift in the Pt-Pt signal compare to Ni/Pt foil, causing lattice contraction.⁴⁷ Further analysis by wavelet transform (WT) reveals a shift in the maximum intensity of Pt-Pt to a lower k region, from approximately $12 \text{ \AA}^{-1}$ to $10 \text{ \AA}^{-1}$ (Figure 3-15c and f). The strong interaction between Pt and Ni in PtNi-NW/C enhances oxidation resistance and changes the Pt coordination environment, which is considered to be favorable for ORR activity.⁴⁸

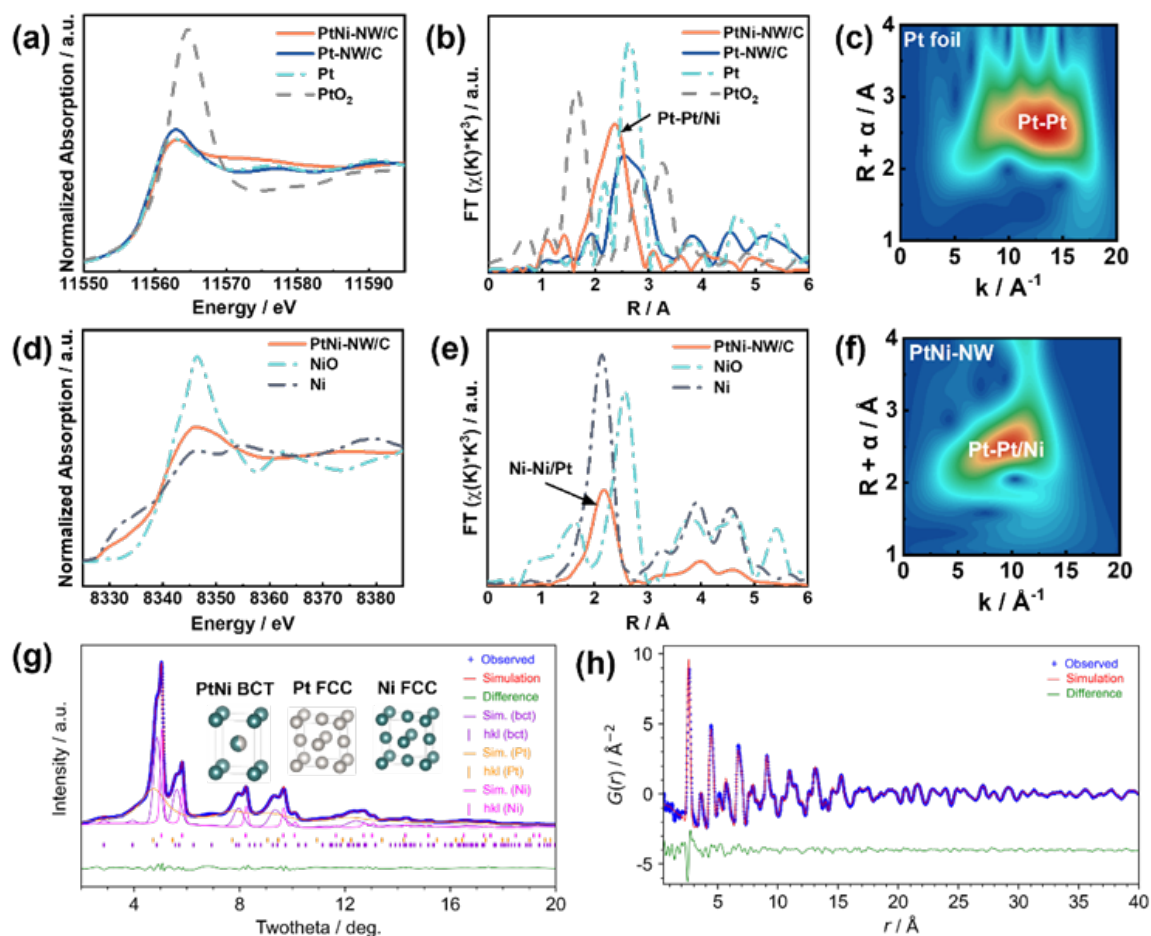


Figure 3-15. (a) Pt L₃-edge XANES spectra and (b) FT-EXAFS spectra of PtNi-NW/C, Pt-NW/C, and Pt/C, (d) Ni K-edge and (e) FT-EXAFS spectra of PtNi-NW/C. Wavelet transform of the k^3 weighted Pt L₃-edge EXAFS spectra of (c) Pt foil and (f) PtNi-NW/C. (g) Powder XRD patterns, and (h) PDF patterns of PtNi-NW/C.

Table 3-3. Fitting model and the extracted parameters of PtNi nanowire

	BCT	Pt FCC	Ni FCC
a axis / Å	2.62603	3.78991	3.55550
C axis / Å	3.61090	-	-
Component wt%	12.96	74.58	12.45
Pt-Pt / Å	2.62603	2.67987	-

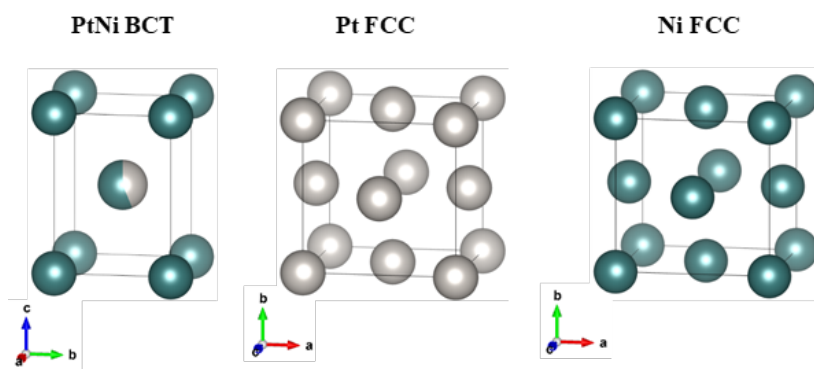


Figure 3-15g and h present the PXRD and PDF analysis for the PtNi-NW/C catalyst, revealing the presence of a tetragonal phase attributed to the $L1_0$ structure in the PtNi alloy core.⁴⁹ Further analysis identifies a phase near pure Pt, characterized by a compressed fcc structure with a lattice constant of 3.79 Å and a shorter Pt-Pt distance of 2.67 Å compared to bulk Pt (Table 3-3), consistent with the Pt-rich layer observed in TEM images. Interestingly, PXRD did not show clear peaks for the tetragonal phase; instead, displayed broad intensities in regions where these peaks were expected, along with sharp Bragg peaks associated with pseudo-cubic phases. This pattern, combined with PDF data, suggests the formation of large pseudo-cubic crystals composed of randomly oriented *c*-axes of tetragonal phases. Additionally, the analysis indicated the presence of a pure fcc Ni phase within PtNi-NW/C, attributed to excess Ni content. Both the bct PtNi alloy and pure fcc Ni phases synergistically influence the core, positively impacting the structure and properties of the Pt-rich surface layer.

3.3.3 Electrochemical measurement

The RDE method was used to assess the electrocatalytic ORR activity of the catalysts in a 0.1 M HClO₄ electrolyte. The cleaning CV was performed in an N₂ environment for 50 cycles. Figure 3-16 shows the cleaning CVs of the different NWs catalysts during the first and fiftieth cycles. In the initial cycle, the underpotential deposition of hydrogen (H_{UPD}) and Pt redox peaks were discrete, likely due to residual surfactants and organic matter on the Pt surface. After 50 cycles, a standard CV curve was obtained, with a significantly reduced peak around 1.1~1.2 V vs. RHE, indicating the removal of organic matter from the Pt surface. Additionally, the PtNi-NW/C catalysts before and after annealing exhibited different CV shapes (Figure 3-16b and c), with the unannealed PtNi-NW/C showing electrochemical behavior similar to that of Pt-NW/C after cleaning.²³ This indicates that the Pt-rich surface layer formed after annealing effectively protects the internal Ni from dissolution.

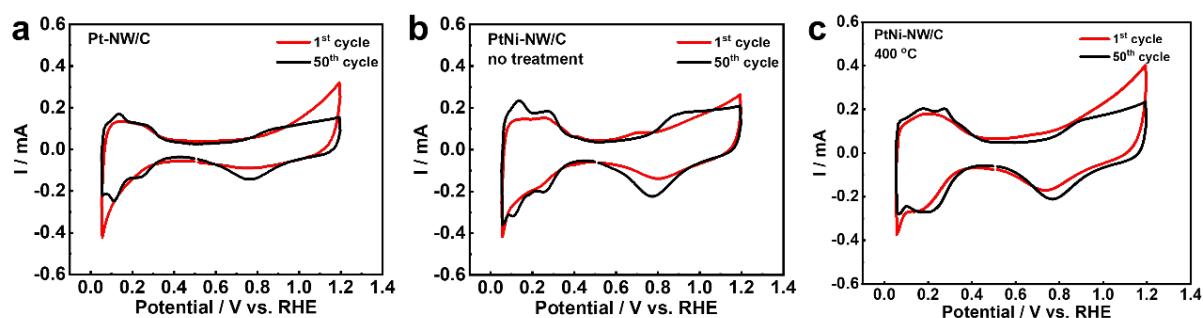


Figure 3-16. CV curves of (a) Pt-NW/C, (b) PtNi-NW/C before annealing and (c) PtNi-NW/C after 400 °C treatment at a scanning rate for 100 mV/s.

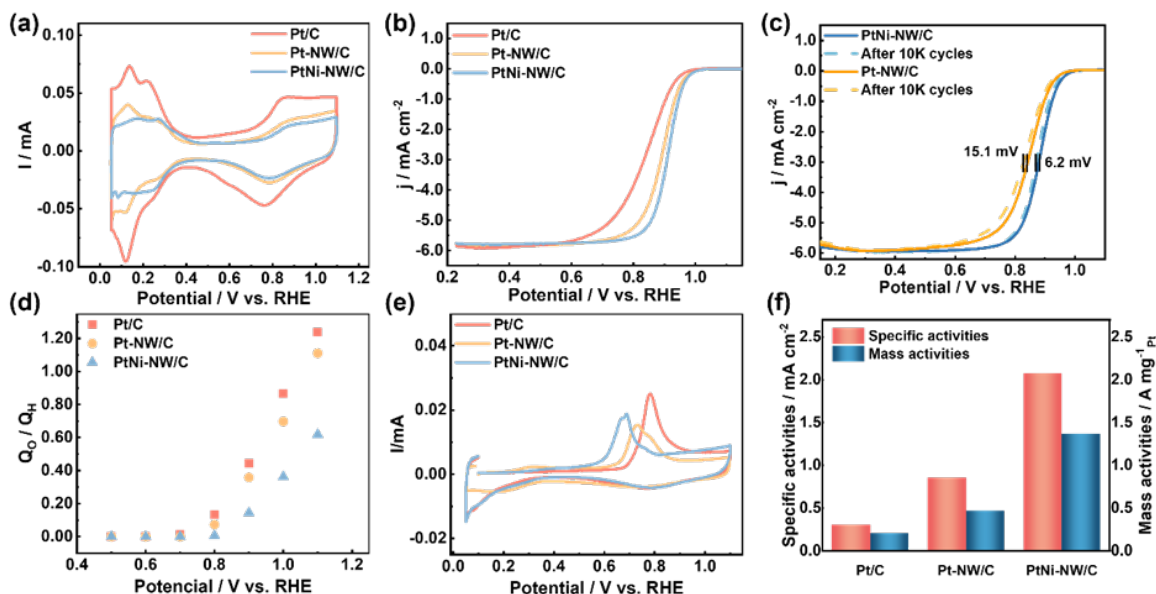


Figure 3-17. (a) CV and (b) ORR polarization curves (1600 rpm) for Pt /C, Pt-NW/C, and PtNi-NW/C catalysts, respectively in O₂-saturated 0.1M HClO₄. (c) ORR polarization curves before and after the ADT. (d) Oxygen coverage and (e) The CO-stripping curves of the Pt-NW/C and PtNi-NW/C. (f) Comparison of specific and mass activity.

Figure 3-17a presents the CV curves of the Pt-NW/C, PtNi-NW/C, and Pt/C catalysts after 50 cleaning cycles. The redox peak associated with oxide formation/reduction in the NW catalysts shifted to higher potentials compared to the Pt/C catalyst. In oxygen-saturated 0.1 M HClO₄, LSV was conducted at 1600 rpm (Figure 3-17b and Figure 3-18), with mass-transfer correction applied for kinetic current calculation. A four-electron pathway for ORR was identified,⁵² as shown in the Koutecky-Levich plot. Further comparison of PtNi-NW/C catalysts, accounting for variations in Ni content and annealing temperature (Figure 3-19 and Table 3-4), showed that catalysts with higher Ni content and annealed at 400°C displayed enhanced ORR activity. This aligns with previous studies, where increasing Ni content in Pt_xNi_y alloys induces lattice contraction, shortening Pt-Pt bond lengths in the Pt-rich surface layer due to strain effects, thereby enhancing catalytic activity (Figure 3-20).⁵⁰ Notably, the NW-structured catalysts exhibited a positive shift in the half-wave potential relative to Pt/C, supported by the Tafel plots (Figure 3-21), confirming the significant boost in ORR activity from one-

dimensional NW catalysts. Under the combined influence of strain and ligand effects, PtNi-NW/C achieved an impressive specific activity of 2.07 mA cm^{-2} at 0.9 V vs. RHE , nearly 7-fold that of Pt/C and 2.5-fold that of Pt-NW/C. Additionally, it exhibited the highest mass activity of $1.37 \text{ A mg}_{\text{Pt}}^{-1}$, surpassing Pt/C ($0.21 \text{ A mg}_{\text{Pt}}^{-1}$) and Pt-NW/C ($0.47 \text{ A mg}_{\text{Pt}}^{-1}$) (Figure 3-17f).

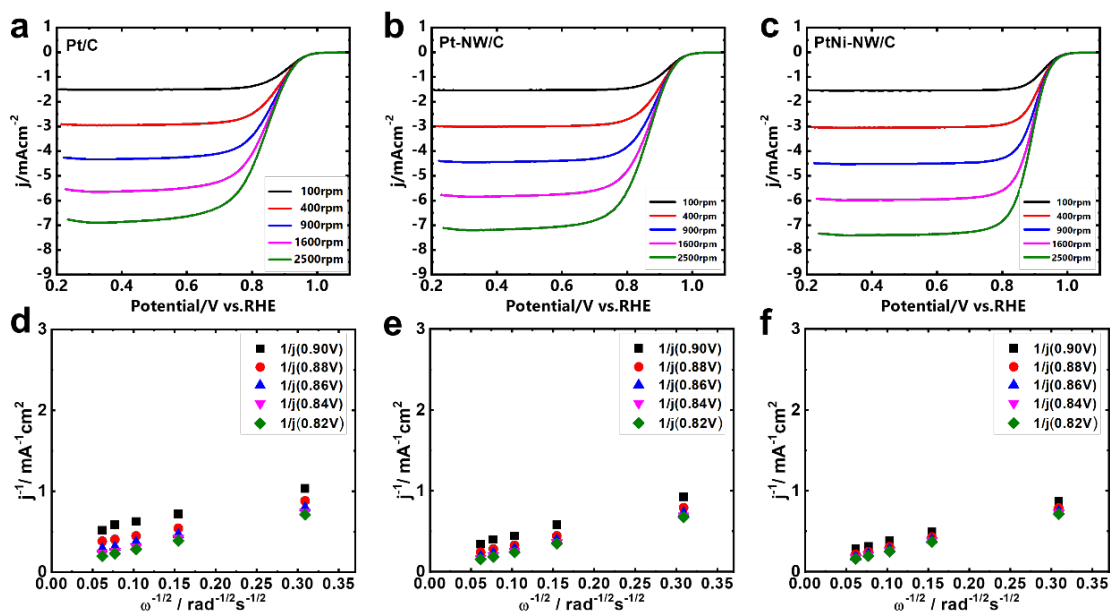


Figure 3-18. LSV curves and Koutecky-Levich plots for (a, d) Pt/C, (b, e) Pt-NW/C, and (c, f) PtNi-NW/C in O_2 -saturated 0.1 M HClO_4 solution at different rotating speed.

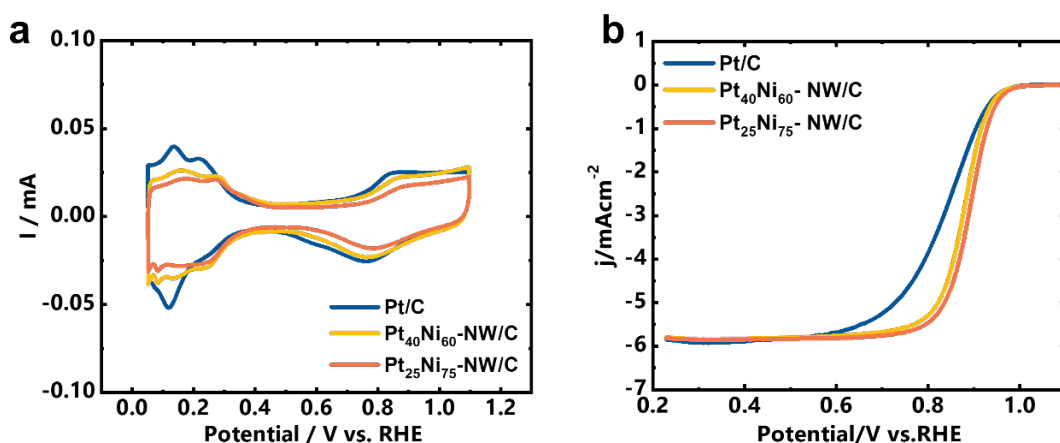
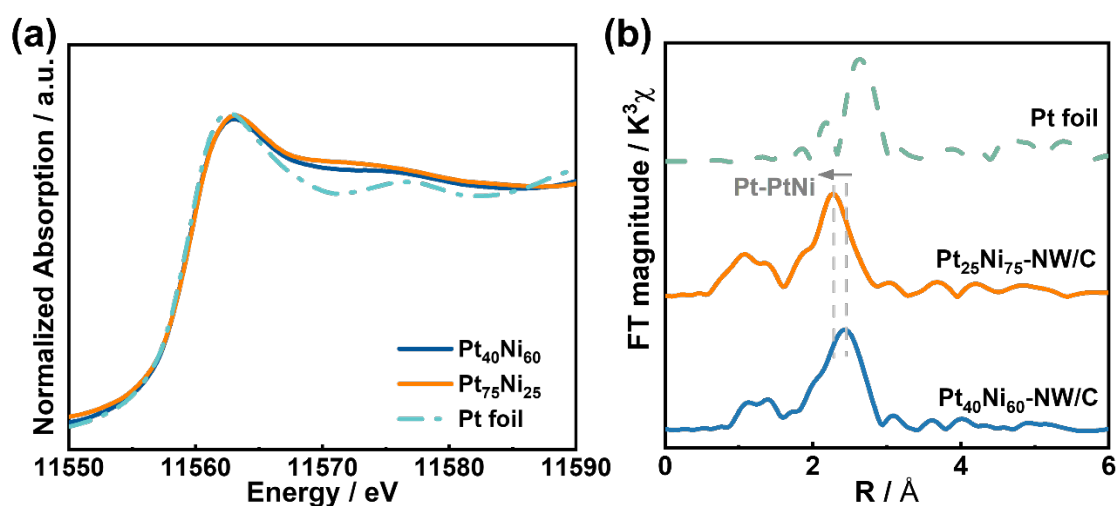


Figure 3-19. (a) CV and (b) LSV curves of PtNi-NW/C catalyst with different Ni content.

Table 3-4. ORR activity of PtNi-NW/C with different Ni content.

Temperature	Specific activity (mA cm^{-2})		Mass activity (A g^{-1})	
	$\text{Pt}_{40}\text{Ni}_{60}$	$\text{Pt}_{25}\text{Ni}_{75}$	$\text{Pt}_{40}\text{Ni}_{60}$	$\text{Pt}_{25}\text{Ni}_{75}$
No treat	850	928	515	529
250°C	1264	1375	709	821
400°C	1811	2074	1050	1366

**Figure 3-20.** (a) Pt L₃-edge XANES spectra and (b) FT-EXAFS spectra of PtNi-NW/C with different Ni content.

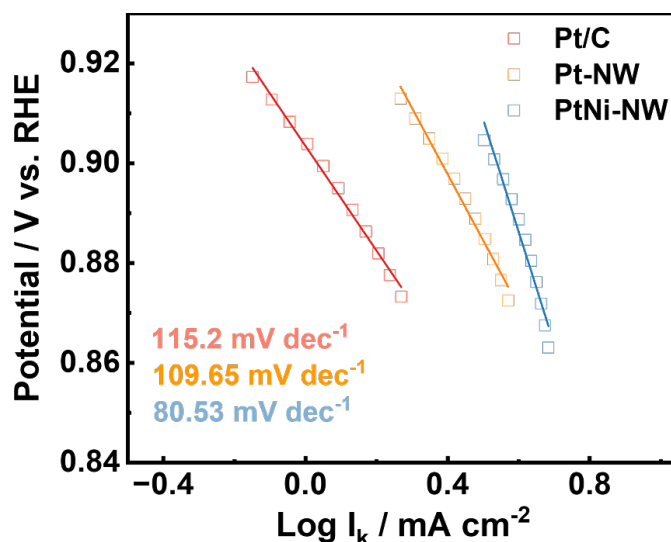


Figure 3-21. Tafel plots of specific activity.

The durability of the catalysts was evaluated by ADT between 0.60 V and 1.0 V *vs.* RHE. Figure 3-17c shows a significant negative shift in half-wave potentials for Pt-NW/C compared to PtNi-NW/C after 10k ADT cycles. TEM and STEM-EDS spectra revealed structural disruption, but the PtNi-NW/C catalyst retained a high Ni content of 60.3 at%, while the unannealed PtNi-NW/C showed approximately 95 at% Ni dissolution, confirming that the Pt-rich surface layer effectively shielded the inner Ni atoms (Figure 3-22 to 3-24). Oxygen coverage was also analyzed at various potentials (Figure 3-17d and Figure 3-25), showing the relationship between oxygen species binding and the Pt surface. At 0.8 V *vs.* RHE, oxygen coverage increased, with the Q_O/Q_H value exceeding 0.0, marking the formation of Pt-OH on the catalyst surface, consistent with previous research.⁵¹ A notable change occurred at 1.1 V *vs.* RHE, where the Q_O/Q_H values for Pt/C and Pt-NW/C exceeded 1.0, indicating the transformation of Pt-OH to Pt-O, which requires two electron transfers per Pt site. This transformation reduced ORR activity by occupying surface-active sites.³² Interestingly, PtNi-NW/C exhibited lower oxygen coverage than Pt/C and Pt-NW/C, suggesting that the Pt-rich layer in PtNi-NW/C lowers oxygen adsorption energy at higher potentials, which could improve ORR performance. This finding is further supported by CO stripping results (Figure 3-17e), where CO_{ads} electrooxidation shifted to a negative potential in PtNi-

NW/C due to the synergistic effects of surface steps, grain boundaries, and core-shell structures.⁵² These structural factors, as noted in previous studies, disrupt the interfacial water network, reduce the activation barrier for O-species conversion, and weaken oxygenated species adsorption, promoting CO_{ads} electrooxidation and enhancing ORR activity.⁵³

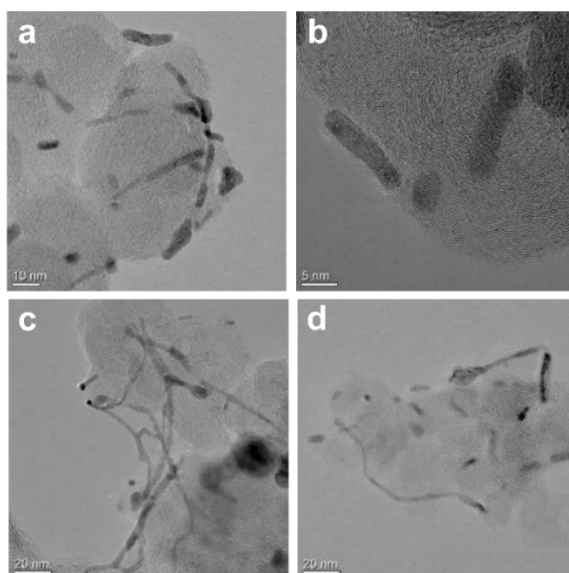


Figure 3-22. TEM images of (a,b) Pt-NW/C and (c,d) PtNi-NW/C catalyst after 10K ADT cycles.

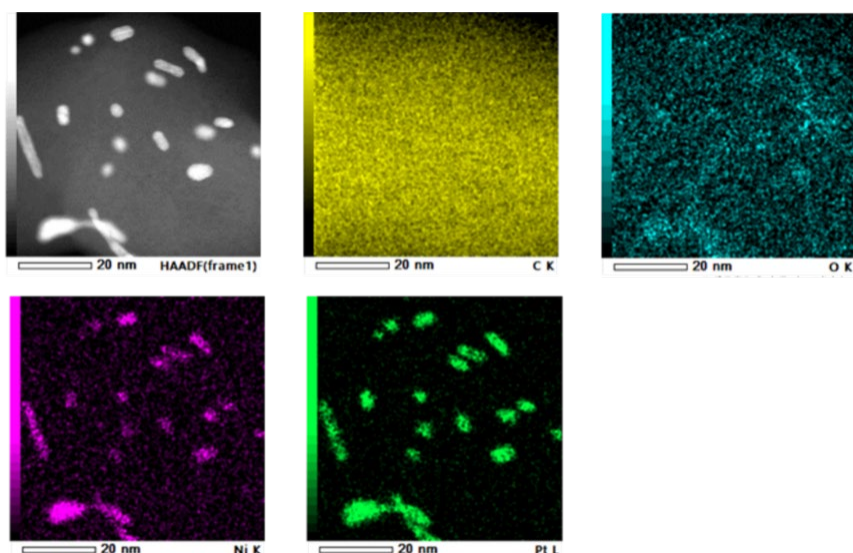


Figure 3-23. STEM image and EDS element mapping for PtNi-NW/C catalyst after 10K ADT cycles.

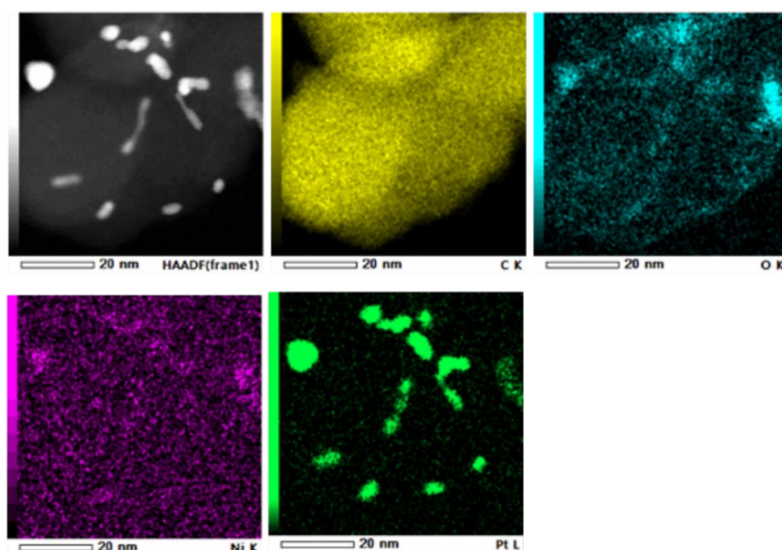


Figure 3-24. STEM image and EDS element mapping for unannealed PtNi-NW/C catalyst after 10K ADT cycles.

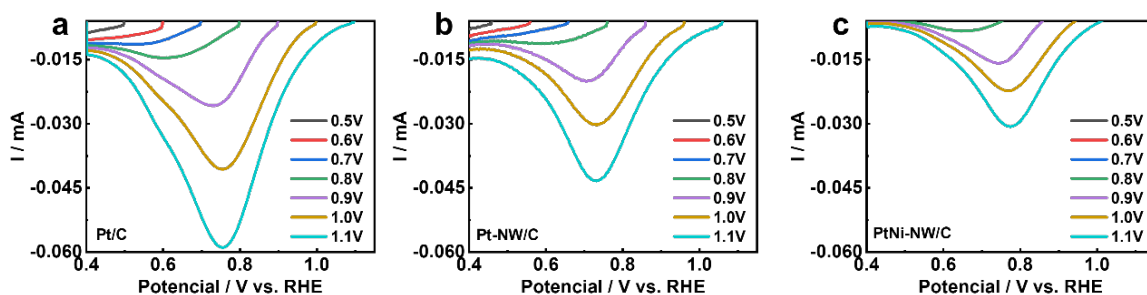


Figure 3-25. Reduction current profiles of oxide species on (a) Pt/C and (b) Pt-NW/C and (c) PtNi-NW/C from 0.50 to 1.0 V vs. RHE.

3.3.4 Chemisorption observation from *operando* HERFD-XANES

To investigate the electronic state of Pt in the Pt/C, Pt-NW/C, and PtNi-NW/C catalysts under ORR condition, *operando* HERFD-XANES analysis was conducted. This technique provides enhanced resolution compared to conventional XAS,⁵⁴ and allows for the distinct identification of changes in the white line, enabling differentiation between chemisorbed oxygen species, Pt oxides, and Pt metal.^{55, 56} For measurements, the catalysts were mounted on RDE and evaluated in an *operando* cell. The primary intensity of the Pt L₃-edge white line increased and shifted positively with increasing

polarization potential, particularly for the Pt/C catalyst (Figure 3-26 and Figure 3-27). This broadening and shifting in the spectrum is attributed to Pt adsorption and subsequent oxidation.⁵⁷ Between 0.5 and 0.8 V vs. RHE, signs of hydroxyl (OH) adsorption on Pt caused a slight shift in peak position and an increase in white line intensity,⁵⁸ with Pt oxidation becoming more pronounced above 1.0 V vs. RHE.^{51, 59} The initial steps involve the dehydration of chemisorbed OH, leaving oxygen atoms on the Pt surface, which eventually form Pt-O bonds.²⁵

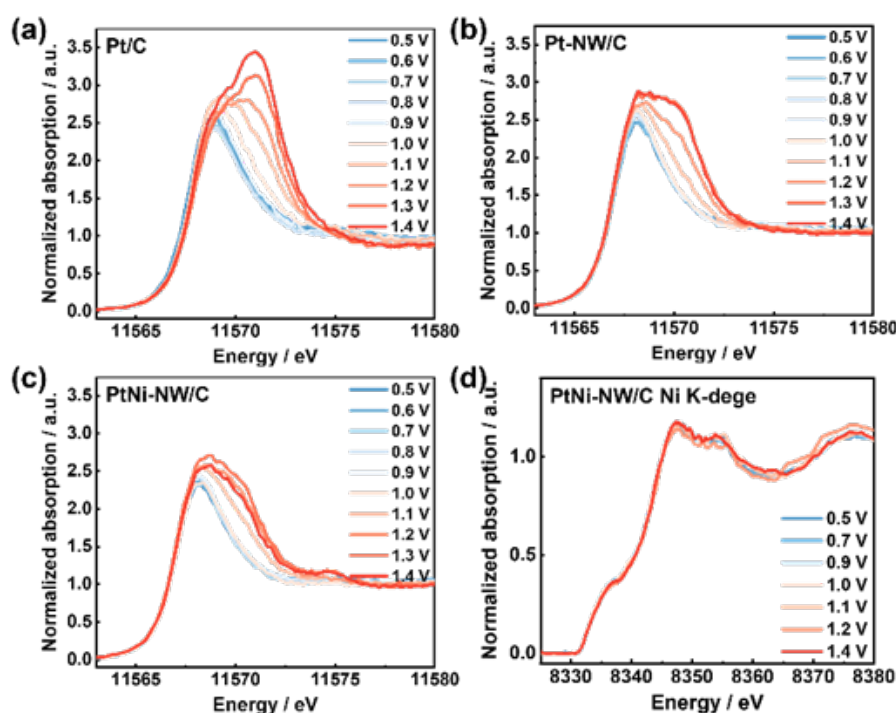


Figure 3-26. *operando* HERFD- Pt L₃-edge XANES analysis for (a) Pt/C, (b) Pt-NW/C, and (c) PtNi-NW/C catalyst varying different polarization potential. (d) *operando* HERFD- Ni K-edge XANES analysis for PtNi-NW/C.

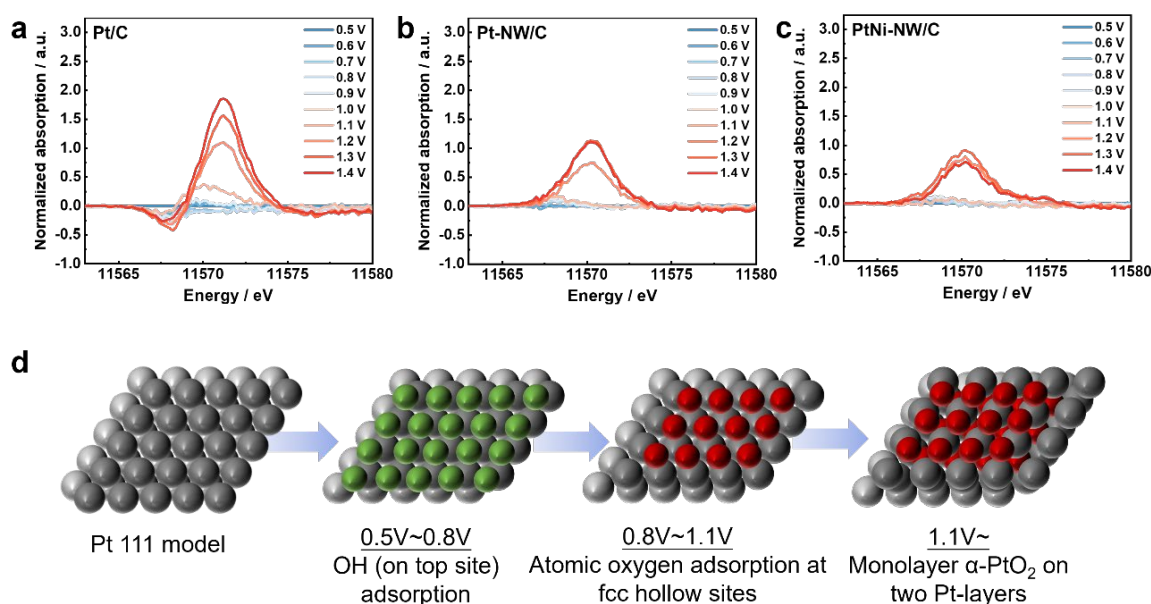


Figure 3-27. (a, b, c) The difference spectra of **Figure 3-26** at various potentials, the spectrum tested at 0.5 V was used as a reference spectrum. (d) The catalyst oxidation process reported by Imai et al.

The subsequent oxidation of the Pt surface leads to the formation of PtO, which not only remains on the surface but also penetrates deeper, forming higher-order oxides such as α -PtO₂, β -PtO₂, and Pt₃O₄ at high polarization potentials.^{51, 60} Computational results from FEFF calculations suggest that as PtO fully converts to α -PtO₂, there is a significant shift of approximately 2 eV towards the higher-energy side, along with a noticeable increase in intensity.⁵⁹ However, in the case of PtNi-NW/C, this shift is smaller, indicating the catalyst does not undergo further oxidation to PtO₂, which is attributed to the Pt-rich surface layer and strain effects.⁴⁶

Catalysts with high transition metal content often tend to adsorb OH species at reaction potentials. The strong affinity of Ni or Co atoms for oxygen (oxyphilicity) accelerates the oxidation of Pt at high polarization potentials. This effect extends to internal Ni atoms, which are prone to oxidation due to interfacial place exchange with surface Pt atoms and adsorbed oxygen.^{61, 62} The *operando* Ni K-edge spectra (Figure 3-26d) show that the PtNi-N/C catalyst with a stable Pt-rich surface layer, minimizing Ni oxidation and resulting in no significant spectral intensity changes. This demonstrates

the effectiveness of post-annealing treatment in forming Pt-rich layer, which prevents Ni dissolution during the ORR process and suppresses the "positional exchange" effect.

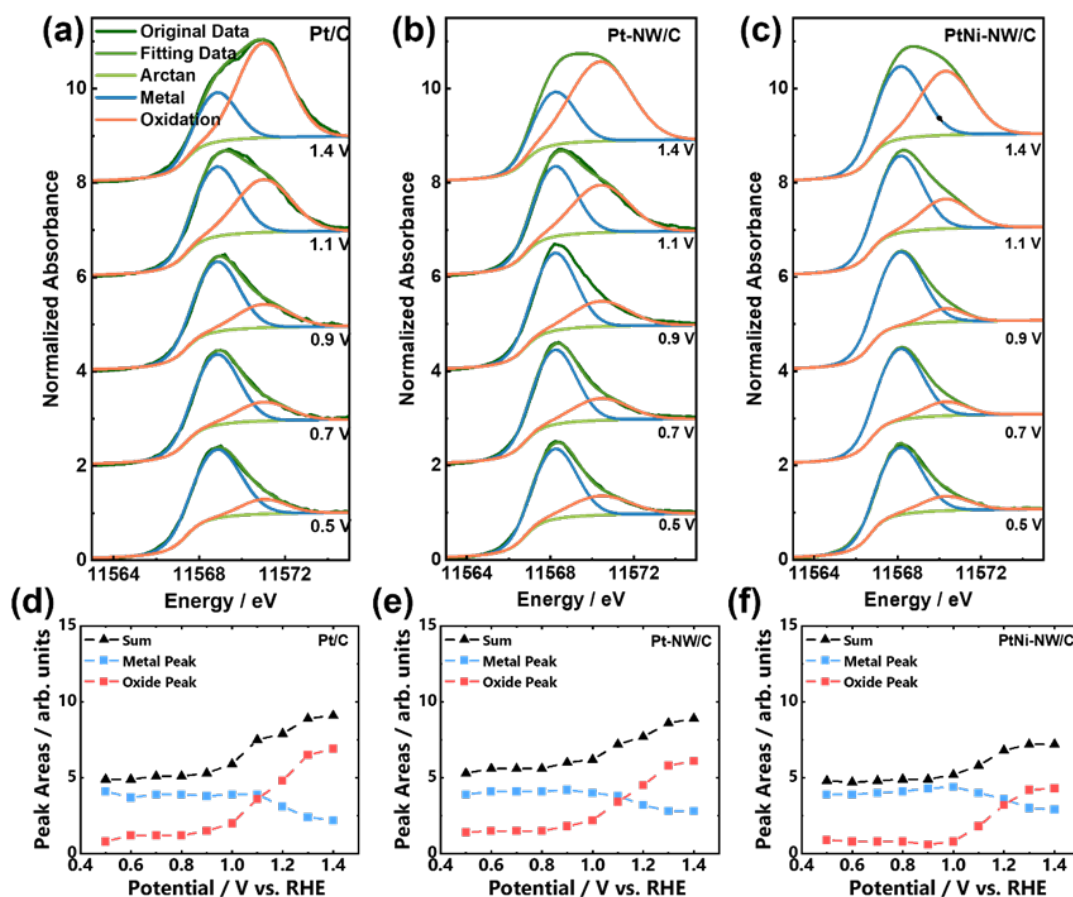


Figure 3-28. Least-square fits by two peaks (metal peak and oxides peak) of all HERFD-XANES spectra from **Figure 3-26** for (a) Pt/C, (b) Pt-NW/C, (c) PtNi-NW/C. Integrated peak areas of metal peak, oxides peak, and sum peak for (d) Pt/C, (e) Pt-NW/C, (f) PtNi-NW/C.

To examine changes in the electronic state of Pt at varying potentials, the spectra were analyzed using an arctangent function combined with two pseudo-Voigt peaks (Figure 3-28a–c). The peaks at 11568.1 eV and 11570.3 eV correspond to the metallic and oxidized states of Pt, respectively. Figure 3-28d–f illustrates the variations in the metallic, oxide, and combined peaks as a function of potential. The PtO_x component increased with rising polarization potential, though this oxidation was mitigated by the NW-structured catalyst, due to its specific surface structure.²⁴ While Pt-NW/C limits PtO_x formation, Pt still tends to convert into PtO_x in highly polarized regions, which can

lead to Pt dissolution and catalyst degradation.⁶³ In contrast, a significant reduction in the oxidized composition was observed for PtNi-NW/C compared to Pt-NW/C, indicating that the Pt-rich surface layer and strain effect of the PtNi alloy hinders PtO_x formation. With lower oxygen adsorption energies and reduced conversion to Pt oxide, PtNi-NW/C catalysts exhibit enhanced activity and stability.

3.3.5 Conventional *operando* XAS measurements

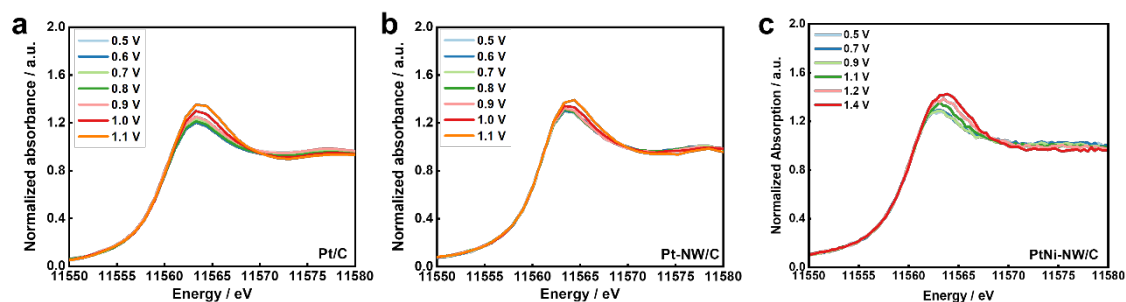


Figure 3-29. Pt L₃-edge XANES spectra of (a) Pt/C, (b) Pt-NW/C and (c) PtNi-NW/C.

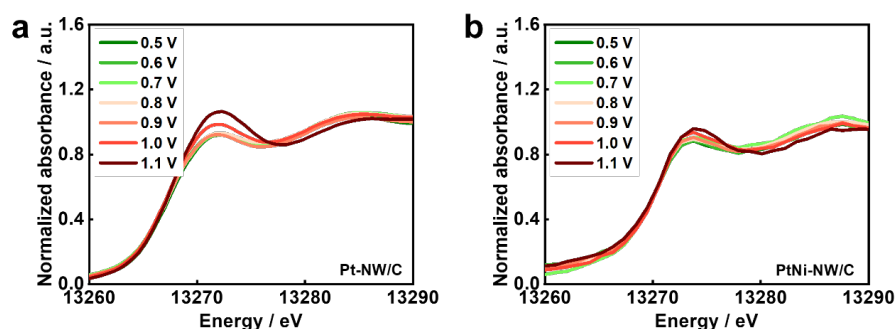


Figure 3-30. Pt L₂-edge XANES spectra of (a) Pt-NW/C, (b) PtNi-NW/C.

The electronic states of Pt in these catalysts were also analyzed using conventional XAS, as shown in Figure 3-29 and Figure 3-30, which display the spectra of the Pt L₂ and L₃-edge at varying potentials. An increase in white line intensity was observed as the potential increased, indicating electron depletion in the Pt d-orbitals due to oxidation. To further investigate changes in Pt valence, $\Delta\mu$ (defined as $\Delta\mu = \mu_E - \mu_{\text{edge}}$) was calculated and depicted in Figure 3-31 and Fig. 7d. The consistent increase in $\Delta\mu$ reflects the presence of chemisorbed oxygen.³⁴ Notably, the minimal increase in white line

intensity observed in the PtNi-NW/C catalyst aligns with the results from HERFD-XANES analysis, confirming its resistance to oxidation.

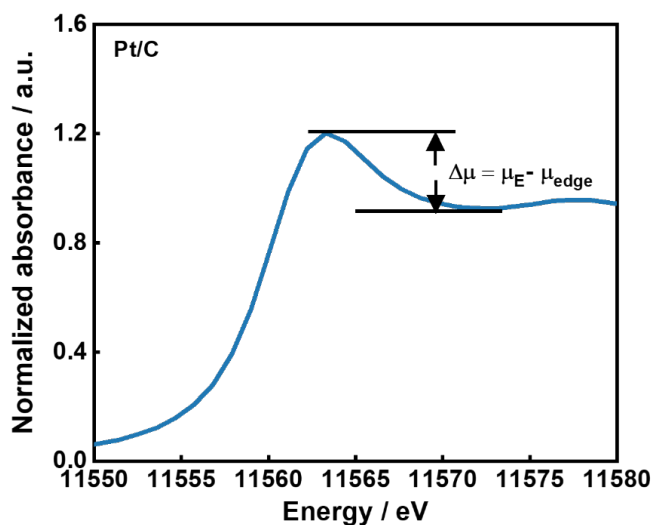


Figure 3-31. XANES spectra showing the determination of the intensity on white line ($\Delta\mu$) for Pt/C.

Figure 3-32a-c and Figure 3-33 present the FT-EXAFS analysis, showing an increase in the Pt-O signal (1.6 Å) and a decrease in the Pt-Pt signal (2.5 Å) as the potential increases. The wavelet-transform EXAFS spectra further confirm the formation of Pt-O bonds at high polarization potentials (Figure 3-34). Compared to Pt/C catalysts, Pt-NW/C and PtNi-NW/C catalysts exhibit less fluctuation in these signals, indicating weaker oxygen binding energies and reduced Pt-O formation on the surface. Pt-Pt bond lengths, calculated by Artemis' IFEFFIT (Table 3-5 to 3-7 and Figure 3-32e), play a crucial role in influencing the d-band center state, which directly impacts ORR activity.⁶⁴ For Pt/C and Pt-NW/C catalysts, a simple fcc Pt model was applied, showing bond lengths of 2.751 Å and 2.746 Å at 0.5 V *vs.* RHE, respectively. As the potential increased, the bond lengths expanded to 2.825 Å and 2.779 Å at 1.1 V *vs.* RHE, due to the combined effect of reduced Pt-Pt coordination number and Pt oxidation.

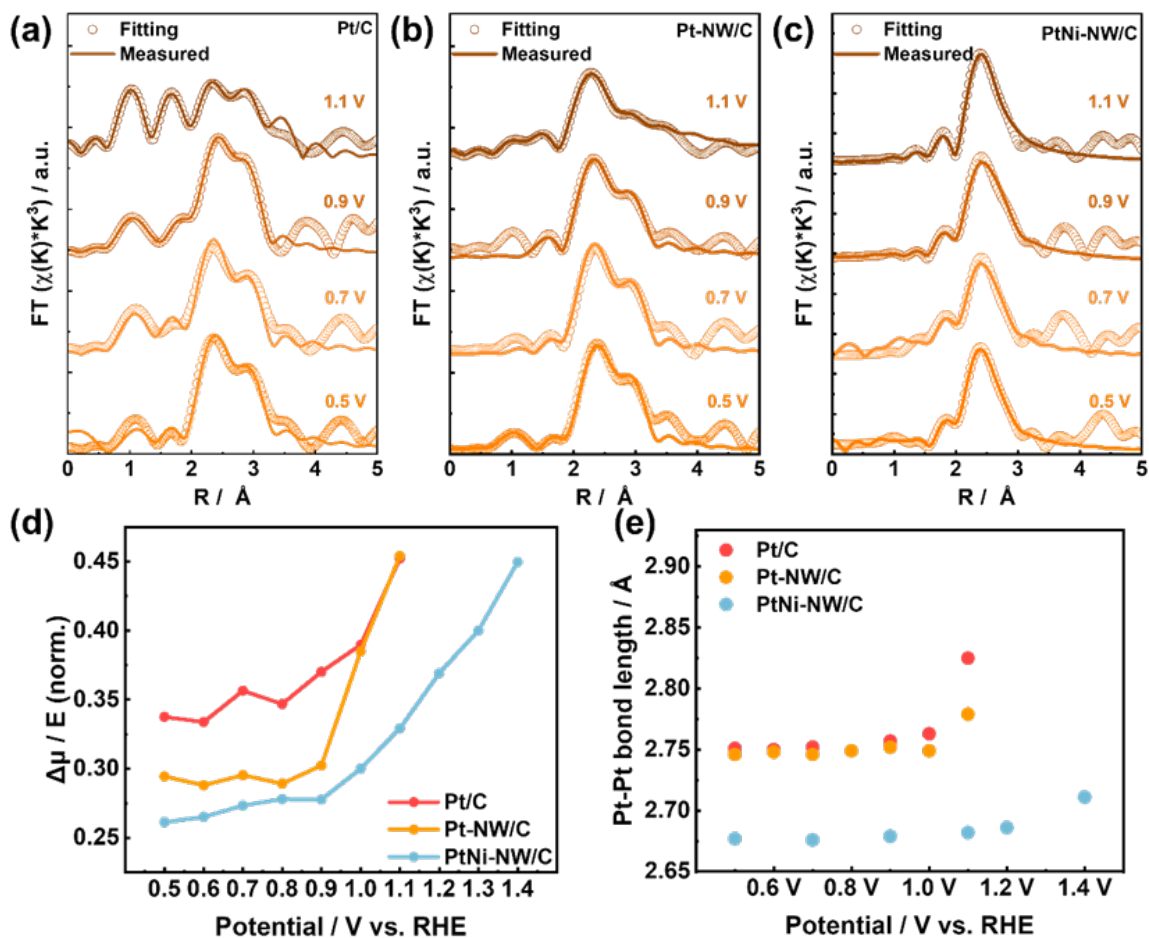


Figure 3-32. Pt L₃-edge FT-EXAFS spectra and corresponding fits for (a) Pt/C, (b) Pt-NW/C, and (c) PtNi-NW/C varying different polarization potential. (d) $\Delta\mu$ of the white line peak heights and (e) Pt-Pt bond length from the corresponding fitting results for Pt/C, Pt-NW/C, and PtNi-NW/C catalysts.

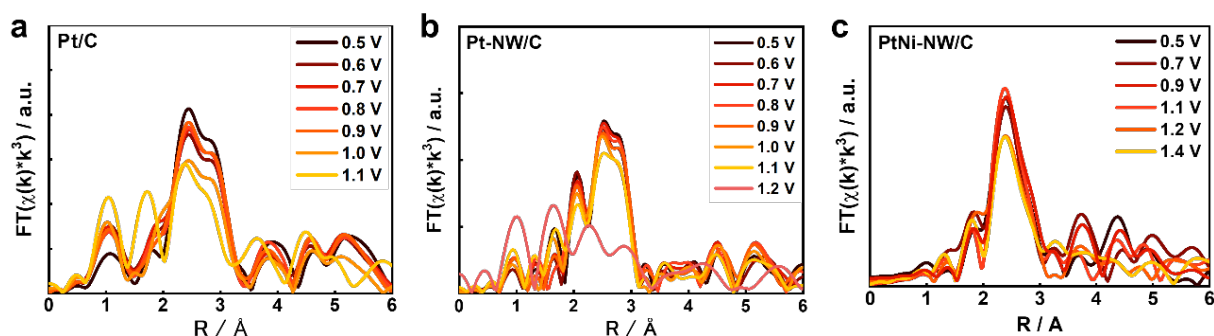


Figure 3-33. The FT-EXAFS spectra for (a) Pt/C, (b) Pt-NW/C and (c) PtNi-NW/C.

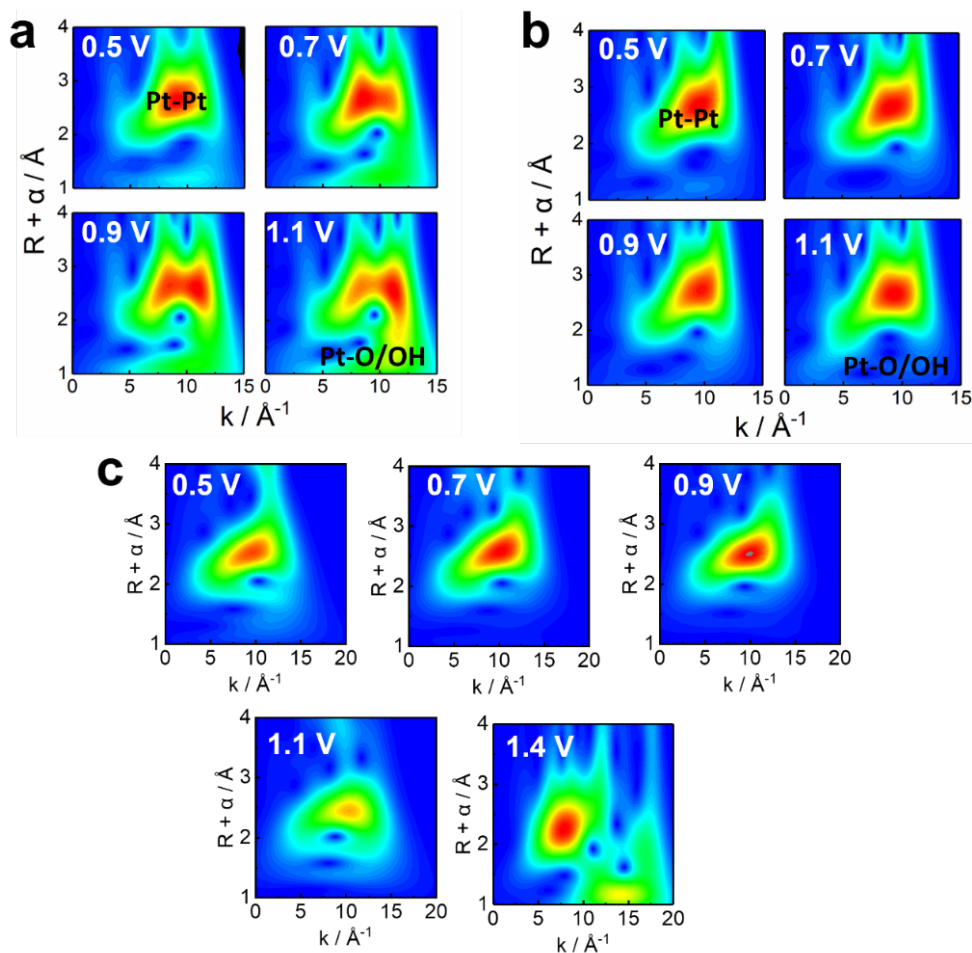


Figure 3-34. WT for (a) Pt/C, (b) Pt-NW/C and (c) PtNi-NW/C at different potential.

For the PtNi-NW/C catalysts with a Pt-rich layer structure, fitting was performed using both fcc Pt and bct PtNi models. At a potential of 0.5 V vs. RHE, the Pt-Pt and Pt-Ni bond lengths were determined to be 2.677 Å and 2.639 Å, respectively, consistent with the PDF results. Although these bond lengths increase with rising potential, the expansion is significantly smaller than that observed in the Pt-NW/C catalyst. The Pt-Pt bond length increases by approximately 0.01 Å at 1.1 V vs. RHE, and even at a high polarization potential of 1.4 V vs. RHE, it remains at 2.711 Å. DFT computational studies support the idea that Pt skins in Pt-Ni catalysts suppress the d-band center, effectively reducing ΔE_o .^{46, 65} This theory, aligned with *operando* XAS results, confirms that the Pt-rich layer and high Ni content in PtNi-NW/C catalysts contribute to enhanced catalytic activity.

Table 3-5. The corresponding R space curve fitting results of Pt L₃-edge for the Pt/C catalysts varying different potential. Fitting details: S_0^2 was fixed at 0.90, which was obtained by fitting the reference foils. Fits were undergone in R-space for $1.5 \leq R \leq 3.3$ Å, and the k_{1,2,3} weighting for $\Delta k = 3 - 11$ Å⁻¹. The path of the Pt-Pt is from the crystal structure of FCC Pt phase (*fm-3m*).

	Bond	Length/Å	CN	$\Delta E/eV$	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.751(2)	9.0(2)	9.516	0.005	1.3%
0.6 V	Pt-Pt	2.750(8)	9.9(2)	10.08	0.007	1.8%
0.7 V	Pt-Pt	2.752(5)	9.5(6)	9.221	0.007	1.1%
0.8 V	Pt-Pt	2.749(9)	8.1(6)	11.50	0.005	0.7%
	Pt-O	2.109(2)	1.0(5)	1.098	0.001	
0.9 V	Pt-Pt	2.757(5)	8.0(3)	10.66	0.005	1.9%
	Pt-O	2.110(4)	1.5(5)	7.088	0.008	
1.0 V	Pt-Pt	2.763(11)	8.2(8)	10.22	0.007	2.3%
	Pt-O	2.109(3)	1.6(9)	9.925	0.008	
1.1 V	Pt-Pt	2.825(13)	5.1(9)	14.88	0.004	2.0%
	Pt-O	2.122(5)	4.1(3)	10.40	0.012	

Table 3-6. The corresponding R space curve fitting results of Pt L₃-edge for the Pt-NW/C catalysts varying different potential.

	Bond	Length/Å	CN	$\Delta E/\text{eV}$	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.746(3)	9.1(1)	8.794	0.008	0.2%
0.6 V	Pt-Pt	2.748(5)	8.9(2)	9.357	0.007	0.7%
0.7 V	Pt-Pt	2.746(5)	9.0(6)	11.32	0.006	1.5%
0.8 V	Pt-Pt	2.749(9)	9.0(5)	8.886	0.007	2.0%
0.9 V	Pt-Pt	2.752(9)	8.8(9)	10.42	0.007	0.9%
	Pt-O	2.110(4)	0.9(5)	-8.333	0.011	
1.0 V	Pt-Pt	2.748(9)	8.2(5)	-3.547	0.008	1.9%
	Pt-O	2.109(3)	1.1(5)	9.942	0.007	
1.1 V	Pt-Pt	2.779(7)	8.0(8)	7.905	0.009	2.3%
	Pt-O	2.150(4)	1.6(9)	18.85	0.005	
1.2 V	Pt-Pt	2.875(12)	3.5(9)	3.345	0.002	2.1%
	Pt-O	2.159(4)	5.1(3)	2.811	0.025	

Table 3-7. The corresponding R space curve fitting results of Pt L₃-edge for the PtNi-NW/C catalysts varying different potential. The corresponding R space curve fitting results of Pt L₃-edge for the Pt/C catalysts varying different potential. The path of the Pt-Pt and Pt-Ni are from the crystal structure of BCT PtNi phase (*P4mmm*) for core structure and FCC Pt phase (*fm-3m*) for Pt layer.

	Bond	Length/Å	CN	$\Delta E/\text{eV}$	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.677(8)	3.3(7)	2.421	0.001	0.2%
	Pt-Ni	2.639(9)	6.5(3)	7.235	0.011	
0.7 V	Pt-Pt	2.676(6)	3.3(2)	-2.419	0.008	2.0%
	Pt-Ni	2.620(9)	6.3(5)	2.149	0.011	
0.9 V	Pt-Pt	2.679(2)	3.5(5)	2.752	0.004	0.3%
	Pt-Ni	2.640(13)	6.0(5)	7.572	0.013	
1.1 V	Pt-Pt	2.682(10)	3.1(3)	5.647	0.001	1.4%
	Pt-Ni	2.651(11)	5.7(2)	5.816	0.012	
	Pt-O	2.110(4)	0.1(3)	-9.320	0.017	
1.2 V	Pt-Pt	2.686(7)	2.7(8)	-0.377	0.007	1.9%
	Pt-Ni	2.642(3)	3.5(3)	12.02	0.002	
	Pt-O	2.150(4)	1.6(3)	25.31	0.004	
1.4 V	Pt-Pt	2.711(12)	1.7(9)	17.56	0.002	0.9%
	Pt-Ni	2.647(9)	2.5(7)	6.513	0.011	
	Pt-O	2.141(4)	2.0(3)	23.96	0.012	

Table 3-8: Acidic ORR activity and durability of PtNi-NW/C and state-of-the-art Pt-based nanocatalysts from recent years-published work.

Catalysts	Mass activity at 0.9 V (A mg _{Pt} ⁻¹)	Specific activity at 0.9 V (mA cm _{Pt} ⁻²)	Degradation of mass activity after ADT test		References
			Loss (%)	Cycles	
IMC-PtFeMo/C nanowire	2.56	5.41	11	10k	<i>Nano Energy</i> , 2024, 129 , 110079
PtNi/C nanowire	0.28	0.25	0	10k	<i>ACS Catal.</i> , 2024, 14 , 1750–1758
PtNi NW/C	1.85	1.64	23.6	10k	<i>Chin. Chem. Lett.</i> , 2024, 35 , 108445
PtNiGa NW/C	2.37	1.89	12.8	10k	
Pt ₂ Ni ₁ /C nanowire	0.095	0.24	18.9	3k	<i>Int. J. Hydrogen Energy.</i> , 2024, 51 , 1487
L ₁ ₂ -Pt ₃ Co/C nanowire	0.31	2.47	6.2	5k	<i>Adv. Funct. Mater.</i> , 2024, 34 , 2311618.
A ₁ -Pt ₃ Co/C nanowire	0.12	1.1	8.3	5k	
O-PtCu/C nanowire	0.48	0.47	4.2	10k	<i>Nano Res.</i> , 2024, 17 , 7001
Waved Pt nanowire/C	0.71	1.55	Na	Na	

Regular Pt nanowire/C	0.56	0.99	Na	Na	<i>Appl. Catal. B: Environ.</i> , 2023, 324 , 122268
Pt@Pt-skin Pt ₃ Ni nanowire	6.69	8.42	2.9	50k	<i>Nat. Commun.</i> , 2023, 14 , 1518
Pt–Ni Nanochains	1.78	3.11	35.9	10k	<i>Adv. Mater.</i> , 2023, 35 , 2206508
Pt–Ni Nanowires	1.25	2.92	58.7	10k	
Pt–Ni Bunched-Nanocages	1.95	3.55	17.4	20k	<i>Adv. Energy Mater.</i> 2023, 13 , 2204257.
PtNiCo branched nanocages	1.03	2.75	13	5k	<i>J. Mater. Chem. A</i> , 2021, 9 , 23444
PtNi branched nanocages	0.37	1.39	NA	NA	
Pt -Co nanoframes/C	0.4	0.8	15.0	10k	<i>Nano Lett.</i> , 2020, 20 , 1974
fct -PtFeIr nanowires/C	2.03	2.40	11.1	10k	<i>Angew. Chem.</i> 2022, 134 , e202113278
fcc -PtFeIr nanowires/C	1.11	1.29	31.6	10k	
Pt _{4.31} Ga nanowires/C	1.89	3.28	15.8	30k	<i>J. Am. Chem. Soc.</i> 2019, 141 , 18083
Jagged Pt nanowires/C	13.6	11.5	12	6k	<i>Science</i> , 2016, 354 ,1414

Pt ₃ Ni nanowires/C	0.546	0.9	63	50k	<i>ACS Catal.</i> , 2019, 9 , 4488
L1 ₀ -PtCo/C NW	1.30	3.55	NA	10k	<i>ACS Appl. Mater. Interfaces</i> , 2022, 14 , 25246
Re-PtNiGa tetrametallic NWs/C	3.49	3.17	10.6	20k	<i>Appl. Catal. B: Environ.</i> , 2022, 303 , 120918
PtNi NWs/C	2.11	2.40	48.9	20k	
WO _{x-(0.25)} -PtNi NWs/C	0.85	1.29	23.89	30k	<i>J. Colloid Interface Sci.</i> , 2022, 607 , 1928
PtNi NWs/C	0.33	0.60	45.94	30k	
Pt/W _{0.02} -SnO ₂ -C	0.23	0.37	10.0	50k	<i>J. Mater. Chem. A</i> , 2024, 12 ,10799
L1 ₂ -PtCu ₃ /C	1.33	2.63	27.1	20k	<i>J. Mater. Chem. A</i> , 2024, 12 ,10385
PtZn-CoNC	0.45	0.55	12.8	30k	<i>J. Mater. Chem. A</i> , 2023, 11 , 24371
PtNi-NW/C	1.37	2.07	5.1	10k	This work

3.4 Conclusions

In summary, high-Ni-content PtNi-NW/C catalysts were synthesized and characterized using techniques such as TEM, XRD, PDF, and XAS, revealing an intriguing fcc Pt-rich surface layer and bct PtNi alloy core structure. Advanced *operando* HERFD-XANES analysis was used to examine the changes in Pt bonding to oxygenated species under reaction conditions, emphasizing the contribution of the Pt-rich layer and PtNi alloy core in suppressing Pt oxidation and preventing Ni dissolution. EXAFS fitting analysis showed minimal changes in Pt-Pt bond lengths in PtNi-NW/C catalysts as applied potential increased, indicating structural stability. This study provides valuable insights into the relationship between catalyst structure, activity, and stability, offering guidance for future catalyst design and optimization.

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Chapter 4. Intermetallic PtCoNi Nanowires for Oxygen Reduction Reaction Catalysts: *operando* Analysis of Structure-Activity Relationships

The sluggish kinetics of the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells demands highly active and stable catalysts to improve efficiency. In this study, we synthesized intermetallic PtCoNi nanowires (PtCoNi-NW) as catalysts for the oxygen reduction reaction. Designed to leverage the ordered atomic structure of PtCoNi intermetallic compounds (I-PtCoNi-NW), these nanowires demonstrate enhanced catalytic activity and stability due to minimized dissolution of transition metals. Structural characterization via X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed a highly ordered L1₀ intermetallic phase with stable nanowire morphology even after high-temperature treatments. Electrochemical analysis confirmed the catalysts' significant ORR activity and stability, attributed to the Pt-rich surface and ordered structure. Utilizing *operando* X-ray absorption spectroscopy (XAS) and high-energy-resolution fluorescence detection (HERFD-XAS), providing critical insights into the electronic and structural dynamics, showing that the shortened Pt-Pt bond length in the L1₀ phase aids in suppressing Pt oxidation while maintaining Co and Ni in the structure.

4.1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are highly regarded as efficient and eco-friendly systems for sustainable energy conversion. Their potential to operate with high efficiency makes them suitable for green energy applications.^{1, 2} However, the slow oxygen reduction reaction (ORR) kinetics at the cathode remains a challenge, requiring substantial amounts of costly platinum-based catalysts to achieve desired power output levels. This reliance on high Pt loading significantly limits the broader application and commercialization of PEMFCs.^{3, 4} Consequently, enhancing the performance of Pt-based catalysts while reducing their precious metal content is a critical challenge that must be addressed to advance PEMFC

applications.

Alloying platinum with 3d transition metals has emerged as an effective strategy to improve catalytic activity and decrease Pt loading.⁵⁻⁷ Extensive experimental studies have confirmed that such alloying leads to enhanced ORR performance, primarily due to ligand and strain effects that arise from the deliberate adjustment of the catalyst's near-surface composition.⁸

Compared to traditional disordered alloys, Pt-based intermetallic compounds (IMCs) exhibit ordered atomic structures and precise stoichiometries, resulting in stronger interactions between Pt and transition metal atoms.^{9, 10} This ordered arrangement not only enhances catalytic activity but also improves stability by reducing the dissolution of less noble metals during operation.¹¹ However, synthesizing Pt-based IMCs nanocatalysts with well-defined morphologies presents significant challenges, largely due to the high-temperature treatments typically required to achieve an ordered phase.^{12, 13} Such conditions often lead to increased particle size and aggregation, complicating the synthesis of nanocatalysts with desired structural features.¹⁴

One-dimensional Pt-based alloy nanowires are extensively studied in electrocatalysis because their unique anisotropic properties, excellent electrical conductivity, and high surface area enhance catalytic activity.^{15, 16} By designing these nanowires to expose high-index facets rich in unsaturated atomic steps and kinks—which serve as active sites for bond cleavage—their catalytic performance can be further optimized.¹⁷ Despite these advantages, ultrafine 1D nanowires are susceptible to breakage and agglomeration during the high-temperature processes required to achieve ordered structures, ultimately leading to decreased catalytic performance.¹⁸ To mitigate these issues, strategies such as incorporating high-melting-point metals and protective shells have been employed.¹⁹ For example, Li et al. enhanced the thermal stability and catalytic activity of Pt-based nanowires by introducing molybdenum and coating them with a silica shell.²⁰ However, the inclusion of additional metals and the use of etching agents like hydrofluoric acid make the synthesis process more complex. While increasing the diameter of nanowires can improve their stability at elevated temperatures, it may limit Pt utilization efficiency. Conversely, nanowires that are too thin may suffer from reduced

durability. As noted by Bu et al., employing 1D Pt structures for ORR applications often involves a trade-off between maximizing Pt utilization and ensuring long-term durability.²¹

To establish a clear relationship between the observed catalytic performance and the structural characteristics of nanowires, *in situ* studies are essential. Such investigations provide a comprehensive understanding of how the structure and chemistry of nanowires evolve under real-time electrochemical conditions, closely simulating the environments encountered in practical applications.²² *Operando* X-ray absorption spectroscopy (XAS) is a powerful technique for examining real-time changes, especially useful in studying the formation of Pt oxide species during ORR process.²³ High-energy-resolution fluorescence-detected (HERFD) XAS provides enhanced analytical precision by selectively capturing X-rays emitted from excited core electrons, which reduces core-hole lifetime broadening and improves signal-to-noise ratios.²⁴ This advanced method yields detailed information on the electronic states of Pt atoms, offering a deeper understanding of catalyst behavior under operating conditions.

In this study, we report the successful synthesis of carbon-supported PtCoNi intermetallic nanowires with an average diameter of approximately 15 nm using a hydrothermal method. The relatively larger diameter of these nanowires allows them to maintain their structural integrity during high-temperature annealing processes. The formation of intermetallic phases with transition metals effectively tunes the electronic properties of Pt, resulting in enhanced catalytic activity for the ORR.

4.2 Experimental Methods

4.2.1 Materials

Pt(II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 98%), Ni(II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%), and Co(III) acetylacetonate ($\text{Co}(\text{CO})_3$, 98%) were obtained from Sigma-Aldrich. Ethanol (99.5%), 2-propanol (99.7%), oleylamine (OAm, 85%), cyclohexane (99.5%), glucose, and hexadecyltrimethylammonium chloride (CTAC, 99%) were sourced from Fujifilm. The electrolyte was prepared using ultrapure water (Milli-Q, 18.2 M Ω) and

ultrapure perchloric acid from Kanto Chemical Co. Inc. Vulcan XC-72 carbon was supplied by Cabot Corporation, and gases such as O₂ (99.995%), N₂ (99.999%), and H₂ (5% in N₂ balance) were purchased from Kyoto Teisan Co., Ltd. A commercial Pt/C catalyst (29.1 wt%; TEC10V30E) was obtained from Tanaka Kikinzoku Kogyo Co., Ltd., Japan.

4.2.2 Synthesis of the PtCoNi nanowire catalyst

To synthesize PtCoNi nanowire catalysts, a precise amount of Pt(acac)₂, Ni(acac)₂, Co(CO)₃, and CTAC was dissolved in 5 mL of oleylamine (OAm) and sonicated for 1 hour at room temperature. The mixture was then heated in a 60°C water bath until a uniform, clear solution was achieved. This solution was transferred to an autoclave and heated at 200°C for 10 hours, producing nanowire-structured catalysts. The resulting product was cooled, washed with a cyclohexane/ethanol mixture to remove any residual organics, and dried to yield a black powder. This powder was then dispersed in a cyclohexane/ethanol solution with Vulcan XC-72 carbon black, sonicated in an ice bath for 2 hours, and centrifuged to obtain PtCoNi-NW/C (12.3 wt% Pt). To promote specific crystal structures, the nanowires were calcined in a 5% H₂ and 95% N₂ atmosphere at 400°C and 550°C for 10 hours.

4.2.3 Characterization

The structure of the PtCoNi nanowires was characterized using synchrotron X-ray diffraction (XRD) at beamline BL02B2 at SPring-8, Japan, with background corrected using Match! 3 software and calibrated to a wavelength of 0.35437 Å using CeO₂ as a reference. Morphological and structural analysis was performed using a JEM-2200FS transmission electron microscope (JEOL, Ltd.) operating at 200 kV, and high-resolution TEM (HR-TEM) and energy-dispersive X-ray spectroscopy (EDS) mapping were conducted on a JEOL-JEM-ARM200F microscope to obtain detailed compositional insights.

4.2.4 Electrochemical measurements

Electrochemical measurements were carried out in a three-electrode cell at room temperature,

utilizing a reversible hydrogen electrode (RHE) with 5% H₂ as the reference, a Pt mesh as the counter electrode, and a glassy carbon rotating disk electrode (RDE) with a 5 mm diameter as the working electrode, which was coated with the catalyst. The RDE was polished with alumina and rinsed thoroughly to remove any contaminants. Catalyst ink was prepared by dispersing 2 mg of catalyst in a solution of ultrapure water and 2-propanol (0.3:1.7) with 40 μ L of 5 wt% Nafion® as a binder. This ink was sonicated for 30 minutes and then drop-cast onto the RDE, with a Pt loading of 6.5 μ g/cm².

For catalyst activation, cyclic voltammetry (CV) was conducted in N₂-saturated 0.1 M HClO₄ for 50 cycles, scanning between 0.02 and 1.2 V vs. RHE at 100 mV/s to remove residual surfactants. A stable CV curve was then recorded at a scan rate of 50 mV/s. For oxygen reduction reaction (ORR) studies, linear sweep voltammograms (LSVs) were recorded in O₂-saturated 0.1 M HClO₄, with scans from 0.2 to 1.2 V vs. RHE at 10 mV/s. Additional LSV measurements were conducted at various rotation speeds from 100 to 2500 rpm, with background corrections made using N₂-saturated solutions. Data at 0.9 V vs. RHE were analyzed using the Koutechy-Levich (K-L) equation. Electrochemical active surface area (ECSA) was estimated from the hydrogen adsorption charge in the CV curve, based on a monolayer adsorption value of 210 μ C/cm².

Catalyst durability was evaluated through an accelerated degradation test (ADT), where potential was cycled between 0.60 V and 1.00 V vs. RHE, each held for 3 seconds over 10,000 cycles. Post-ADT LSV measurements were used to assess stability.

4.2.5 *operando* XAS measurement

X-ray absorption spectroscopy (XAS) for PtCoNi alloy nanowires was performed at the BL36XU beamline at SPring-8, Japan, using a Si (111) monochromator and a 4 mrad total reflection Ru mirror to produce monochromatic X-rays. The *operando* cell, made from polyether ether ketone (PEEK), was equipped with an Ag/AgCl reference electrode (saturated KCl), a platinum mesh counter electrode, and a glassy carbon rotating disk electrode (RDE) coated with the catalyst as the working electrode. Gas was introduced at the cell's base through

a PTFE tube, with a check valve at the top to maintain pressure during bubbling. X-rays were transmitted through a 25 μm Kapton® film window, and data were processed using ATHENA and ARTEMIS software from the IFEFFIT suite.

For high-energy resolution fluorescence detection (HERFD)-XAS at the Pt L₃-edge, measurements were conducted at the BL39XU beamline under O₂-saturated 0.1 M HClO₄ conditions, with potentials referenced to the reversible hydrogen electrode (RHE). X-ray emission spectroscopy (XES) was utilized to monochromatize the emitted fluorescent X-rays before data acquisition, with Si (220) monochromators and a 4.5 mrad total-reflection Rh mirror used to collimate and monochromate the beam. HERFD-XAS spectra were analyzed using an arctan function for background adjustment, combined with two pseudo-Voigt functions (Gaussian-Lorentzian) for peak fitting. Here, A_{bg} adjusted the arctan height to match μ_E values between 11568 and 11570 eV, with E_{bg} and E_n values aligned to prior studies, and m_n was fixed at 0.5.

$$\frac{A_{bg}}{\pi} \left[\tan^{-1} \left(\frac{E-E_{bg}}{\Delta E_{bg}} \right) + \frac{\pi}{2} \right] \quad (4-1)$$

$$\frac{A_n}{1+4m_n \frac{(E-E_n)^2}{\Delta E_n^2}} \exp \left[-4 \cdot \ln 2 \cdot (1-m_n) \cdot \frac{(E-E_n)^2}{\Delta E_n^2} \right] \quad (4-2)$$

4.3 Results and Discussion

4.3.1 Identification of the PtCoNi nanowire structure

Using a straightforward wet chemical synthesis method, we successfully prepared PtCoNi alloy nanowires through the simultaneous reduction of Pt(acac)₂, Ni(acac)₂, and Co(acac)₃ in OAm. ICP analysis confirmed the complete reduction of metals during the reaction, yielding an atomic ratio of Pt₅₀Co₃₆Ni₁₄. The morphology of the as-synthesized nanowires was thoroughly characterized by TEM, HR-TEM, and HAADF-STEM (Figure 4-1). The results revealed that the nanowires have an average diameter of approximately 15 nm with irregular surface features.

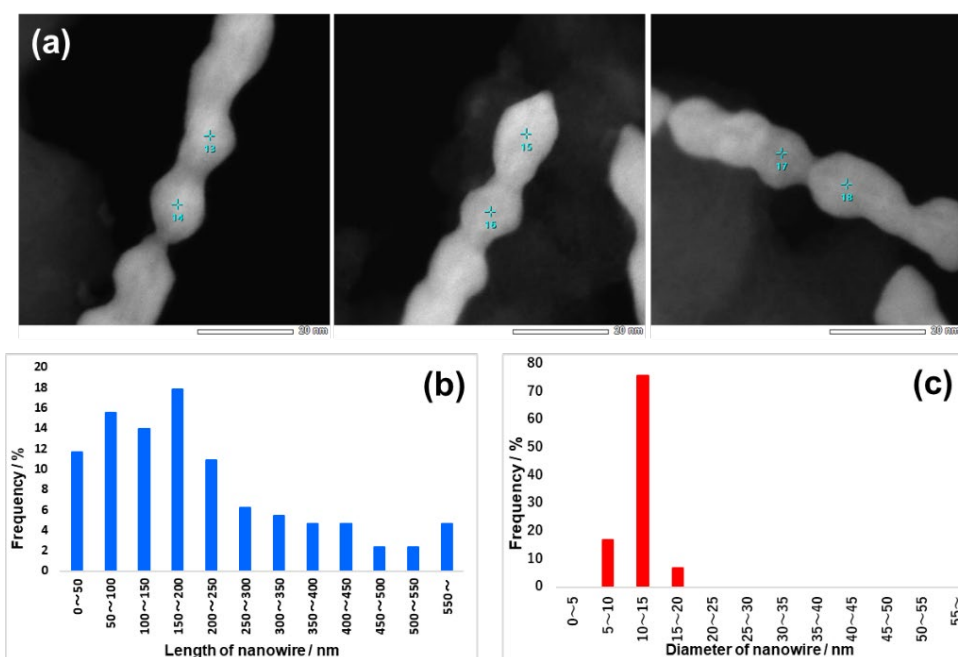


Figure 4-1. (a) STEM images, (b) length distribution and (c) diameter distribution of D-PtCoNi-NW/C.

Selected area electron diffraction (SAED) patterns exhibited distinct polycrystalline diffraction rings. The first to third rings correspond to the (111), (200), and (220) planes of face-centered cubic (fcc) structured PtCoNi alloy, indicating $Fm-3m$ symmetry (denoted as D-PtCoNi-NW/C) (Figure 4-2). The XRD pattern of D-PtCoNi-NW/C also displayed characteristic fcc phases, with the three main diffraction peaks ((111), (200), and (220)) positioned between those of pure Pt and Co (Figure 4-3). Further atomic arrangement analysis (Figure 4-4b and c) showed alignment with the PtCoNi $Fm-3m$ [0 -1 1] and [0 0 -1] crystal structural models. Most nanowires exhibited a lattice spacing of 0.223 nm, corresponding to the (111) plane of typical fcc PtCoNi nanocrystals. Moreover, the nanowire surfaces displayed evident stepped structures, exposing more high-index facets such as (221), (211), and (311), which are beneficial for enhancing catalytic activity.²⁵

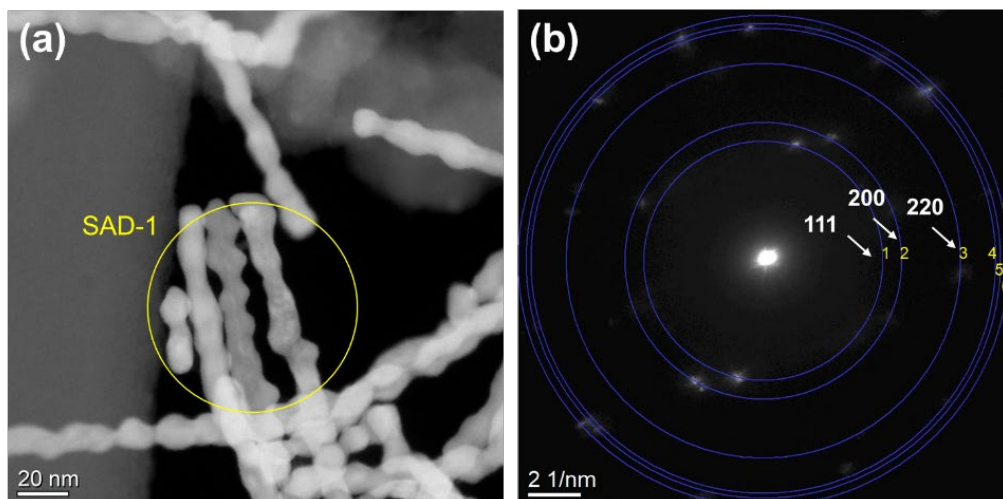


Figure 4-2. (a) HAADF-STEM image, (b) SAED image from the yellow area of D-PtCoNi-NW/C.

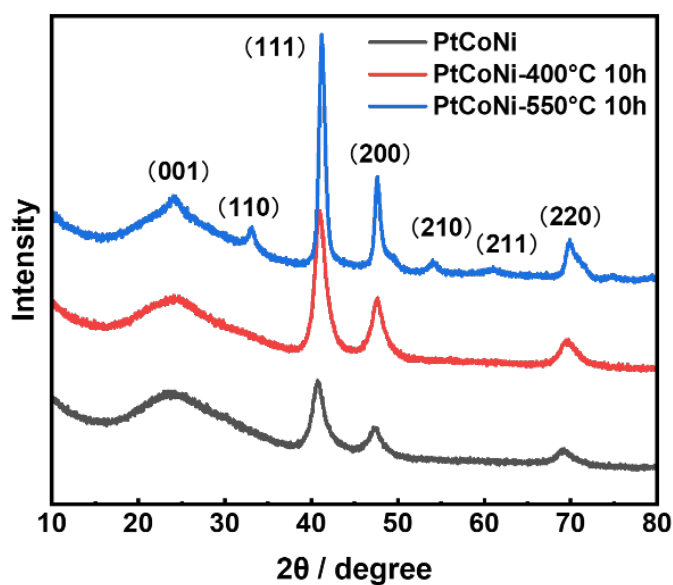


Figure4-3. XRD pattern for PtCoNi-NW/C.

EDS mapping and EELS imaging via STEM revealed a lack of ordered arrangement and non-uniform elemental distribution in the as-prepared catalyst (Figure 4-4d and Figure 4-5). Line scan results indicated a Pt-rich surface on the catalyst (Figure 4-6). PXRD patterns with a wavelength of $\lambda = 0.354 \text{ \AA}$ were used to analyze the crystal structure of D-PtCoNi-NW/C (Figure 4-7). Simulations using the fcc PtNiCo model yielded a lattice constant of $a = 3.845 \text{ \AA}$, indicating a more compact structure compared to standard Pt crystals ($3.925 \text{ \AA}$).

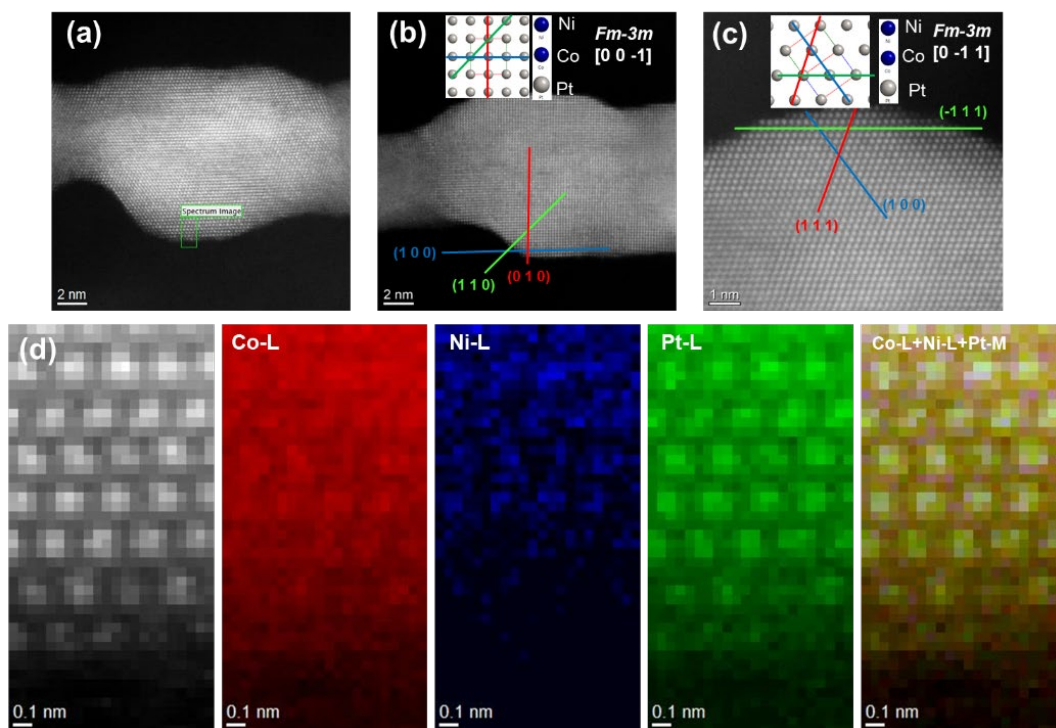


Figure 4-4. (a-c) HAADF-STEM image, (d) STEM-EELS mappings for D-PtCoNi-NW/C.

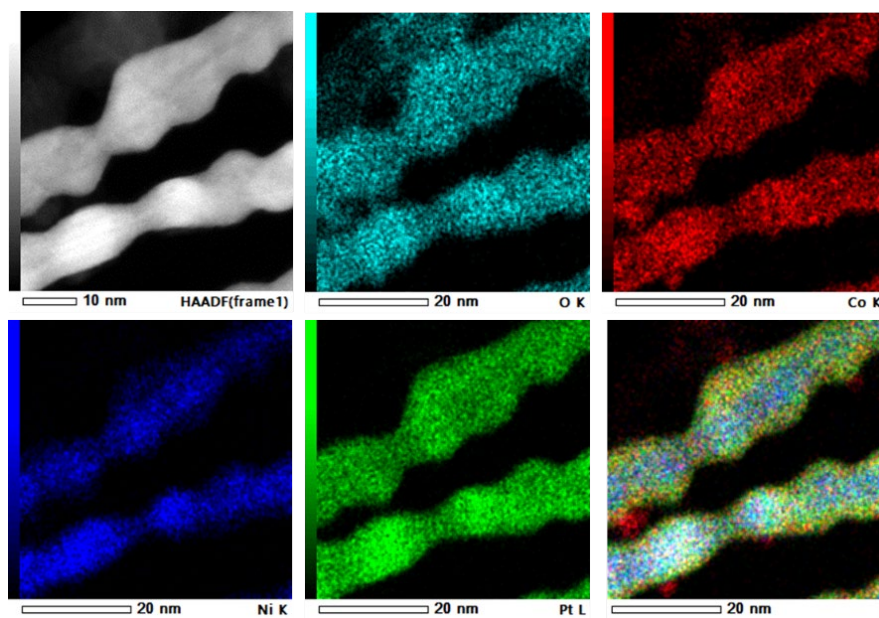


Figure 4-5. STEM-EDS element mapping spectrum of D-PtCoNi-NW/C

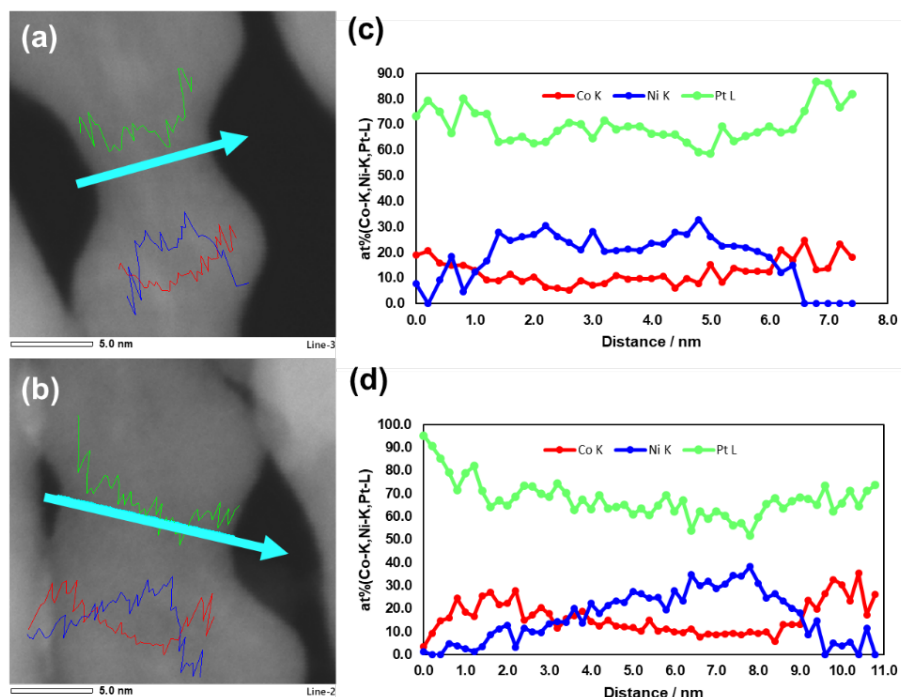


Figure 4-6. (a, b) STEM images, and (c, d) corresponding line scanning profiles of D-PtCoNi-NW/C.

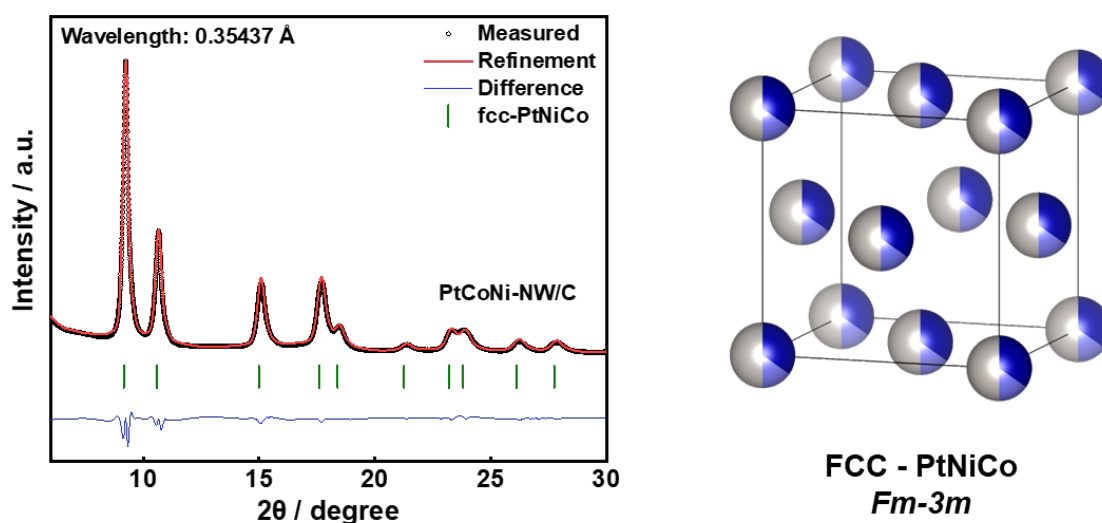


Figure 4-7. Powder XRD pattern of D-PtCoNi-NW/C.

After annealing at various temperatures for 10 hours in a reducing atmosphere (5% H_2/N_2), it was found that only at 550 °C did D-PtCoNi-NW/C transform from the fcc phase to an ordered $L1_0$ face-centered tetragonal (fct) intermetallic structure (denoted as I-PtCoNi-NW/C).

²⁵ By recording XRD spectra at different annealing temperatures, the phase transition from fcc

to fct was traced. After annealing at 550 °C for 10 hours, new diffraction peaks corresponding to the (001), (110), and (210) planes emerged, indicating the formation of the L1₀ structure (Figure 4-3). TEM and HR-TEM images of the annealed nanowires showed that they largely retained their initial morphology. Although high temperatures caused some nanowires to break, reducing the average length to about 100 nm, the diameter remained unchanged at approximately 15 nm (Figure 4-8). This unique stability eliminates the need for protective coatings to prevent sintering during high-temperature annealing. Unlike thinner nanowires that tend to break and aggregate at temperatures above 450 °C,²⁶ increasing the nanowire diameter effectively maintains their morphology while promoting the formation of ordered alloy structures.

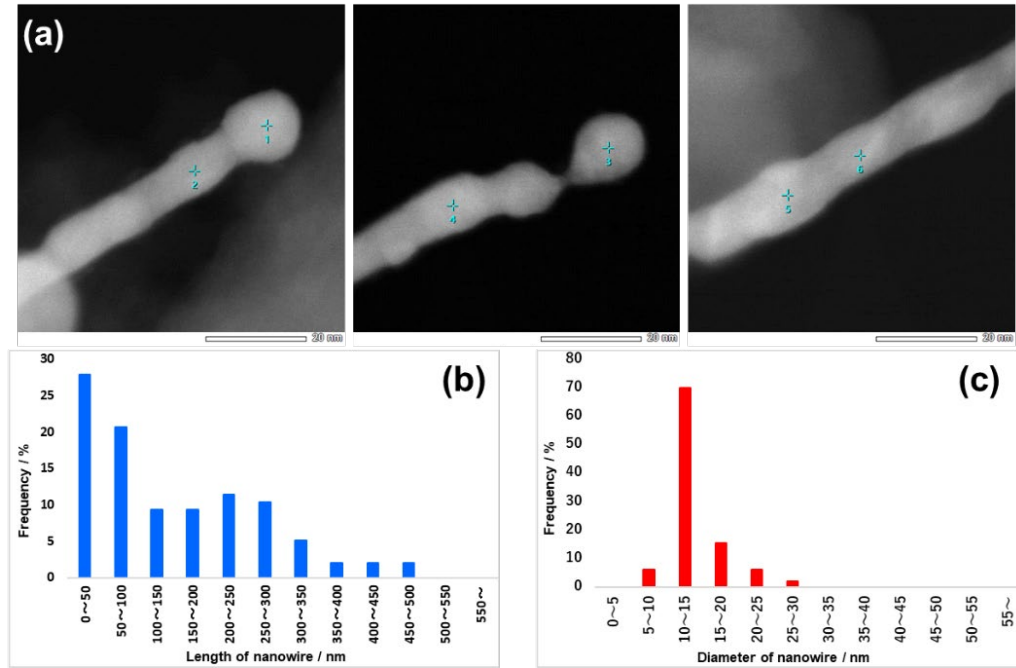


Figure 4-8. (a) STEM images, (b) length distribution and (c) diameter distribution of I-PtCoNi-NW/C.

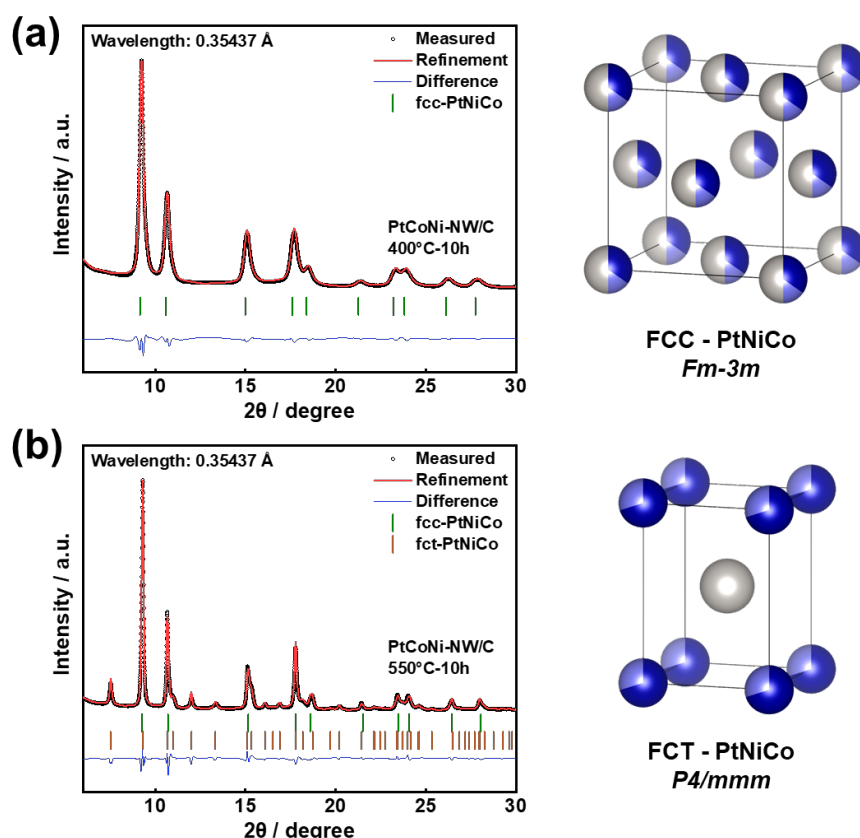


Figure 4-9. Powder XRD pattern of PtCoNi-NW/C after annealing at (a) 400°C and (b) 550°C for 10h.

Further fitting of the XRD results in Figure 4-9 revealed that samples annealed at 400 °C did not show significant $L1_0$ phase but exhibited a compressed fcc structure with a lattice constant of $a = 3.836 \text{ \AA}$. The I-PtCoNi-NW/C catalyst annealed at 550 °C for 10 hours presented a mixed configuration of fcc and fct phases, with the fct phase being predominant, accounting for about 60% of the total mass. The lattice constants were $a = 3.799 \text{ \AA}$ for the fcc phase and $a = 2.696 \text{ \AA}$, $c = 3.701 \text{ \AA}$ for the fct phase.

The SAED pattern displayed distinct polycrystalline diffraction rings, where the first to fifth rings corresponded to the (001), (100), (101), (110), and (002) planes of fct-PtCoNi, respectively, exhibiting $P4/mmm$ symmetry (Figure 4-10). Figure 4-11b further analyzed the atomic arrangement of I-PtCoNi-NW/C, confirming that its structure matches the PtCoNi $P4/mmm$ [0 -1 0] crystal structural model. Notably, a minor presence of the $L1_2$ structure Pt_3Co

($Pm-3m$) was detected in some regions, possibly due to uneven distribution of transition metals within the nanowires (Figure 4-11c).

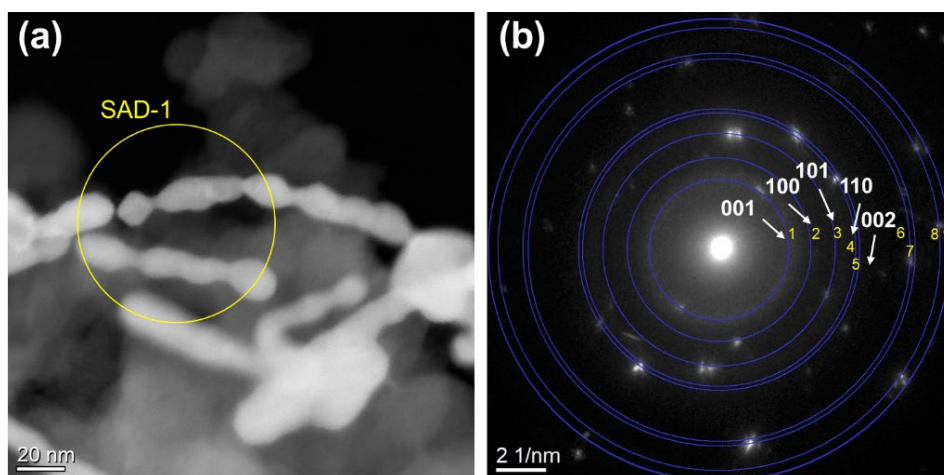


Figure 4-10. (a) HAADF-STEM image, (b) SAED image from the yellow area of I-PtCoNi-NW/C.

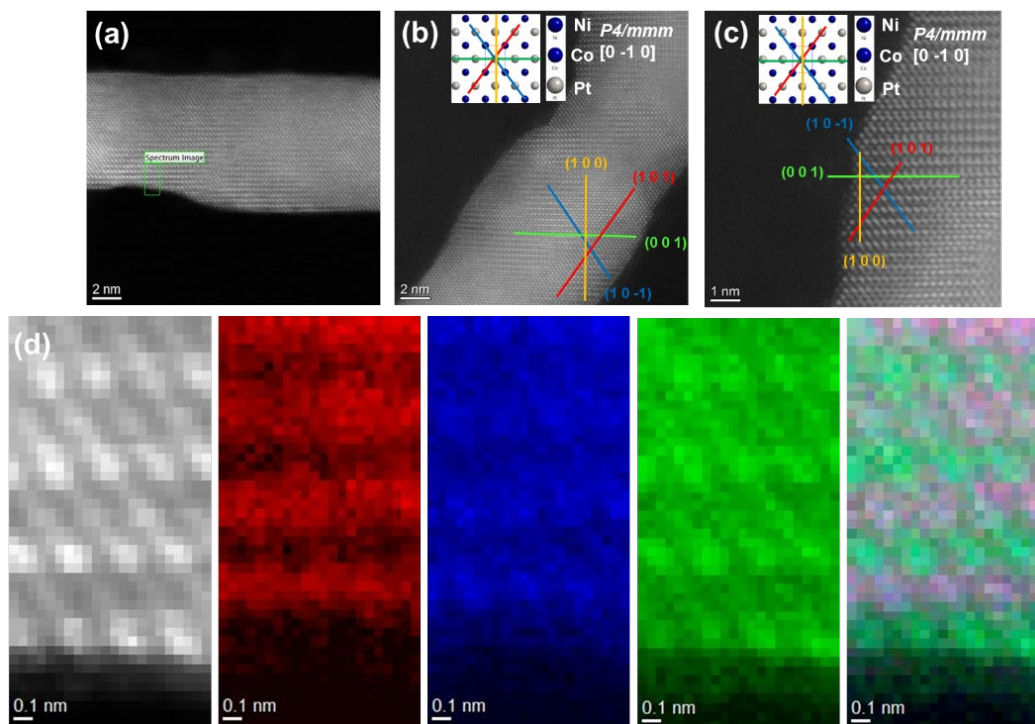


Figure 4-11. (a-c) HAADF-STEM image, (d) STEM-EELS mappings for I-PtCoNi-NW/C.

Previous studies have reported that while thermodynamics permit surface transformations at lower temperatures,²⁷ the slow atomic diffusion within the nanowires hinders the migration of

phase boundaries between the newly formed intermetallic phase and the random alloy phase.²⁸ Once inside, the phase transformation kinetics significantly slow down.²⁹ This suggests that larger-diameter nanowires exhibit slower internal elemental diffusion during annealing compared to typical nanoparticles, leading to uneven distribution.

STEM EDS mapping and line scan results showed that Pt tends to enrich in specific regions near the core, helping forming an L_{12} -Pt₃M₁ structure (Figure 4-12 and 4-13). Unlike the body-centered tetragonal structure of L_{10} , the L_{12} structure is an ordered arrangement within a face-centered cubic lattice; therefore, it does not exhibit the anisotropy characteristic of the L_{10} structure but possesses highly symmetric isotropy. EELS imaging indicated that Pt atoms alternately arrange with Co/Ni atoms, forming an ordered L_{10} structure (Figure 4-11d). Additionally, the edges of the annealed I-PtCoNi-NW/C still exhibited stepped features, indicating that the annealing process did not alter the surface structural characteristics of the catalyst.

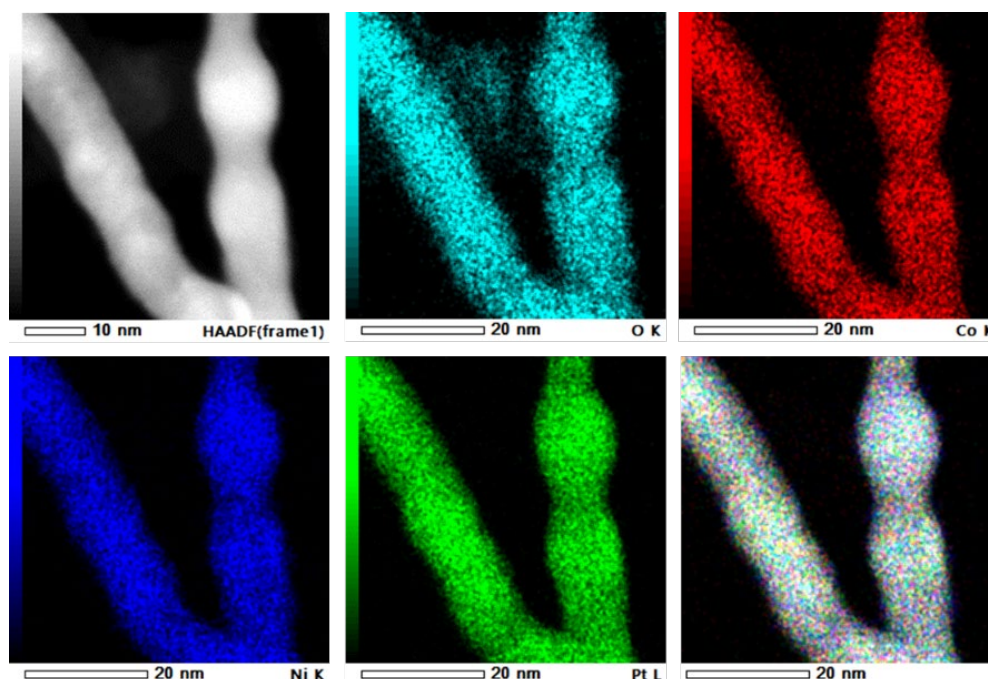


Figure 4-12. STEM-EDS element mapping spectrum of I-PtCoNi-NW/C.

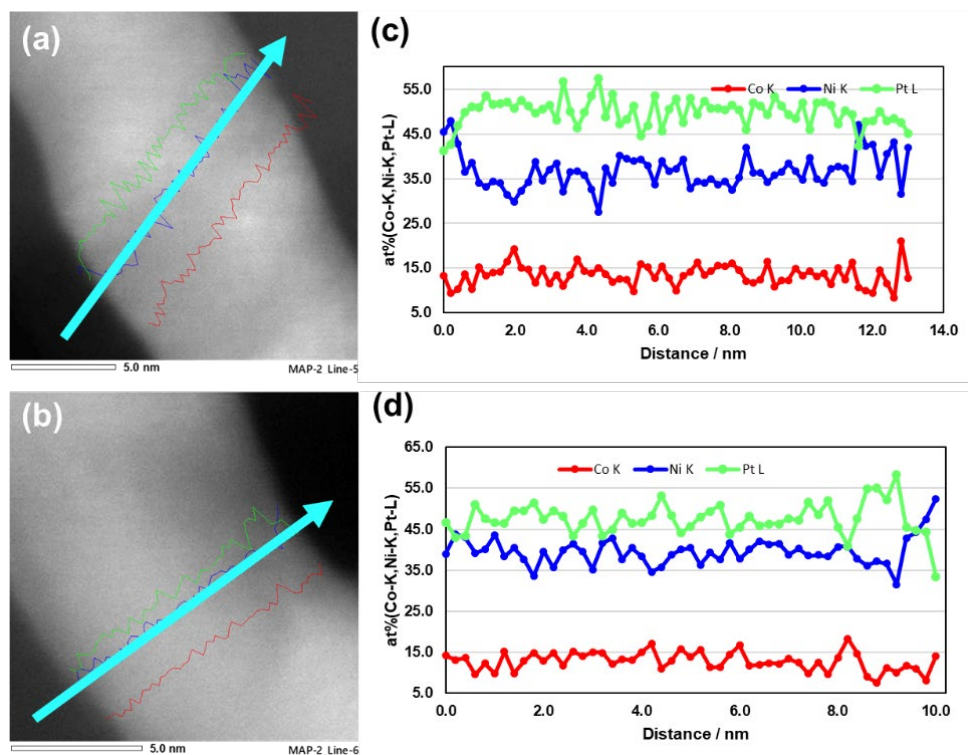


Figure 4-13. (a, b) STEM images, and (c, d) corresponding line scanning profiles of I-PtCoNi-NW/C.

4.3.2 Electrochemical measurement

Before measuring the ORR activity of the catalysts, an electrochemical leaching process was performed to remove residual surfactants and organic matter from the Pt surface and to generate a dynamically stable Pt-rich structure.²⁶ In a typical procedure, cleaning CV was conducted with 50 cycles in an N₂-saturated environment. The CV curves of the PtCoNi-NW/C catalysts before and after annealing exhibited different shapes, which is associated with the fracture of nanowire structures and internal element segregation during high-temperature calcination (Figure 4-14a-c).

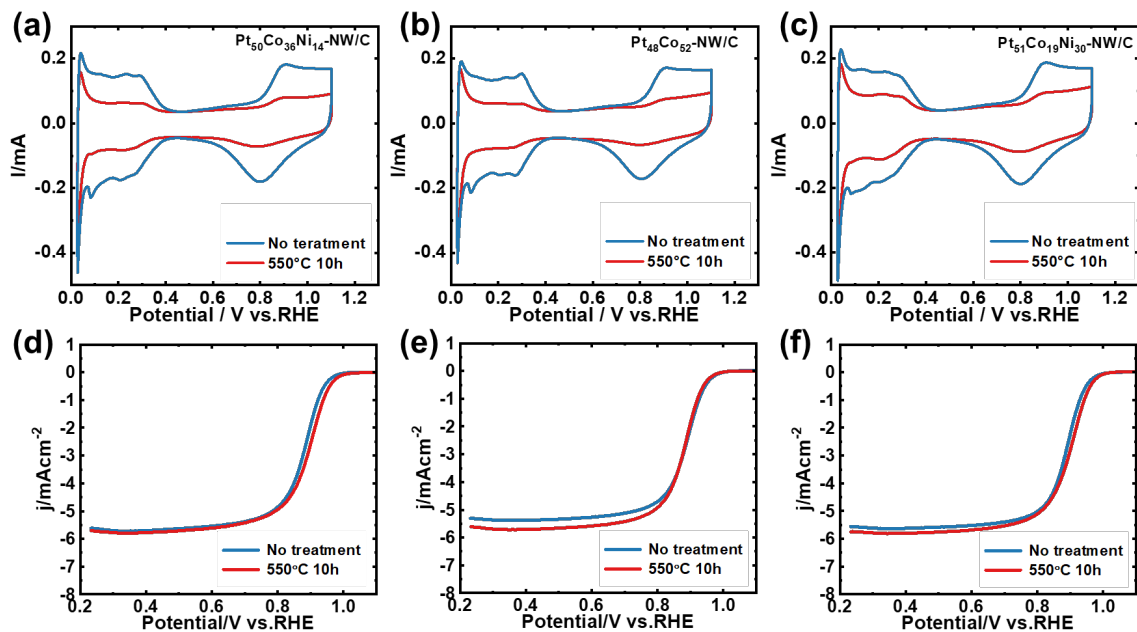


Figure 4-14. CV and ORR polarization curves (1600 rpm) for (a, d) Pt₅₀Co₃₆Ni₁₄-NW/C, (b, e) Pt₄₈Co₅₂-NW/C, and (c, f) Pt₅₁Co₁₉Ni₃₀-NW/C catalysts.

We performed a full comparison of three catalysts with different Co/Ni ratios. Pt₅₀Co₃₆Ni₁₄-NW/C exhibits the most excellent catalytic activity. The electrochemically active surface area (ECSA) of the catalysts was calculated from the H_{upd} region and decreased progressively with increasing heat treatment temperature. The D-Pt₅₀Co₃₆Ni₁₄-NW/C (donated as D-PtCoNi-NW/C) catalyst exhibited a higher ECSA of 57 m²/g, whereas the I- Pt₅₀Co₃₆Ni₁₄-NW/C (donated as I-PtCoNi-NW/C) catalyst showed only 38 m²/g. Contrary to the decrease in ECSA, the specific activity (SA) at 0.9 V vs. RHE displayed a positive correlation with the heat treatment temperature. The LSV curves in Figure 4-14d-f demonstrate that the I- PtCoNi-NW/C catalyst treated at higher temperatures exhibited a slight positive shift. As shown in Figure 4-15, the I-PtCoNi-NW/C catalyst achieved a record-high specific activity of 3594 $\mu\text{A cm}_{\text{Pt}}^{-2}$, approximately 2.5 times higher than that of D-PtCoNi-NW/C. Additionally, the mass activity of I-PtCoNi-NW/C reached as high as 1431 A g_{Pt}⁻¹.

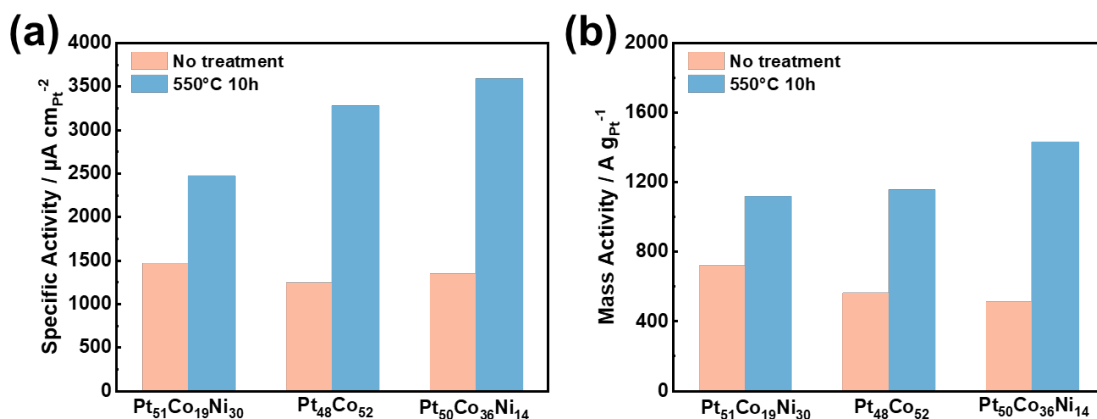


Figure 4-15. Comparison of (a) specific and (b) mass activity.

As to why Pt₅₁Co₃₆Ni₁₄-NW/C exhibits the best ORR performance, for Pt-based alloy catalysts in ORR applications, PtNiCo alloys generally exhibit superior catalytic activity compared to PtCo alloys.³⁰ This enhancement is mainly attributed to multiple synergistic effects resulting from the simultaneous introduction of Ni and Co into Pt. Co-doping with Ni and Co adjusts the electronic properties of Pt more effectively than adding Co alone, optimizing the d-band center of Pt. This modification enhances the adsorption and reduction of oxygen molecules, thereby accelerating ORR kinetics. Moreover, forming a ternary alloy creates more favorable surface geometries and increases the density of active sites, which is more advantageous for ORR than binary alloys.³¹ The reason why Pt_{0.5}Co_{0.35}Ni_{0.15} with high Co content shows higher activity than Pt_{0.5}Co_{0.15}Ni_{0.35} with high Ni content is that Pt_{0.5}Co_{0.35}Ni_{0.15} is more prone to form a order L1₀ structure, which improves the activity. Compared to the annealing temperature required for forming L1₀-PtCo, the formation of L1₀-PtNi generally requires higher temperatures.³² Specifically, L1₀-PtCo can typically form an ordered structure through annealing at lower temperatures (500°C to 600°C), whereas L1₀-PtNi requires higher annealing temperatures, usually above 700°C, to achieve the transition from disordered to ordered phases. This is because Ni atoms diffuse more slowly in the Pt lattice, necessitating higher temperatures to accelerate atomic movement and ordering.³³ Therefore, selecting Pt_{0.5}Co_{0.35}Ni_{0.15} facilitates the formation of an ordered alloy based on the ternary system, further enhancing catalytic activity.

The durability of the catalysts was evaluated through ADT between 0.60 V and 1.0 V vs. RHE. As shown in Figure 4-16, compared to I-PtCoNi-NW/C (~ 5 mV), the half-wave potential of D-PtCoNi-NW/C exhibited a significant negative shift (~ 24 mV) after 10,000 ADT cycles. TEM images revealed partial structural degradation; however, we found that the surfaces of the nanowires became more irregular (Figure 4-17). Yu et al. reported similar changes in nanowire structures during the ADT process: a small amount of unstable nanoparticles dissolve first, and Pt atoms subsequently deposit continuously on the nanowire surface, forming a Pt skin, thereby ensuring the retention of catalytic activity.³⁴

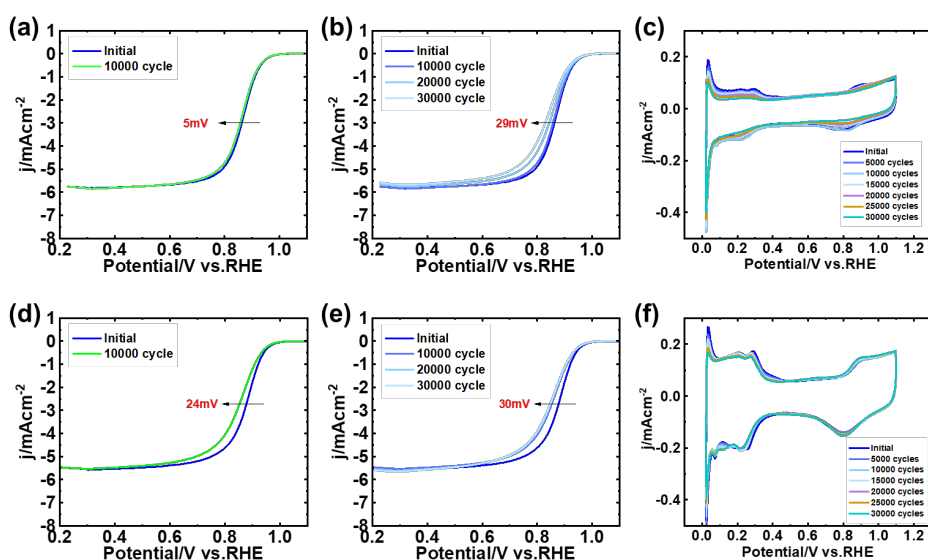


Figure 4-16. ORR polarization curves and CV curves before and after the ADT of (a-c) I-PtCoNi-NW/C and (d-f) D-PtCoNi-NW/C.

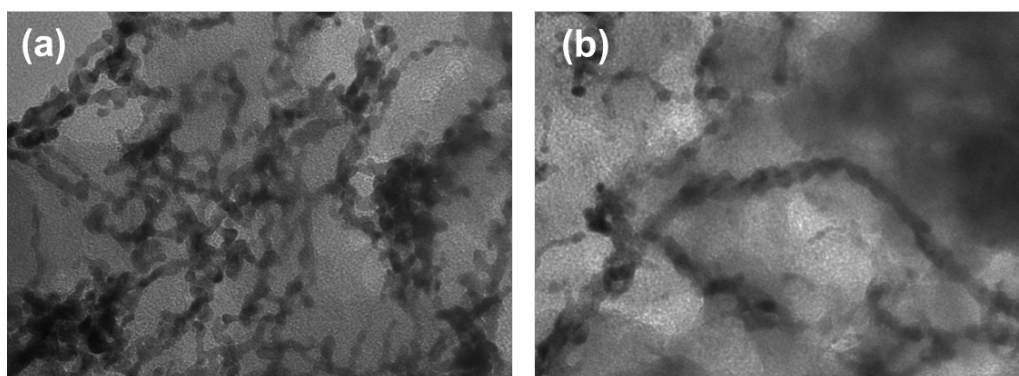


Figure 4-17. TEM images of (a) I-PtCoNi-NW/C and (b) D-PtCoNi-NW/C catalyst after 10K ADT cycles.

4.3.3 Electronic and coordination study by *operando* XAS

To investigate the alterations in electronic structure and coordination environments of PtCoNi-NW/C catalysts with two distinct crystal structures during the ORR, we conducted *operando* high-energy-resolution fluorescence-detected X-ray absorption near-edge structure (HERFD-XANES) analysis. The catalysts underwent cleaning CV treatments on glassy carbon electrodes prior to measurement. HERFD-XAS spectra were collected over a potential range from 0.5 V to 1.4 V vs. RHE, where 0.5 V is considered the metallic state devoid of oxidation charges based on CV curves.

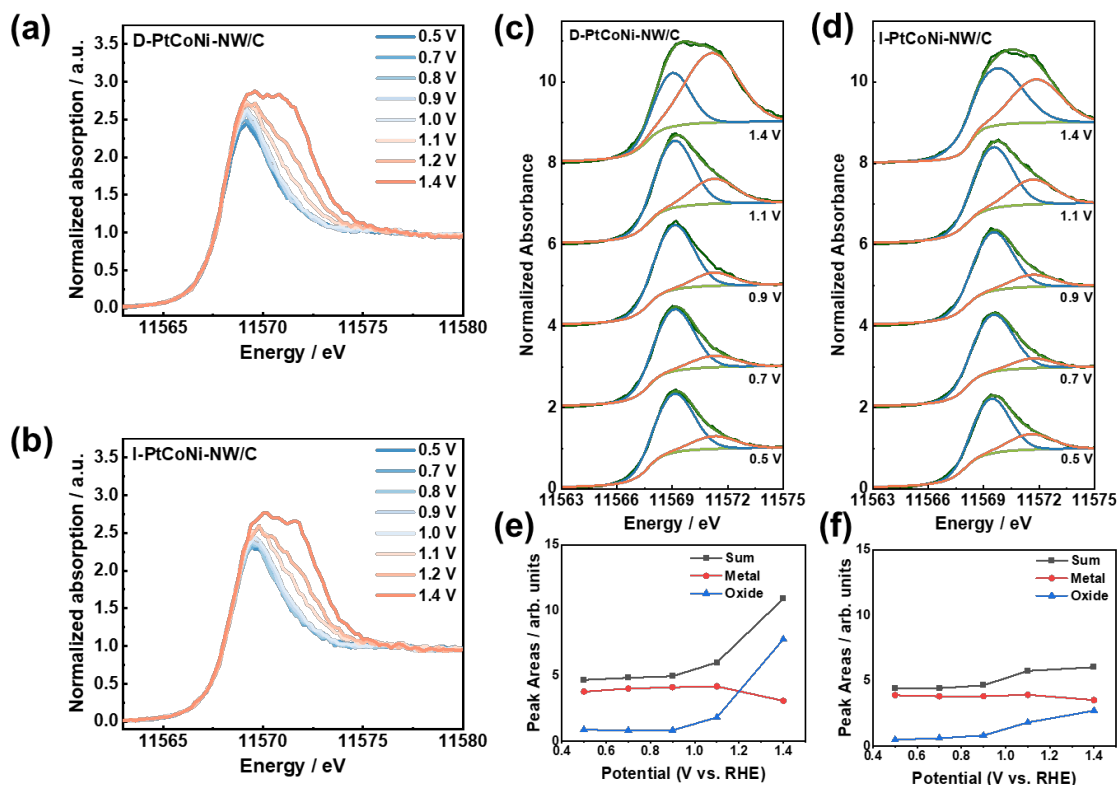


Figure 4-18. *operando* HERFD- Pt L₃-edge XANES analysis for (a) D-PtCoNi-NW/C, and (b) I-PtCoNi-NW/C catalyst varying different polarization potential. Least-square fits by two peaks (metal peak and oxides peak) of all HERFD-XANES spectra for (c) D-PtCoNi-NW/C, and (d) I-PtCoNi-NW/C. Integrated peak areas of metal peak, oxides peak, and sum peak for (e) D-PtCoNi-NW/C, and (f) I-PtCoNi-NW/C.

As illustrated in the Figure 4-18, an increase in potential led to a rise and positive shift in the white-line intensity at the Pt L₃-edge. This effect was more pronounced in the disordered D-PtCoNi-NW/C catalyst, indicating more substantial Pt oxidation, whereas the ordered I-PtCoNi-NW/C catalyst exhibited suppressed Pt oxidation. To further elucidate the differing oxidation behaviors, the spectra were fitted using an arctangent function alongside two pseudo-Voigt peaks.³⁵ Peaks positioned at 11,569.7 eV and 11,572.0 eV were attributed to metallic and oxidized Pt species, respectively. The analysis revealed that, although both catalysts showed some degree of Pt oxidation at higher potentials, the oxide content was lower in the I-PtCoNi-NW/C catalyst. This underscores the advantage of the L1₀ crystal structure in weakening the Pt–O bond strength.

It is noteworthy that in the D-PtCoNi-NW/C catalyst, the dissolution of transition metals during operation can adversely affect durability and diminish the benefits conferred by alloying. Previous studies by Gao et al. have suggested that Co can adsorb hydroxyl species (OH_{ad}) even at operational potentials, accelerating the oxidation of both transition metals and Pt.^{24, 36} In contrast, the I-PtCoNi-NW/C catalyst demonstrates enhanced structural stability. Following minor dissolution of Co and Ni and the formation of a Pt-enriched surface layer, the catalyst effectively shields internal transition metals from further dissolution and oxidation.³⁷ *operando* HERFD-XAS spectra at the Co K-edge for the I-PtCoNi-NW/C catalyst (Figure 4-19) showed minimal shifts in the pre-edge and main peak positions with increasing potential, indicating negligible oxidation of Co during the ORR process.

Collectively, the I-PtCoNi-NW/C catalyst maintains a higher retention of Co within its core structure and exhibits a reduced Pt–O bonding energy, leading to a lower degree of oxidation and less formation of PtOx species. This contributes to its enhanced catalytic activity and stability.

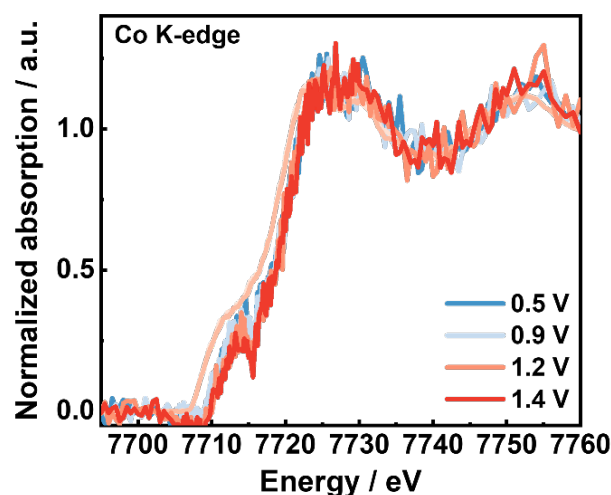


Figure 4-19. *operando* HERFD- Co K-edge XANES analysis for I-PtCoNi-NW/C.

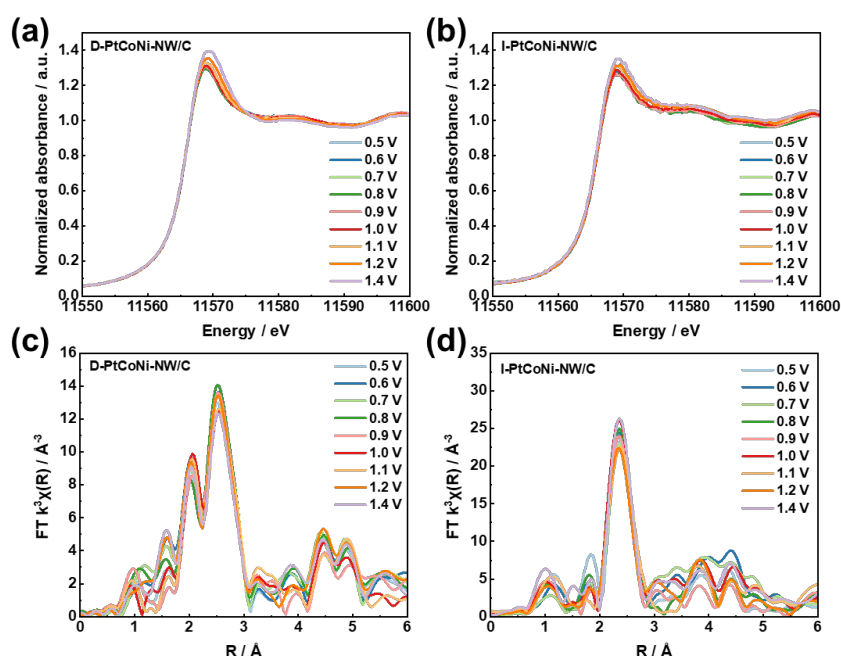


Figure 4-20. Pt L₃-edge XANES spectra of (a) D-PtCoNi-NW/C and (b) I-PtCoNi-NW/C. FT-EXAFS spectra for (c) D-PtCoNi-NW/C and (d) I-PtCoNi-NW/C.

In addition, we employed *operando* conventional XAS to assess changes in the electronic state of Pt active sites under operational conditions. As depicted in Figure 4-20a and b, the white-line intensities for both catalysts increased with higher potentials, signifying partial oxidation of Pt at elevated polarization potentials.²³ Importantly, the I-PtCoNi-NW/C catalyst showed a smaller change in white-line intensity, suggesting a lower Pt–O bond strength and inhibited formation of Pt oxides, aligning with the HERFD-XAS findings

Further structural insights were obtained through Fourier-transform extended X-ray absorption fine structure (FT-EXAFS) analysis in Figure 4-20c and d. We observed that in the I-PtCoNi-NW/C catalyst, the main peak around 2.3 Å—comprising Pt–Pt and Pt–Co/Ni coordination—shifted to shorter distances compared to that in D-PtCoNi-NW/C.³⁸ This shift is attributed to lattice compression associated with the L1₀ structure. With increasing potential, there was a slight increase in the Pt–O signal near 1.5 Å, more evident in the D-PtCoNi-NW/C catalyst.

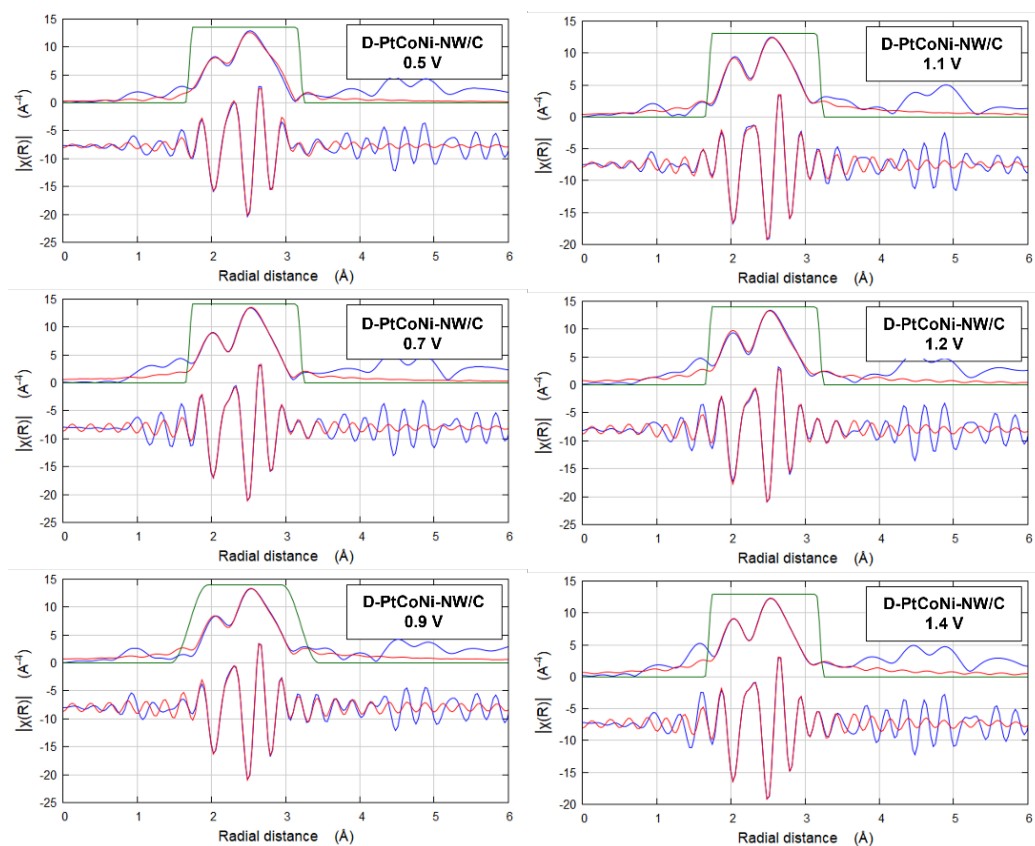


Figure 4-21. Fourier transformed k^3 -weighted Pt L_3 -edge EXAFS spectra of D-PtCoNi-NW/C at different potentials. Blue line is the FT-EXAFS spectrum and red line is the fitted spectrum.

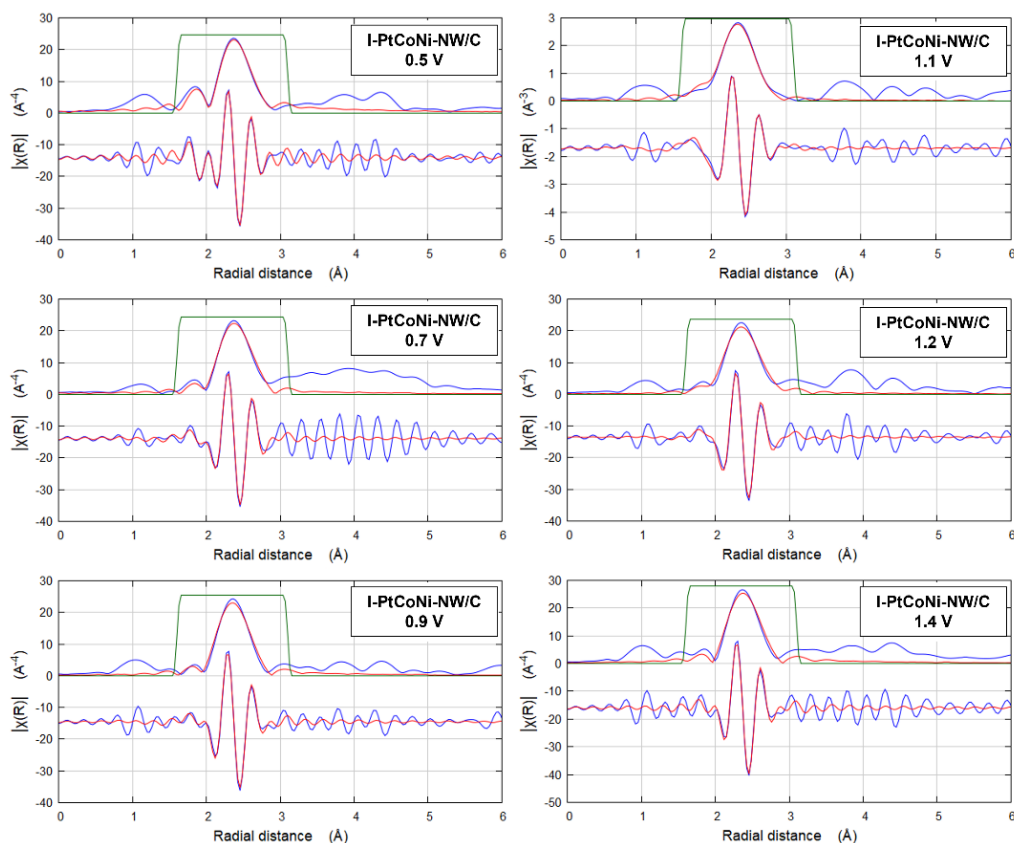


Figure 4-22. Fourier transformed k^3 -weighted Pt L_3 -edge EXAFS spectra of I-PtCoNi-NW/C at different potentials.

To quantitatively analyze structural changes under operational potentials, EXAFS data were fitted using reference models for fcc and fct PtCoNi structures (Figure 4-21 and 4-22). During tests at potentials between 0.5 V and 0.6 V, a slight decrease in Pt–Pt bond length was noted for D-PtCoNi-NW/C, possibly due to the dissolution of surface Ni and Co atoms leading to Pt atom rearrangement (Figure 4-23). As the potential increased further, the Pt–Pt bond distances expanded relative to the initial catalyst, likely due to the formation of Pt–O or Pt–OH species during electrochemical oxidation. In the ordered I-PtCoNi-NW/C catalyst, the increase in Pt–Pt bond length was less pronounced, especially at higher potentials such as 1.1 V, reflecting its superior stability compared to the disordered catalyst. However, significant structural changes were observed in I-PtCoNi-NW/C at potentials reaching 1.2 V, primarily attributed to the instability of Ni and Co under these conditions.³⁹ Catalysts with an ordered $L1_0$ structure, such as I-PtCoNi-NW/C, demonstrate enhanced structural stability during the ORR process. They

effectively inhibit the dissolution of Ni and Co, reduce the Pt–O bonding energy, and suppress oxide formation, thereby exhibiting superior catalytic performance in terms of both activity and durability.

Table 4-1. The corresponding R space curve fitting results of Pt L₃-edge for the D-PtCoNi-NW/C catalysts varying different potential.

	Bond	Length/Å	CN	$\Delta E/\text{eV}$	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.728	9.5	11.40	0.008	0.4%
	Pt-Co/Ni	2.674	2.1	11.97	0.005	
0.6 V	Pt-Pt	2.721	6.4	12.06	0.006	0.4%
	Pt-Co/Ni	2.701	2.3	18.89	0.001	
0.7 V	Pt-Pt	2.722	7.1	10.58	0.007	0.1%
	Pt-Co/Ni	2.713	2.1	19.10	0.002	
0.8 V	Pt-Pt	2.723	6.3	10.32	0.005	0.1%
	Pt-Co/Ni	2.714	2.0	17.63	0.003	
0.9 V	Pt-Pt	2.725	6.0	12.25	0.007	0.1%
	Pt-Co/Ni	2.699	2.3	10.10	0.001	
1.0 V	Pt-Pt	2.729	6.2	12.38	0.006	0.1%
	Pt-Co/Ni	2.696	2.5	9.711	0.001	
1.1 V	Pt-Pt	2.729	3.6	12.03	0.004	0.1%
	Pt-Co/Ni	2.703	2.9	10.05	0.001	
1.2 V	Pt-Pt	2.735	3.4	20.41	0.009	0.3%

	Pt-Co/Ni	2.709	2.5	8.701	0.003	
1.4 V	Pt-Pt	2.745	3.4	21.04	0.010	
	Pt-Co/Ni	2.712	2.8	8.562	0.001	0.5%

Table 4-2. The corresponding R space curve fitting results of Pt L₃-edge for the I-PtCoNi-NW/C catalysts varying different potential.

	Bond	Length/Å	CN	$\Delta E/eV$	Debye–Waller factor	R-factor
0.5 V	Pt-Pt	2.678	5.6	0.127	0.002	
	Pt-Co/Ni	2.677	4.6	12.40	0.001	2.2%
0.6 V	Pt-Pt	2.679	8.8	9.800	0.127	
	Pt-Co/Ni	2.651	5.3	13.94	0.004	2.1%
0.7 V	Pt-Pt	2.684	9.2	5.686	0.013	
	Pt-Co/Ni	2.657	5.6	18.06	0.007	3.3%
0.8 V	Pt-Pt	2.683	8.1	7.485	0.011	
	Pt-Co/Ni	2.665	4.6	13.40	0.002	0.9%
0.9 V	Pt-Pt	2.689	8.3	5.346	0.016	
	Pt-Co/Ni	2.664	4.3	17.03	0.004	1.2%
1.0 V	Pt-Pt	2.690	6.2	6.591	0.008	
	Pt-Co/Ni	2.665	4.3	15.59	0.002	2.1%
1.1 V	Pt-Pt	2.693	6.0	6.869	0.008	0.8%

	Pt-Co/Ni	2.664	4.2	13.54	0.004	
1.2 V	Pt-Pt	2.705	6.0	5.593	0.011	2.1%
	Pt-Co/Ni	2.622	5.3	7.028	0.006	
1.4 V	Pt-Pt	2.731	4.9	9.700	0.010	3.5%
	Pt-Co/Ni	2.707	4.1	12.00	0.002	

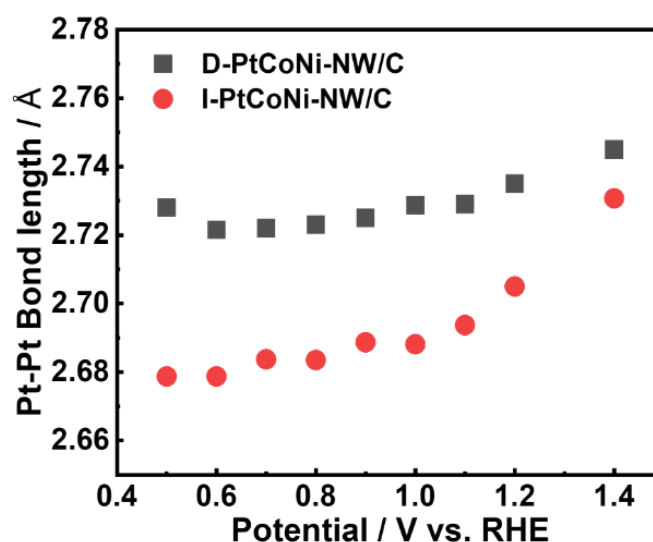


Figure 4-23. Pt-Pt bond length from the corresponding fitting results for I-PtCoNi-NW/C and D-PtCoNi-NW/C catalysts.

4.4 Conclusion

This work highlights the successful synthesis and optimization of PtCoNi intermetallic nanowires for ORR applications, with a combination of XRD and TEM providing confirmation of the ordered $L1_0$ phase and stable nanowire morphology. The electrochemical results revealed that the PtCoNi nanowires exhibit substantial ORR activity and durability, supported by a stable Pt-rich surface layer and order Pt–Co/Ni distribution. *Operando* XAS and HERFD-XAS

analyses offered essential insights into the catalysts' structural and electronic stability, showing that the L1₀ phase suppresses Pt oxidation and enhances Co/Ni retention, with the shortened Pt-Pt bond lengths contributing to higher specific activity. These advanced XAS methods provided a detailed view of the electronic and structural evolution under operational conditions, thus guiding the design of highly durable and active ORR catalysts based on PtCoNi intermetallic nanostructures.

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Chapter 5. *operando* Deciphering the Role of Structural and Anionic Environmental Determinants during Oxygen Evolution Reaction in Iridium Oxide Catalysts

Enhancing the efficiency of proton-exchange membrane water electrolysis requires addressing the kinetic challenges of the oxygen evolution reaction (OER) and understanding the effect of anion poisoning on catalytic activity. This study investigates the structural and electrocatalytic behaviors of two iridium oxide (IrO_x) catalysts—SA3.5 (amorphous) and SA58 (crystalline)—under varying electrolytic conditions. By employing *operando* X-ray absorption spectroscopy and pair distribution function analysis, the relationship between the catalysts' crystal structure and OER performance is elucidated. The results reveal that SA3.5, mix of orthorhombic ($Pbcn$) and monoclinic ($C2/m$) structure rich in coordinatively unsaturated sites ($\mu_1\text{-O}/\mu_2\text{-O}$) that contribute to the formation of $\text{Ir}^{\text{IV}+\delta}$, exhibits enhanced OER activity but is more susceptible to anion poisoning, highlighting a trade-off between activity and stability. In contrast, SA58 demonstrates more stable but lower OER activity, attributed to its rutile structure. Density functional theory calculations and Bader charge analysis clarify that anion adsorption on the Ir surface leads to charge redistribution, significantly weakening catalytic activity. Particularly in amorphous SA3.5 catalysts, the three-point adsorption of anions on the $Pbcn$ (11-1) surface and the notable increase in Bader charge on the $C2/m$ (-100) surface led to pronounced anion poisoning effects.

5.1 Introduction

The transition to a carbon-neutral future depends heavily on hydrogen, a key energy carrier in roadmaps aimed at achieving net-zero emissions.¹⁻⁴ Proton-exchange membrane water electrolysis (PEMWE) is a promising technology for green hydrogen production, especially suitable for dynamic environments driven by intermittent renewable energy sources.⁵⁻⁷

However, the slow kinetics of the oxygen evolution reaction (OER) at the PEMWE anode remains a significant barrier, resulting in efficiency losses and elevated operational costs.^{8, 9} Addressing this challenge requires advanced catalyst materials that enhance both OER activity and stability, with a deeper understanding of the interfacial processes involved.¹⁰⁻¹²

Iridium oxides (IrO_x) are the most effective catalysts for OER in acidic environments. It has been observed that the electrocatalytic performance of IrO_x is closely linked to its elemental composition and crystal structure.^{13, 14} Amorphous and hydrated forms of IrO_x exhibit better OER activity compared to their crystalline counterparts, though they are often less stable.^{15, 16} This enhanced activity is attributed to the presence of coordinatively unsaturated sites (CUS) in amorphous structures, which facilitate the formation of electrophilic O^{((1+δ)-)} species through oxidative deprotonation of OH groups.^{17, 18} Several *operando* techniques, such as Raman,^{19, 20} UV-VIS,^{18, 21} X-ray absorption (XAS),²²⁻²⁴ X-ray photoelectron spectroscopy^{16, 25} coupled with density functional theory (DFT)^{26, 27} have been employed to elucidate these OER mechanisms and identify the reactive sites on the IrO_x surface that drive O–O bond formation during the reaction.^{18, 28}

Despite significant advancements, the role of electrolyte composition, particularly the effects of anions on catalyst performance, has often been underestimated.²⁹⁻³¹ Widely used electrolytes, such as sulfuric acid (H₂SO₄), which shares characteristics with the sulfonate group in Nafion®,³² and perchloric acid (HClO₄), in studies of acidic oxygen evolution reactions,³³ have been shown to exert distinct influences on catalyst behavior. For instance, sulfate anions have been reported to lower OER activity more than perchlorate anions, highlighting the importance of anion-catalyst interactions.³⁴ Furthermore, the challenges faced by standard Nafion® membranes at temperatures over 100°C,³⁵ such as decreased mechanical strength and the risk of dehydration,³⁶ have prompted a shift towards alternatives like polybenzimidazole (PBI) membranes infused with phosphoric acid (H₃PO₄).³⁷ This shift underscores the need to investigate the effect of anion poisoning on catalytic activity. Nevertheless, the interplay between catalyst structure, OER activity, and anion poisoning remains insufficiently understood, necessitating further investigation under *operando* conditions.

This study investigates the crystal structures of two IrO_x catalysts, SA3.5 (amorphous) and SA58 (crystalline), using Pair Distribution Function (PDF) analysis to explore their structural characteristics. The impact of varying concentrations of H₂SO₄ and H₃PO₄ on these catalysts is evaluated to highlight the influence of electrolyte composition on catalytic performance. *Operando* O K-edge and Ir L₃-edge High-Energy Resolution Fluorescence Detected (HERFD) XAS techniques are employed to compare the high activity of amorphous SA3.5, which is rich in unsaturated oxygen sites, with the more stable but less active crystalline SA58. Systematic DFT calculations investigated anion adsorption from acidic electrolytes on the IrO_x catalyst surface. H₂PO₄⁻ shows more stable adsorption than HSO₄⁻, significantly decreasing catalytic activity. In the SA3.5 catalyst, anion adsorption blocks active sites and induces electron transfer and repulsive effects between negatively charged species, further weakening intermediate adsorption during the OER process and reducing overall catalytic performance.

5.2 Experimental Methods

5.2.1 Materials and Characterization

Iridium oxide samples with varying levels of crystallinity, specifically SA58 and SA3.5, were obtained from Tanaka Kikinzoku Kogyo K.K., Chemical & Refining Company. These samples were distinguished based on their Brunauer-Emmett-Teller (BET) surface area measurements.

X-ray Diffraction (XRD) analysis was performed using the BL02B2 beamline at SPring-8 in Japan. Transmission Electron Microscopy (TEM) was conducted with the JEM-2200FS model from JEOL Ltd., operating at an acceleration voltage of 200 kV. Additionally, Scanning Transmission Electron Microscopy (STEM) examinations were carried out using the JEM-ARM200F model (JEOL Ltd.) at the same acceleration voltage.

PDF analysis was carried out at BL04B2, employing an X-ray energy setting of 112.88 keV. We processed the scattering data to calculate the structure factor $S(Q)$, incorporating background, absorption, multiple scattering, and inelastic scattering corrections. This data was

then Fourier transformed into the reduced pair distribution function $G(r)$. For comprehensive analysis, we performed joint curve fitting and simulation on the PDF data using the PDFgui software.³⁸ This approach utilized a unified structural model, with individually assumed lattice constants for each sample to enhance the precision of our PDF analyses.

5.2.2 Electrochemical Measurements

The electrochemical properties of two IrO_x catalyst variants were assessed in differing concentrations of H_3PO_4 and H_2SO_4 . Preparation of the catalyst inks involved a mixture of catalyst powder, 5 wt% Nafion solution (Sigma-Aldrich), ethanol (FUJIFILM Wako Pure Chemical Corporation), and ultra-pure deionized water (18.2 M Ω .cm resistivity, Milli-Q®, Millipore A/S). This mix was sonicated for 30 minutes in an ice bath for uniformity, then applied onto a polished gold rotating disk electrode (RDE, 5 mm diameter, Hokuto-denko).

In the standard three-electrode cell setup connected to an MPG-205-NUC electrochemical workstation (Bio-Logic), electrochemical assessments were conducted. The setup included a platinum mesh as the counter electrode, a reversible hydrogen electrode (RHE) for reference, and the catalyst-coated gold RDE as the working electrode. Cyclic Voltammetry (CV) tests were carried out in a nitrogen-purged electrolyte, scanning from 0.1 V to 1.2 V vs. RHE at a scan rate of 50 mV/s. Linear Sweep Voltammetry (LSV) followed, conducted at a 1600 rpm rotation, covering a potential range of 1.1 to 1.6 V vs. RHE at a scan rate of 10 mV/s. The electrochemically active surface area (ECSA) for each catalyst was determined using the pseudocapacitive charge method, aligning with established methodologies.³⁹ Current density values were normalized to the BET surface area to ensure uniformity in the results.

5.2.3 *Operando* XAS measurement

The O K-edge *operando* measurements were conducted in Total electron-yield (TEY) mode at the BL27SU, SPring-8, using a home-made *operando* cell.⁴⁰ In this setup, a Pt wire and RHE functioned as the counter and reference electrodes, respectively. The catalyst coated membrane (CCM) samples were prepared by spraying the IrO_x catalysts onto Nafion 212 membranes,

achieving an iridium loading of approximately 0.1 mg/cm^2 . The CCM assembly included a glassy carbon (GC) disc with a central hole ($\Phi=1\text{mm}$) and the cell body, as detailed in Figure 5-1. A pair of Si (111) monochromators and a 4 mrad total-reflection Rh mirror were utilized to generate collimated and monochromatic X-rays. Electrode polarization ranged from 0.5 V to 1.9 V vs. RHE in a vacuum environment. XAS signals were recorded after stabilizing each potential for 10 minutes to ensure steady current conditions.

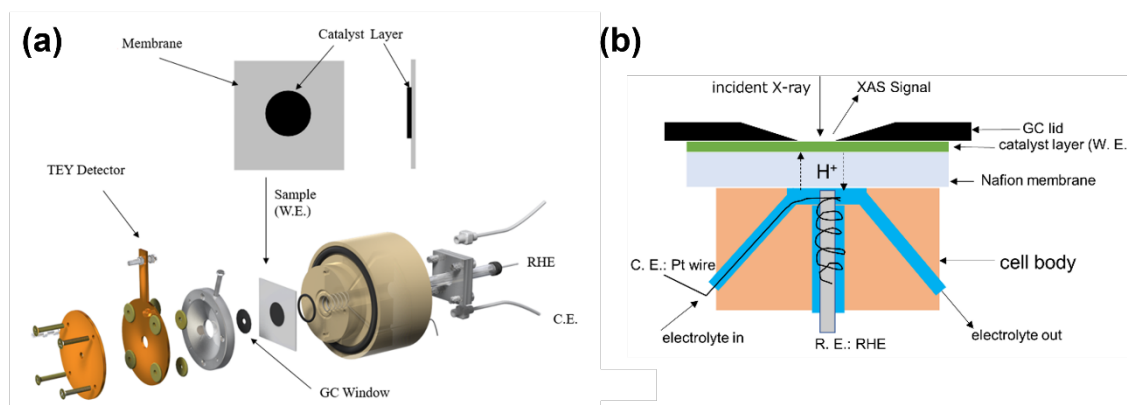


Figure 5-1. (a) Decomposition chart and (b) sectional view of *operando* XAS cell.

For the conventional Ir L_3 -edge XAS, measurements were carried out at the BL37XU, SPring-8, Japan. The home-made flow-type cell's fundamental design was based on our earlier study. Collimated and monochromatic X-rays were achieved using Si (111) monochromators and a total-reflection Ru mirror (4 mrad). Catalyst ink was applied onto an Au (50nm) sputtered polyetherimide film (Mitsubishi Chemical Corporation), serving both as the X-ray window and the working electrode. A flow rate of 0.5 L/min was maintained for the electrolyte using a non-pulsation pump, which helped in mitigating bubble accumulation on the electrode surface.

The HERFD XANES at the Ir L_3 -edge was performed at the BL39XU.⁴¹ This involved testing in both 0.1 M HClO_4 and 0.1 M H_3PO_4 electrolytes, with the potential from 0.5-1.45 V vs. RHE. X-ray emission spectroscopy (XES) was employed to monochromatize fluorescent X-rays prior to XAS signal acquisition. A pair of Si (220) monochromators and a total-reflection Rh mirror (4.5 mrad) were used to generate the necessary X-ray conditions. The collected data were primarily analyzed using ATHENA and ARTEMIS software programs from the IFEFFIT.⁴²

5.2.4 Computational Details

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP), version 5.4.4. The Perdew-Burke-Ernzerhof (PBE) functional was employed, and electron-ion interactions were modeled using the projector-augmented wave (PAW) method. A plane-wave basis set with a cutoff energy of 500 eV was used for the calculations. The convergence criteria for forces and total energy were set to 0.01 eV/Å and 10^{-8} eV, respectively. The Brillouin zone was sampled using Γ -centered k-point meshes with a spacing of $2\pi \times 0.05 \text{ \AA}^{-1}$. To model the surfaces, three-dimensional slab models were applied. The optimized structures presented in this study were visualized using the VESTA software.

5.3 Result and Discussion

5.3.1 Morphology and structure

The BET surface areas of the IrO_x catalysts, measured via N_2 adsorption, are listed in Table 5-1, with SA3.5 and SA58 showing surface areas of $3.5 \text{ m}^2/\text{g}$ and $58 \text{ m}^2/\text{g}$, respectively. XRD analysis (Figure 5-2) reveals distinct structural characteristics: Commercial IrO_2 and the SA58 catalyst, both with rutile-type structures and tetragonal symmetry ($P42/mnm$), exhibit sharp diffraction peaks, though SA58 shows lower intensity, indicating reduced crystallinity. In contrast, SA3.5 displays faint, broad peaks, characteristic of an amorphous structure, as further supported by TEM and HAADF-STEM images (Figure 5-3, Figure 5-4). SA58 consists of nanometer-sized particles with visible lattice fringes and a rutile SAED pattern, while SA3.5, with diffuse SAED rings and randomly distributed Ir atoms, reflects its disordered, amorphous nature.^{23, 43}

Table 5-1. BET surface and ECSA of SA3.5 and SA58.

Sample	BET surface/ $\text{m}^2 \text{g}^{-1}$	BET surface area / cm^2	ECSA / cm^2
SA58	58	10.809	104.8
SA3.5	3.5	0.726	107.0

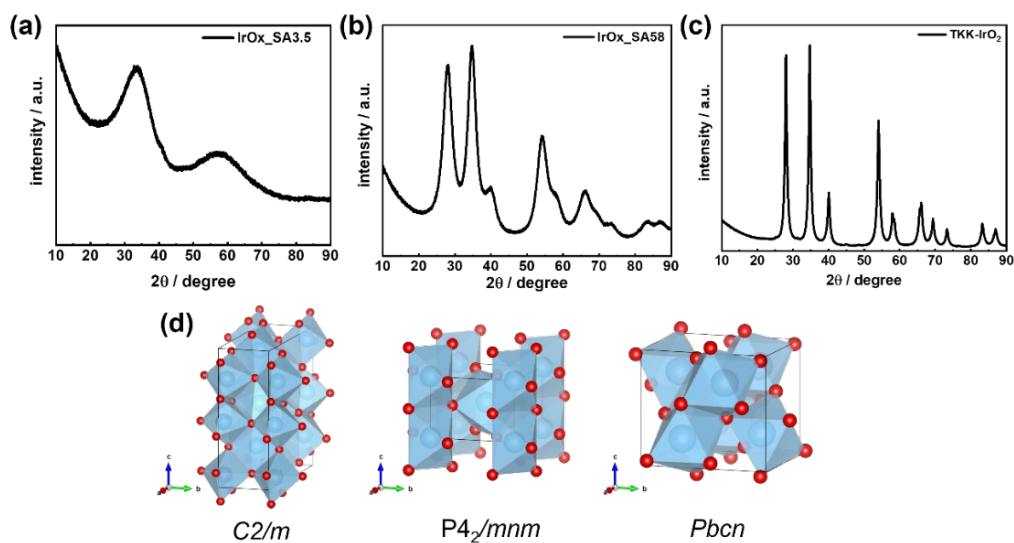


Figure 5-2. XRD patterns of (a) SA3.5, (b) SA58, (c) TKK-IrO₂. (c) Three typical crystal structures of iridium oxide.

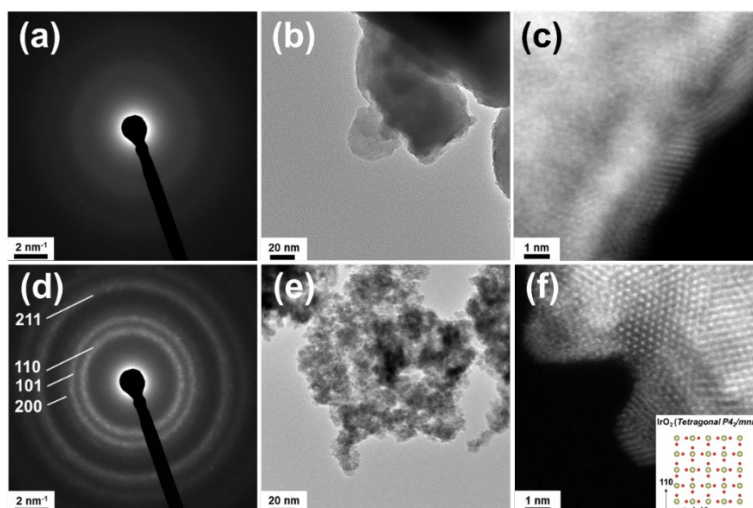


Figure 5-3. SAED pattern, TEM images and HAADF-STEM images of (a, b, c) SA3.5 and (d, e, f) SA58.

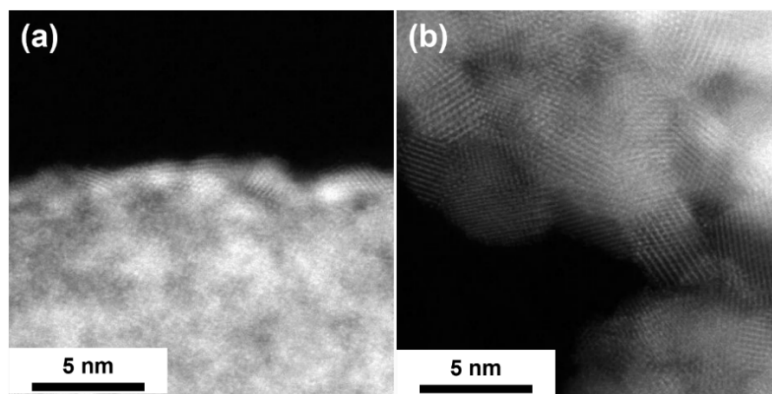


Figure 5-4. STEM- HAAD images of (a) SA58 and (d) SA3.5 catalysts.

Both amorphous and rutile-type IrO_x share similar $[\text{IrO}_6]$ octahedral units,¹⁶ yet in amorphous IrO_x , these units are more "flexible," facilitating rapid OER by acting as effective electrophilic centers.²² Additionally, some research reported amorphous IrO_x shows greater deprotonation of $\mu_2\text{-OH}$ and $\mu_1\text{-OH}$ groups, enhancing activity.¹⁶ To further clarify the relationship between structure and catalytic activity, additional analysis of the crystal structure of the amorphous SA3.5 catalyst is required. Due to the weak, broad XRD peaks of SA3.5, structural analysis via Rietveld refinement is challenging; therefore, PDF analysis was employed to elucidate its short-range order.

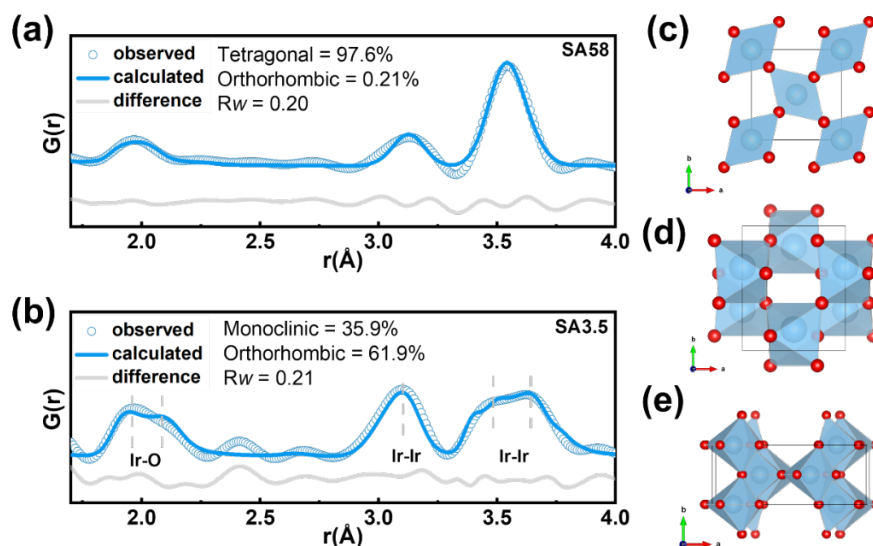


Figure 5-5. PDF analyses of experimental and fitting results of (a) SA58 and (b) SA3.5. Illustrations of crystal structures based on PDF fitting results, (c) tetragonal, (d) orthorhombic and (e) monoclinic, respectively.

PDF analysis, using Fourier-transformed high-energy X-ray diffraction data, provided the reduced pair distribution function $G(r)$, which reveals interatomic distances and local structure.^{44, 45} In Figure 5-5, PDF results for SA3.5 and SA58 show distinct structural features. The long-range ordered structure of SA58 displays discrete peaks at 1.96 Å, 3.15 Å, and 3.55 Å, corresponding to Ir-O, edge-sharing Ir-Ir, and corner-sharing Ir-Ir bonds, respectively, consistent with the rutile structure (Table 5-2).⁴⁶

In contrast, the PDF signal amplitude of SA3.5 diminishes rapidly around 4 Å, indicating a lack of long-range order. Fitting results in Table 5-3 suggest that a combination of orthorhombic ($Pbcn$) and monoclinic ($C2/m$) phases best describes the structure of SA3.5,⁴⁷ with respective proportions of 0.62 and 0.36, aligning with the atomic disorder seen in STEM images.

Table 5-2. The crystal structure parameters obtained from PDF analysis of the SA58.

Phase	Lattice parameter / Å	Space group	scale factor	Phase ratio in mass	R_w
Tetragonal	a = 4.485(1)	$P4_2mm$	0.833(5)	0.976(6)	
	c = 3.133(2)				
Orthorhombic	a = 5.046(2)	$Pbcn$	0.020(5)	0.024(6)	0.20
	b = 5.274(1)				
	c = 4.853(3)				

Table 5-3. The crystal structure parameters obtained from PDF analysis of the SA3.5.

Phase	Lattice parameter / Å	Space group	scale factor	Phase ratio in mass	R_w
Orthorhombic	a = 4.650(7)	<i>Pbcn</i>	0.619(4)	0.652(10)	0.21
	b = 5.609(8)				
	c = 4.924(8)				
Monoclinic	a = 6.790(10)	<i>C2/m</i>	0.359(6)	0.348(10)	0.21
	b = 3.801(3)				
	c = 3.047(6)				
	$\beta = 72.800(6)$				

To clarify the link between structure and electrocatalytic performance, OER tests were conducted on the SA3.5 and SA58 catalysts in 0.1 M HClO₄ solution. The CV curves in Figure 5-6a show that SA3.5 has a prominent oxidation-reduction peak near 0.95 V vs. RHE, marking the Ir^{+III} to Ir^{+IV} transition.⁴⁸ Comparisons of OER activity via LSV (Figure 5-6b-d) reveal that the amorphous SA3.5 has a lower overpotential for OER than SA58, consistent with the higher activity typical of amorphous structures.¹⁸ Despite SA3.5's smaller BET surface area, its electrochemical surface area (ECSA) reached 48.5 cm², as determined from CV curves at varying scan rates (Figure 5-7).

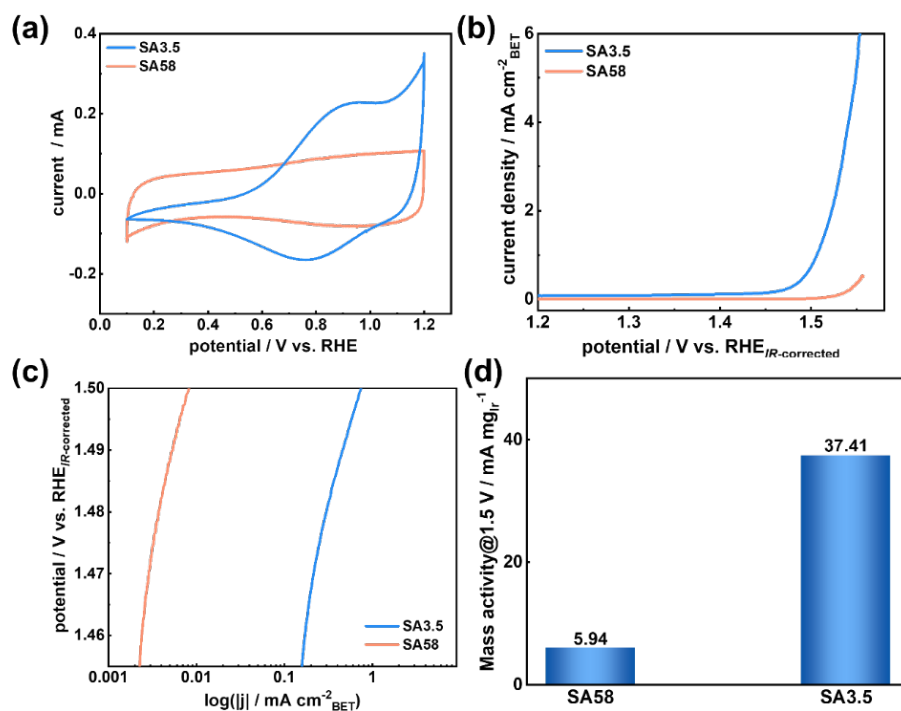


Figure 5-6. (a) CV curves and (b) OER activity normalized by BET surface area. (c) Tafel slope and (d) mass activity of SA3.5 and SA58.

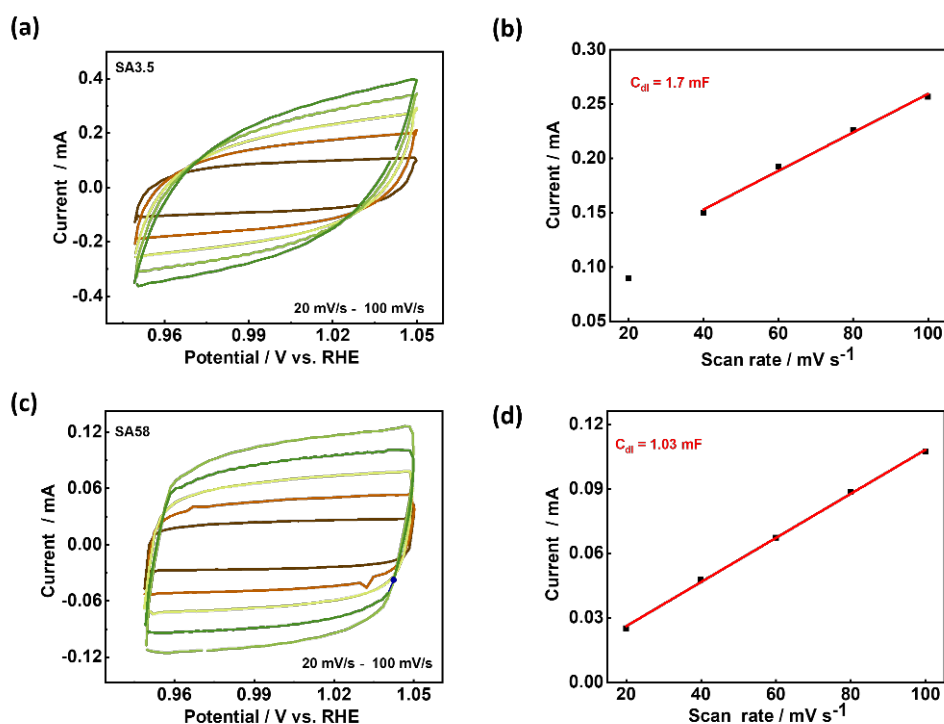


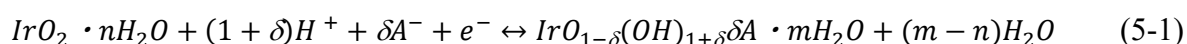
Figure 5-7. Comparison of different electrocatalysts ECSA curves of (a) SA58, (c) SA3.5, and C_{dl} curves of (b) SA58, (d) SA3.5.

PDF fitting results highlight the structural impact on OER activity: the *P42/mnm*-IrO₂ unit cell features a tetragonal arrangement with edge- and corner-sharing [IrO₆] octahedra,⁴⁹ whereas the *C2/m* IrO₂ exhibits a monoclinic structure composed of edge-sharing [IrO₆] octahedra.⁵⁰ In rutile-type IrO₂, the periodic connectivity of [IrO₆] octahedra limits changes in Ir-O distances, restricting variation in the iridium oxidation state.⁵¹ By contrast, in amorphous IrO_x, the randomly connected [IrO₆] octahedra allow for greater redox flexibility, increasing the oxidation state of surface iridium atoms and thereby enhancing OER performance.^{52, 53} Theoretical calculations by Ping et al. further suggest that the *C2/m*-IrO₂ (011) surface promotes O–O bond formation (*O + H₂O → *OOH + H⁺ + e[−]),^{47, 54} lowering the overpotential and increasing activity compared to the rutile-IrO₂ surface.²² This aligns with the superior OER activity of SA3.5, attributed to its substantial monoclinic structure content and flexible [IrO₆] network.

5.3.2 Anion effects on IrO_x during OER

To investigate the effect of anionic species on the OER performance of IrO_x catalysts with varying crystalline structures, electrochemical properties were tested in H₂SO₄ (0.01–0.05 M) and H₃PO₄ (0.02–0.1 M) solutions. The effect of ClO₄[−] in HClO₄ was negligible and is thus omitted from further discussion.³⁴ The CV curves of SA3.5 and SA58 in different electrolytes (Figure 5-8, Figure 5-9 and Figure 5-10) reveal substantial differences, showing that electrolyte type significantly influences electrochemical property. SA3.5, with higher OER activity, exhibited a more pronounced Ir^{+III}/Ir^{+IV} redox peak in 0.1 M HClO₄, which shifted negatively with increased H₂SO₄/H₃PO₄ concentration, indicating the electrolyte's impact on surface reactions. Anions play a crucial role in the oxidation of IrO_x, as shown in the following reaction:

55



where A represents anions present in the solution.

The interaction of anions (ClO_4^- , HSO_4^- , and H_2PO_4^-) with the oxide surface causes shifts in redox potentials, which can be explained by the Nernst equation:⁵⁶⁻⁵⁸

$$E = E^0 + \frac{RT}{F} \ln \frac{[\text{Ir}(+\text{IV})\text{oxide}][\text{H}^+]^{(1+\delta)}[\text{A}^-]^\delta}{[\text{Ir}(+\text{III})\text{oxide}]} \quad (5-2)$$

Here, E is the potential, E^0 is the standard potential, R is the gas constant, T is the temperature, and F is Faraday's constant.

Besides, Owe et al. have shown mass changes in IrO_x catalysts further highlight the electrolyte influence. In pure HClO_4 , the mass change was 98 ng, whereas in HClO_4 containing H_2SO_4 , it reached 100 ng, following the trend $\text{HClO}_4 < \text{H}_2\text{SO}_4 < \text{H}_3\text{PO}_4$.⁵⁹ This suggests that mass changes are largely due to anion adsorption/desorption, surface reactions, and interactions with water molecules, beyond just Ir oxidation or reduction processes.^{33, 56}

No significant changes were observed in the CV profiles of the SA58 catalyst with a tetragonal rutile structure (Figure 5-8b and d), aligning with previous findings.⁵⁹ This stability is attributed to the presence of inert bulk oxygen species.¹⁶ Under OER conditions, CUS is usually present on the IrO_x surface to facilitate the reaction, but the stabilized $[\text{IrO}_6]$ octahedral structure in SA58 has fewer reactive sites and is less susceptible to oxygen or anion binding, which reduces the susceptibility to anion poisoning. A discussion of the active site will be described in detail in the O K-edge XAS section

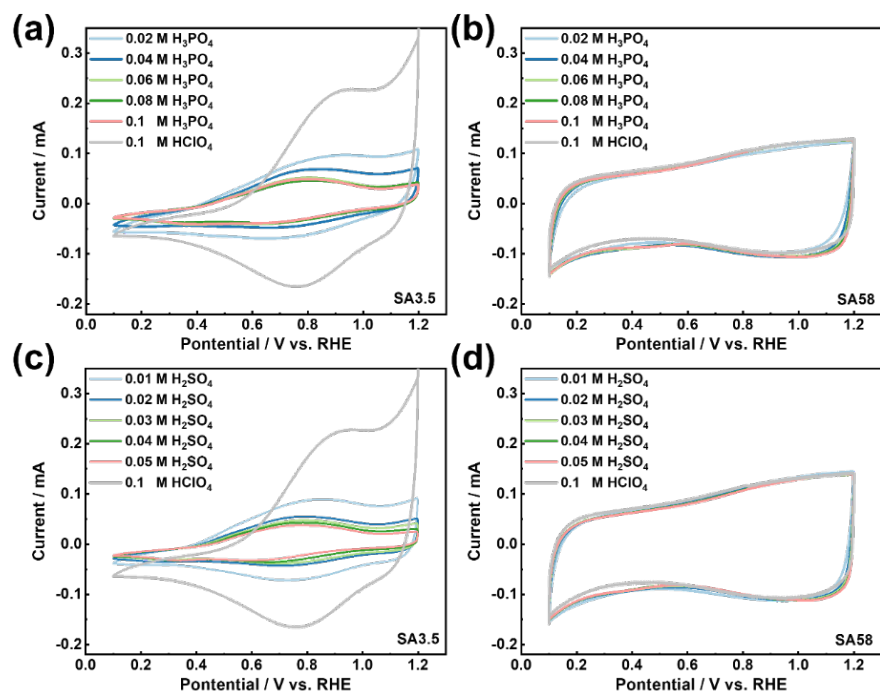


Figure 5-8. CV results of SA3.5 in (a) 0.02 to 0.10 M H_3PO_4 and (b) 0.01 to 0.05 M H_2SO_4 compare with 0.1 M HClO_4 . And CV results of SA58 in (b) 0.02 to 0.10 M H_3PO_4 and (d) 0.01 to 0.05 M H_2SO_4 compare with 0.10 M HClO_4 .

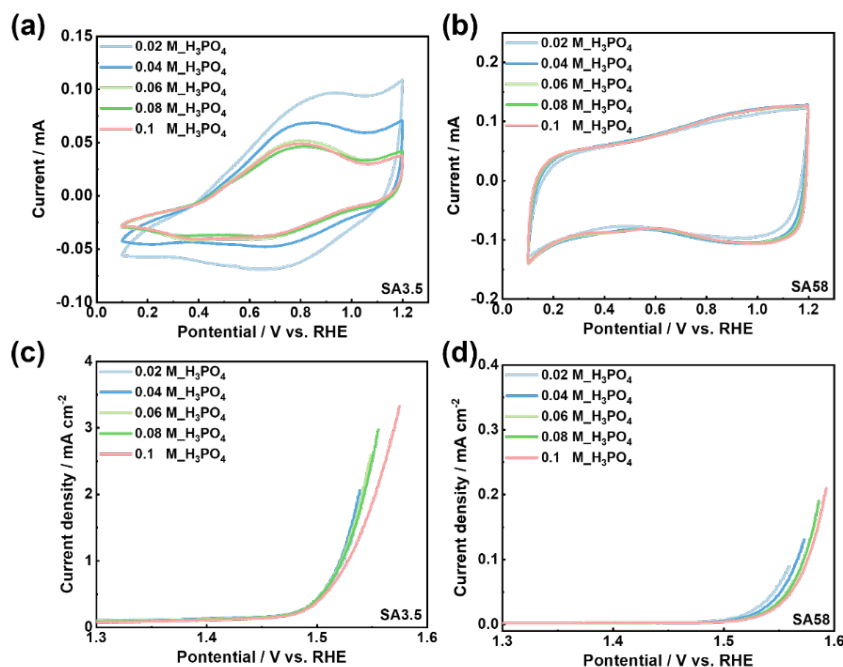


Figure 5-9. Catalytic performance in 0.02~0.1 M H_3PO_4 . CV curves of (a) SA3.5 and (b) SA58. LSV curves of (c) SA3.5 and (d) SA58.

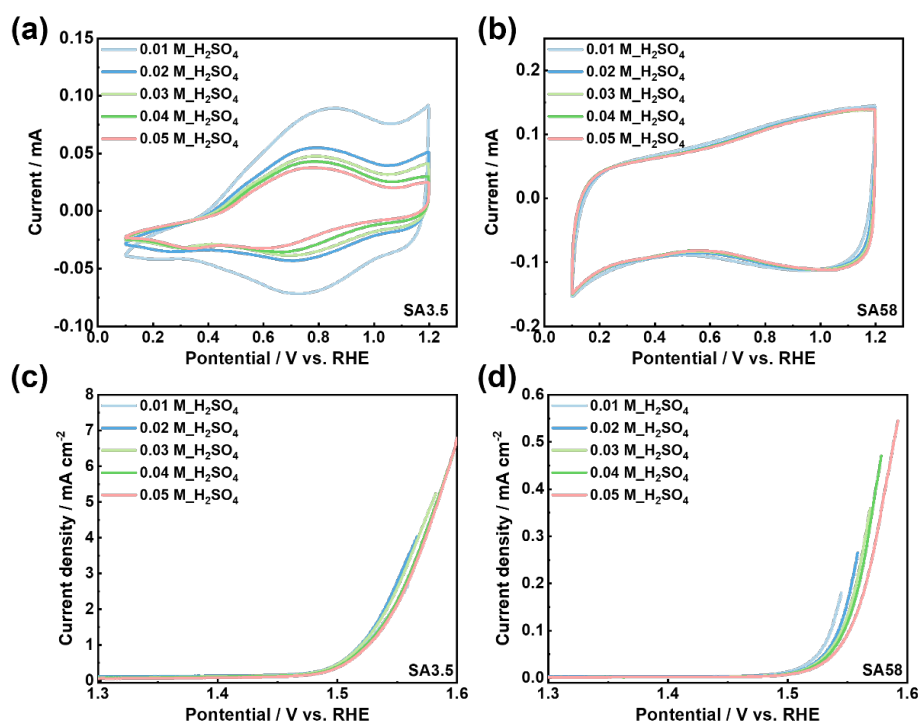


Figure 5-10. Catalytic performance in 0.01~0.05 M H₂SO₄. CV curves of (a) SA3.5 and (b) SA58. LSV curves of (c) SA3.5 and (d) SA58.

LSV tests (Figure 5-11) were conducted in different electrolyte solutions (H₂SO₄ and H₃PO₄) between 1.00 V and 1.60 V vs. RHE to evaluate IrO_x activity. The results showed that IrO_x catalytic performance was lower in these electrolytes than in HClO₄, with performance decreasing as electrolyte concentration increased, especially in 0.1 M H₃PO₄. Tafel slopes (Figure 5-12, Table 5-4) further illustrate this trend. Notably, the overpotential at a current density of 0.1 mA/cm²_{BET} increased in both catalysts, with H₃PO₄ having a more pronounced impact than H₂SO₄. Specifically, SA3.5 showed an overpotential increase of 107 mV in 0.05 M H₂SO₄ and 143 mV in 0.1 M H₃PO₄ compared to HClO₄, while SA58 increased by 23 mV and 107 mV, respectively. This demonstrates that anion adsorption occurs more readily at active surface sites, inhibiting oxygen binding and reducing OER activity.

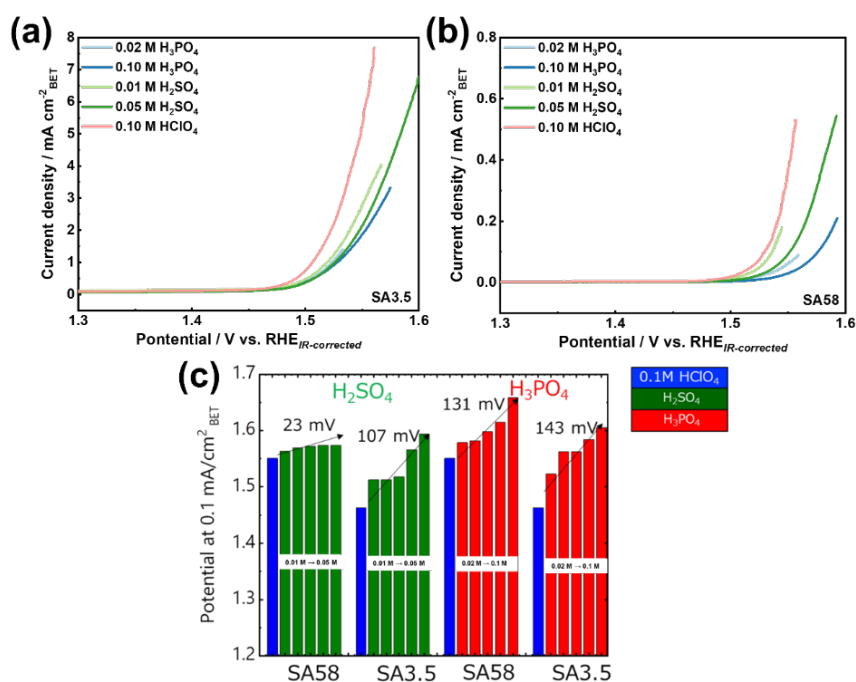


Figure 5-11. OER activity normalized by BET surface area in H₃PO₄ at 0.02 M and 0.10 M; H₂SO₄ at 0.01 M and 0.05 M; and HClO₄ at 0.10 M of (a) SA3.5 and (b) SA58. (c) The summary of OER potential at 0.1 mA/cm² for SA3.5 and SA58 under different types and content of electrolytes.

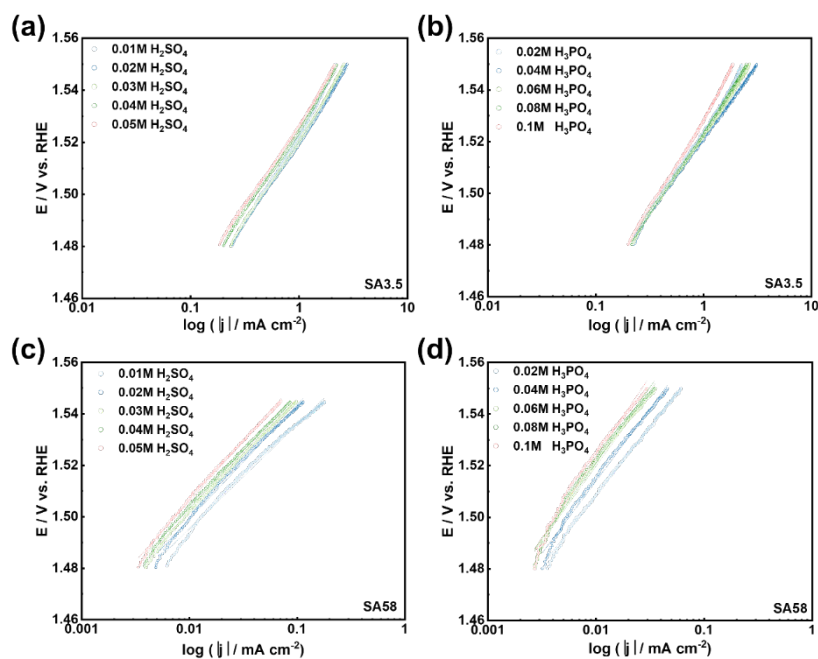


Figure 5-12. Tafel plots of SA3.5 in (a) H₂SO₄ and (b) H₃PO₄. Tafel plots of SA58 in (c) H₂SO₄ and (d) H₃PO₄.

Table 5-4. Tafel slope of SA3.5 and SA58 in H₂SO₄ and H₃PO₄ (mV / dec)

H ₂ SO ₄	0.01 M	0.02 M	0.03 M	0.04 M	0.05 M
SA3.5	62.9	63.46	64.82	64.64	63.14
SA58	40.56	44.39	44.49	44.82	46.75
H ₃ PO ₄	0.02 M	0.04 M	0.06 M	0.08 M	0.1 M
SA3.5	65.01	58.17	62.04	63.60	70.24
SA58	53.62	56.07	58.04	58.80	62.66

Moreover, by examining the OER onset potential under different types and concentrations of anions, we observe that the onset potential increases with rising anion concentration, especially in the presence of H₂PO₄⁻ (Figure 5-13). This is because at lower potentials (0–0.8V), anions such as HSO₄⁻ and H₂PO₄⁻ preferentially adsorb onto the catalyst surface, blocking the adsorption of OER intermediates (such as OOH and OH).⁶⁰ This behavior is primarily attributed to the strong chemical affinity between the anions and coordinatively unsaturated sites, as well as the positive charge effect on the electrode surface.⁶¹ The energy advantage of anion adsorption allows them to stably bind at lower potentials, whereas the adsorption of OER intermediates requires higher potentials to proceed. This preferential adsorption phenomenon has been validated by both experimental and theoretical studies, demonstrating that anion adsorption not only blocks OER active sites but also significantly raises the OER onset potential, thus reducing the catalytic activity.

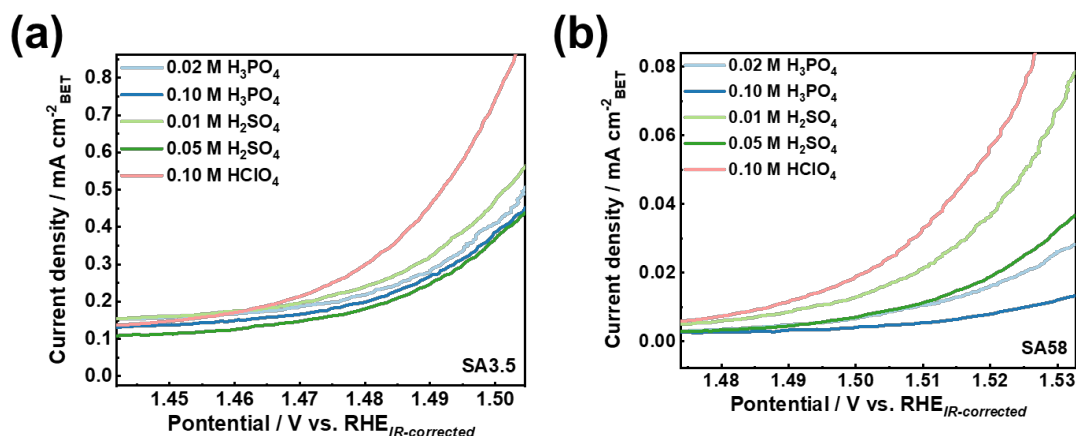


Figure 5-13. Partial enlargement of Figure 5-11.

5.3.3 *Operando* O K-edge XAS measurement

To clarify the observed activity trends, this study focuses on analyzing the near-surface structure and chemical states of IrO_x under electrochemical conditions using *operando* XAS measurements. The CV and LSV curves of SA58 and SA3.5, shown in Figure 5-14 and recorded with both an *operando* cell and a three-electrode RDE setup, demonstrate accurate OER potentials and consistent current-potential relationships, validating the effectiveness of the *operando* approach in capturing intermediates during the OER process.

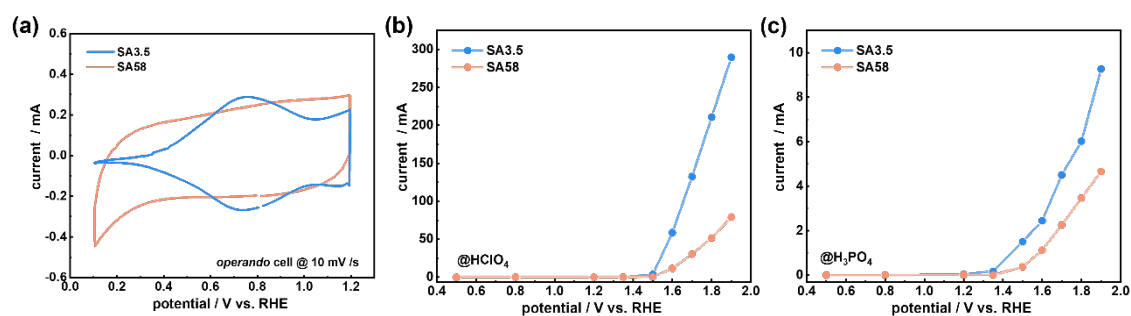


Figure 5-14. Electrochemical performance of SA58 and SA3.5 in the *operando* cell. (a) CV obtained at 0.1 M HClO₄. The relationship between OER current and the applied potential under steady-state *operando* O K-edge measurements at (b) 0.1 M HClO₄ and (c) 0.1 M H₃PO₄.

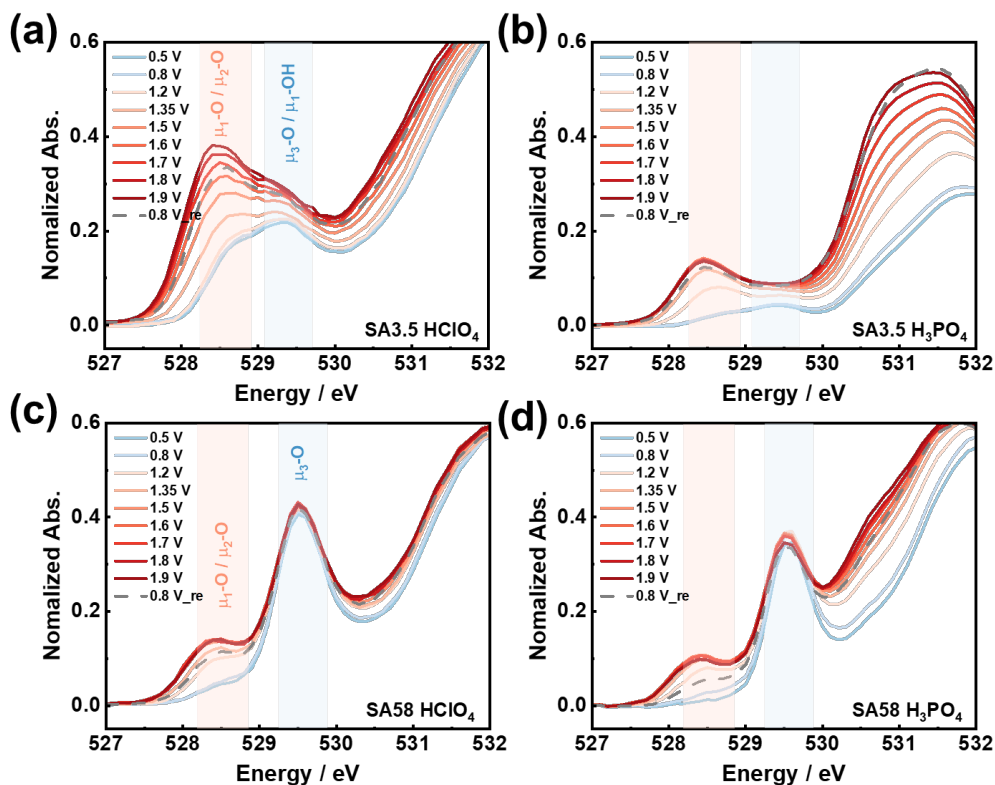


Figure 5-15. Operando O K-edge XAS spectra of SA3.5 in (a) 0.1 M HClO₄ and (b) 0.1 M H₃PO₄ as electrolytes and SA58 in (c) 0.1 M HClO₄ and (d) 0.1 M H₃PO₄ as electrolytes. The spectra were recorded using TEY detection mode.

Operando O K-edge XAS spectra, recorded during the OER process, enabled a detailed analysis of the white line resonance peak within 528–531 eV, providing insights into the near-surface O(H) species.^{16, 25, 62} To accurately describe these oxygen species, this study employs the μ notation from previous research: μ_1 -O (~528.5 eV) represents oxygen at CUS, μ_2 -O (~529 eV) denotes bridging oxygen, and μ_3 -O (~529.6 eV) corresponds to bulk oxygen, which may also appear on the surface.^{16, 23} Figure 5-15a and b demonstrate that as the potential increases, the white line intensity for the amorphous SA3.5 sample shows a significant rise, while the rutile-structured SA58 (Figure 5-15c and d) exhibits only a slight shift and minor intensity increase at higher potentials.

At 0.5 V vs. RHE, SA3.5 displays a strong peak around 528.5 eV and 529.4 eV, indicating substantial hydroxylation in the surface and subsurface regions with predominant μ_1 -O/ μ_2 -O

and μ_1 -OH species with minimal μ_3 -O. The high density of μ_1 -O/ μ_2 -O enhances OER activity by creating a strongly electrophilic environment,⁶³ which facilitates deprotonation of adjacent μ_1 -OH, thereby lowering the O–O coupling barrier for OER.⁶⁴ Conversely, SA58 shows a significant contribution of inert μ_3 -O species at 529.6 eV, indicating that it is the main oxygen species in the bulk of rutile IrO₂.

When the potential reaches 1.9 V vs. RHE, all samples show a pronounced peak near 528.5 eV, linked to the formation of μ_1 -O/ μ_2 -O species in IrO_x during OER. In SA3.5, this peak shifts to lower energies from 0.5 to 1.9 V vs. RHE, suggesting progressive deprotonation of μ_1 -OH at higher potentials.²⁵ Conversely, the inert μ_3 -O peak around 529.6 eV in SA58 remains largely unchanged, indicating limited involvement in the OER process.

This contrast arises from structural differences: the monoclinic SA3.5 structure has μ_1 -O(H) groups distributed both on the surface and in the bulk, enabling significant electronic changes in the oxygen lattice during deprotonation, whereas these groups in rutile SA58 are mainly surface-bound, resulting in minor electronic shifts.^{16, 65} The deprotonation process is also reversible, as seen by the return to the protonated state at lower potentials (0.8 V_{re}), consistent with prior studies.¹⁶

In a 0.1 M H₃PO₄ electrolyte, the SA3.5 catalyst showed significant inhibition of hydroxylation and deprotonation processes, as illustrated in Figure 5-15b. At 0.5 V vs. RHE, the intensities of μ_1 -O/ μ_2 -O and μ_1 -OH signals were noticeably lower, and as the potential increased, the peak enhancement and shift were weaker than those observed in HClO₄. This suggests that phosphate anions occupied active surface sites, thereby diminishing OER activity. In contrast, the SA58 catalyst, with its predominant bulk μ_3 -O composition, was less impacted by anion adsorption due to its stable, inert structure, contributing minimally to the changing in peak intensity (Figure 5-15d).

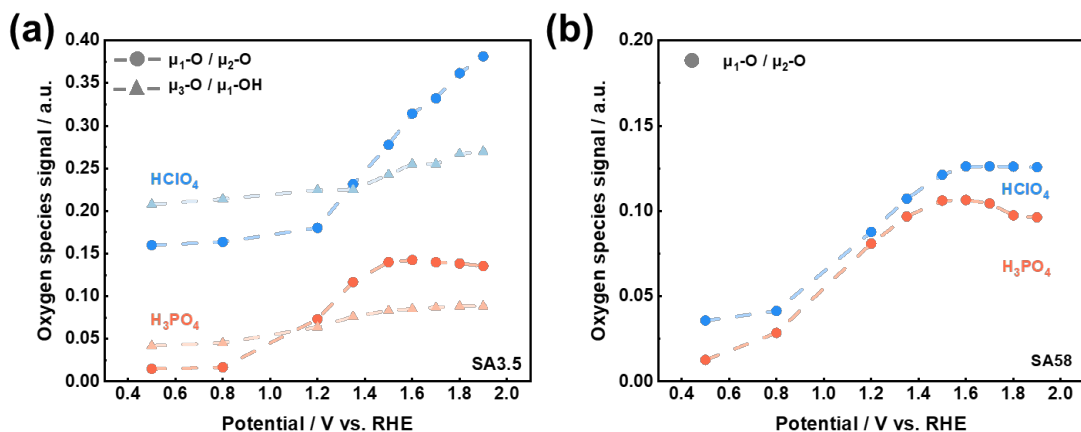


Figure 5-16. Potential dependence of the $\mu_1\text{-O}/\mu_2\text{-O}$ and $\mu_3\text{-O}/\mu_1\text{-OH}$ signals from the data in Figure 5. (a) $\mu_1\text{-O}/\mu_2\text{-O}$ and $\mu_3\text{-O}/\mu_1\text{-OH}$ signals of SA3.5 at 0.1 M HClO_4 and 0.1 M H_3PO_4 . (b) $\mu_1\text{-O}/\mu_2\text{-O}$ signals of SA58 at HClO_4 and H_3PO_4 .

Further quantitative analysis compared the potential-dependent signals of $\mu_1\text{-}$ and $\mu_2\text{-}$ sites in the O K-edge XAS spectra (Figure 5-16) to investigate the impact of anion adsorption on the active sites of catalysts with different structures. The amorphous catalyst SA3.5 exhibited a higher concentration of $\mu_1\text{-}$ and $\mu_2\text{-}$ sites, where the strong $\mu_1\text{-OH}$ signal played a crucial role in the deprotonation process. In contrast, the rutile-structured SA58, primarily composed of inert $\mu_3\text{-O}$, had fewer $\mu_1\text{-}/\mu_2\text{-}$ sites, and its signal saturated around 1.6 V vs. RHE. The presence of phosphate anions significantly affected the formation of $\mu_1\text{-O}/\mu_2\text{-O}$ species, especially in SA3.5, where active sites were covered by H_2PO_4^- , greatly reducing deprotonation and causing the signal to saturate around 1.6 V vs. RHE.⁶³ Additionally, at high polarization potentials (1.8–1.9 V vs. RHE), both catalysts showed a slight decrease in $\mu_1\text{-O}/\mu_2\text{-O}$ signals, which can be attributed to partial irreversible oxidation of Ir induced by anion adsorption, further diminishing the number of active sites.

In summary, $\mu_1\text{-OH}$, $\mu_1\text{-O}$, and $\mu_2\text{-O}$ species are prevalent on the surface of iridium oxide under OER conditions. While SA3.5, with its abundance of $\mu_1\text{-}$ and $\mu_2\text{-}$ active sites, significantly enhances OER activity, it is also more susceptible to anion poisoning.

5.3.4 Operando Ir L₃-edge XAS measurement

To explore the dynamic oxidation state changes of Ir during the OER process, *operando* XAS spectra were recorded at the Ir L₃-edge for IrO_x at varying potentials, capturing transitions from Ir 2p_{3/2} to Ir 5d and 6sp orbitals, which hybridize with O 2p orbitals.^{17, 66} This hybridization produces a distinct white line feature, with variations in its intensity directly correlating with Ir's oxidation state.

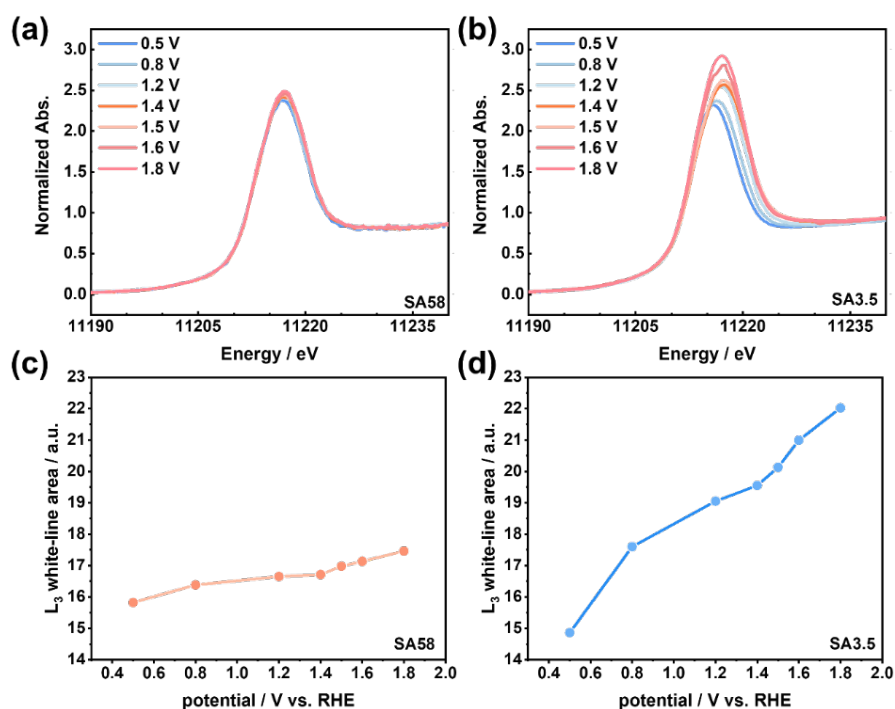


Figure 5-17. *operando* Ir L₃-edge XANES spectra of (a) SA58 and (b) SA3.5. White line intensity of (c) SA58 and (d) SA3.5.

As shown in Figure 5-17, the white line intensity for SA3.5 increases and shifts to higher energy as the potential rises from 0.5 V to 1.8 V vs. RHE, indicating a progressive oxidation of Ir. Additionally, the negative shift in the Ir-O signal in FT-EXAFS spectrum of SA3.5 suggests a shortening of the Ir-O bond (Figure 5-18).⁶⁷ In contrast, SA58 shows minimal changes in Ir L₃-edge XANES spectra across potentials, with weak CV redox peaks, indicating that only limited Ir is oxidized during the OER process.

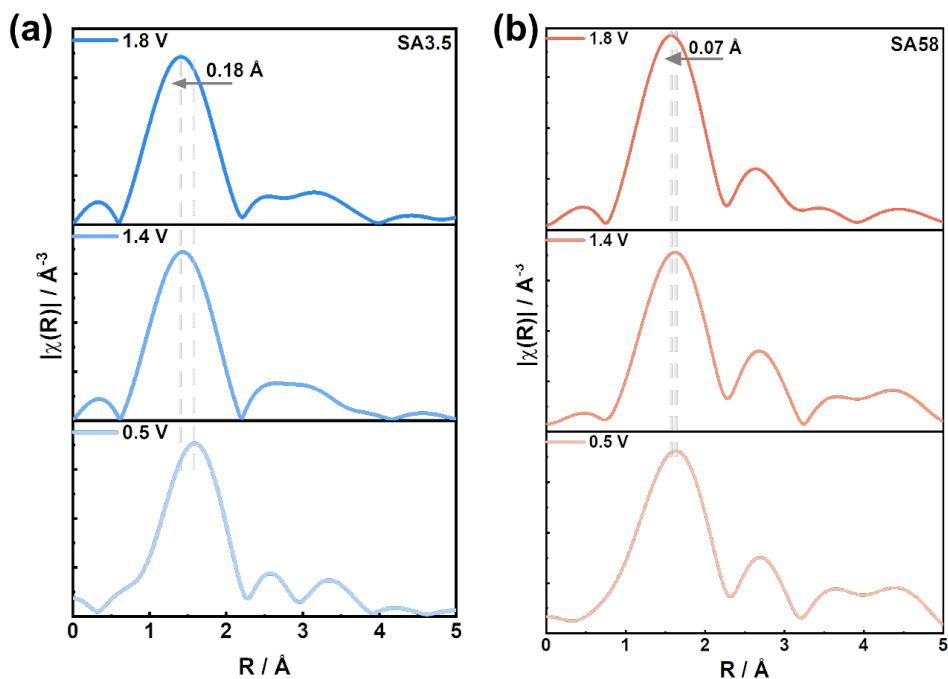


Figure 5-18. *operando* EXAFS spectra of (a) SA3.5 and (b) SA58.

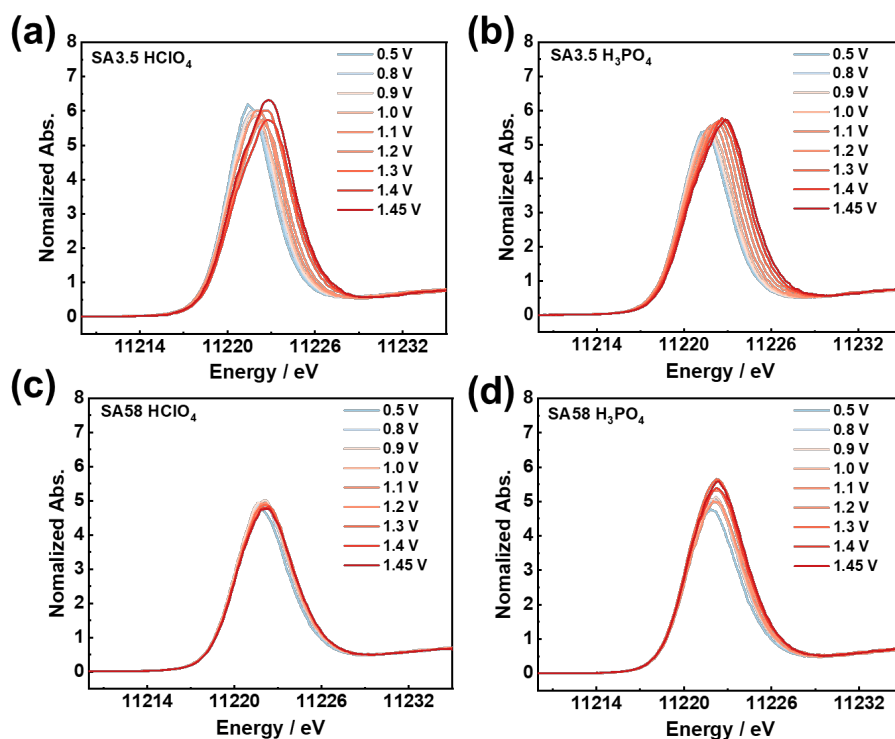


Figure 5-19. *Operando* HERFD- Ir L₃-edge XAS analysis for SA3.5 at (a) 0.1 M HClO₄ and (b) 0.1 M H₃PO₄ and for SA58 at (c) 0.1 M HClO₄ and (d) 0.1 M H₃PO₄ varying different polarization potential.

Further insights into catalyst behavior across electrolyte environments were obtained using high-energy resolution fluorescence-detected XAS (HERFD-XAS) to monitor shifts in the Ir L₃-edge white line as potentials approached OER conditions.⁶⁸ This technique offers the advantage of higher energy resolution, allowing for more precise analysis of electronic structures and local environments and revealing OER mechanism.

Figures 5-19 and 5-20 display Ir L₃-edge XANES white line changes for both catalysts across different electrolytes and potentials, with $\Delta\mu$ spectra quantifying potential-dependent spectral shifts,⁶⁹ showing significant differences between the catalysts and across different electrolyte environments. SA3.5 showed greater spectral variation due to its higher content of active sites. The adsorption of *O, which further oxidizes Ir^{IV} to Ir^{IV+ δ} ,²⁵ is marked by increased white line intensity and energy shifts, primarily involving deprotonated μ_1 -OH intermediates.⁶⁵ In H₃PO₄, however, substantial phosphate anion adsorption on SA3.5 poisons many μ_1 -/ μ_2 -sites, leading to saturation of the O K-edge spectrum near 1.6 V vs. RHE. Interestingly, the Ir L₃-edge XANES white line shifts at high potentials in H₃PO₄ are comparable to those in HClO₄, suggesting that high anion adsorption may increase Ir's oxidation state, forming $IrO(OH)_{1+\delta} \cdot mH_2O$, yet this elevated state minimally contributes to the OER process.⁶¹

For SA58 (Figure 5-19c), the limited change in white-line intensity indicates that Ir^{IV} rapidly reaches saturation at high potentials, possibly due to the fewer CUS occupied by *OO or *OOH intermediates.⁶⁸ Furthermore, the poisoning effect of H₂PO₄⁻ anions in active site of SA58 also facilitates the irreversible oxidation of Ir (Figure 5-19d), which is consistent with conclusions drawn from the O K-edge result.

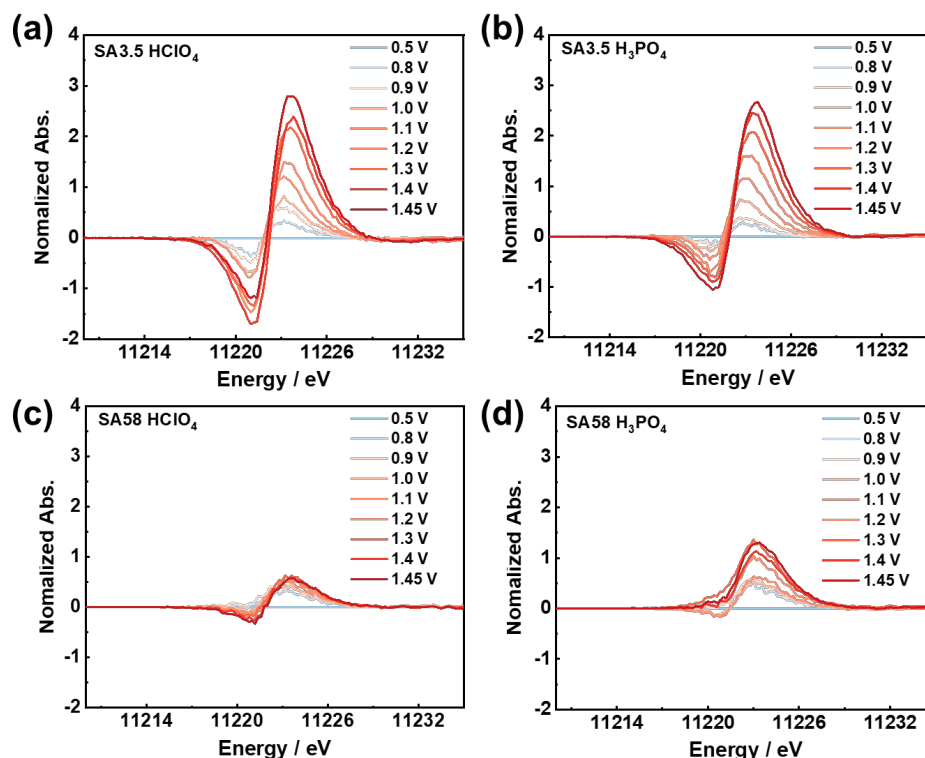


Figure 5-20. $\Delta\mu$ XANES spectra for the catalysts calculated by $\mu p(E) - \mu 0.5V$ according to **Figure 5-19**. $\Delta\mu$ XANES spectra of SA3.5 at (a) 0.1 M HClO_4 and (b) 0.1 M H_3PO_4 . $\Delta\mu$ XANES spectra of SA58 at (c) 0.1 M HClO_4 and (d) 0.1 M H_3PO_4 .

5.3.5 Theoretical investigation of the anion adsorption

To further investigate the effect of acidic electrolyte anion adsorption on IrO_x catalyst surfaces, systematic DFT calculations were performed. Gunasooriya et al. demonstrated that anion adsorption is most stable at the coordinatively unsaturated Ir (Ir-CUS) sites compared to Ir and O bridge sites,⁶¹ with protons in OH groups, especially in HSO_4^- , forming stable hydrogen bonds with lattice oxygen. To identify the most stable adsorption configurations of H_2PO_4^- and HSO_4^- anions, their adsorption stability on Ir-CUS sites was analyzed across three crystal structures: $P42/mnm$ (110), $Pbcn$ (11-1), and $C2/m$ (-100) (Figure 5-21). Results indicate that on $P42/mnm$ (110) and $C2/m$ (-100) surfaces, anions adsorb onto two surface Ir active site, whereas on the $Pbcn$ (11-1) surface, three Ir active site adsorption contribute to the most stable configuration (Figure 5-22a). This indicates that for the SA3.5 catalyst composed of $Pbcn$ and $C2/m$ structures, anions can occupy more iridium active sites, leading to

widespread blockage of catalytic sites. Furthermore, comparison of adsorption energies (Table 5-5) shows that H_2PO_4^- adsorption is more stable than HSO_4^- , resulting in a greater reduction in IrO_x catalytic activity.

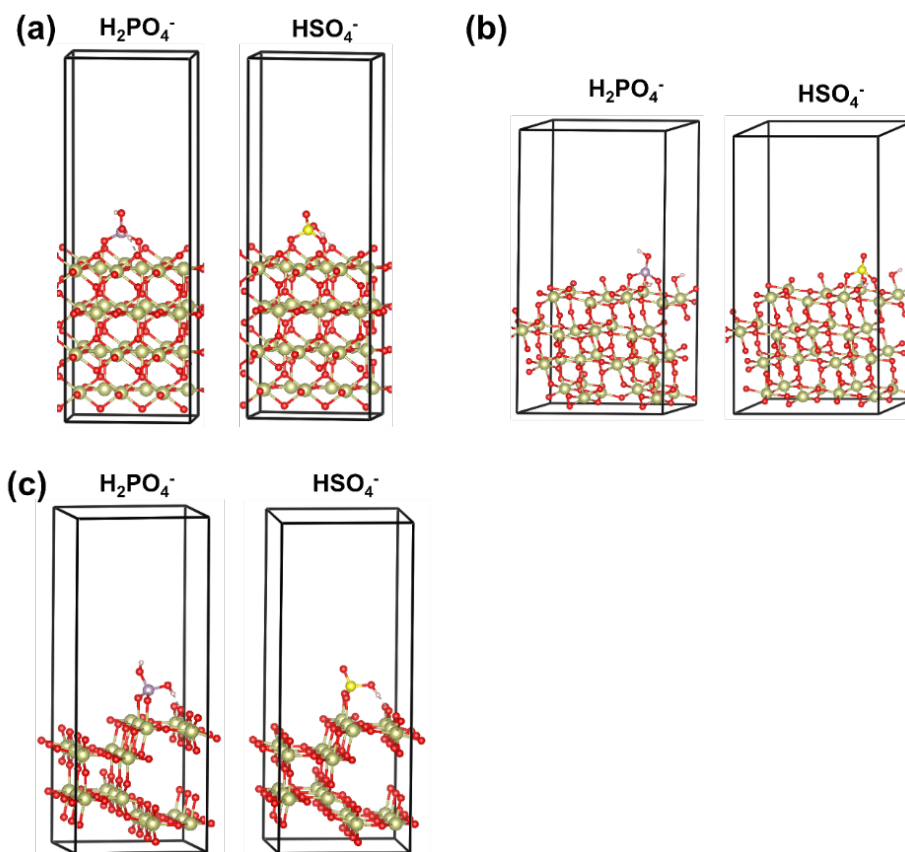


Figure 5-21. (a) The models of IrO_2 (110) of tetragonal crystal ($P42/mnm$), (b) (11-1) plane of orthorhombic crystal ($Pbcn$) and (c) (-100) plane of monoclinic crystal ($C2/m$) to anions such as H_2PO_4^- and HSO_4^- .

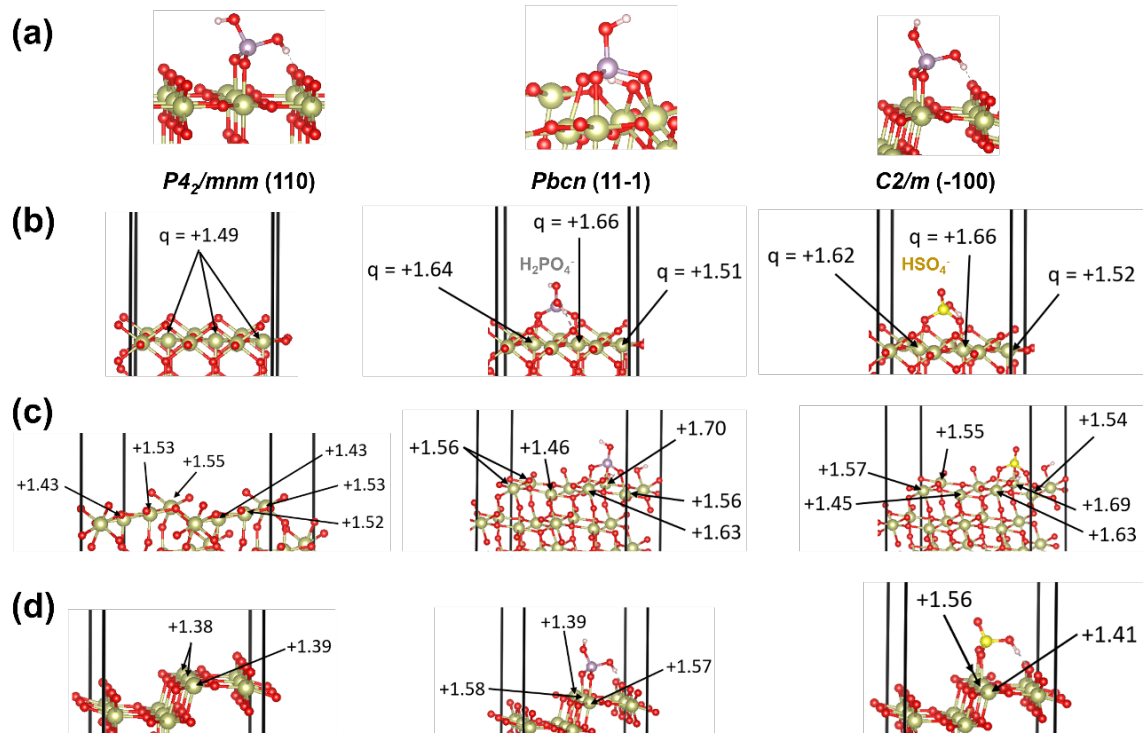


Figure 5-22. (a) Atomistic figures for different anion adsorption in the most stable configuration on the *P4₂/mnm* (110), *Pbcn* (11-1), and *C2/m* (-100) surface. The Bader charge distribution before and after adsorption of H_2PO_4^- and HSO_4^- in (b) *P4₂/mnm* (110), (c) *Pbcn* (11-1), and (d) *C2/m* (-100) surface.

Table 5-5. Adsorption energies of anions on different crystal structure surface.

	$\Delta E_{\text{Adsorption on}}$ <i>P4₂/mnm</i> (110) (eV)	$\Delta E_{\text{Adsorption on}}$ <i>Pbcn</i> (11-1) (eV)	$\Delta E_{\text{Adsorption on}}$ <i>C2/m</i> (-100) (eV)
H_2PO_4^-	-5.305	-4.913	-4.859
HSO_4^-	-4.501	-4.397	-4.238

The effect of anion adsorption on the Bader charge of Ir was also assessed (Figure 5-22b–d). As anticipated, the Bader positive charge of Ir increased upon anion adsorption, indicating an elevated oxidation state and reduced electron density. An excessively high oxidation state in Ir can alter electron distribution and weaken its interactions with critical OER reactants, such as oxygen atoms or hydroxyl groups.⁷⁰ This makes key steps like O–O bond formation and oxygen deprotonation more challenging, thereby decreasing catalytic activity. The increase in the Bader charge of Ir was approximately 0.11 eV on the *P42/mnm* (110) and *Pbcn* (11-1) surfaces, and 0.2 eV on the *C2/m* (-100) surface, suggesting significant reductions in OER activity for SA3.5 due to anion adsorption.

To further analyze anion effects on OER intermediates, Bader charge calculations were conducted for Ir-CUS sites adjacent to adsorbed anions. Although no substantial charge increase was observed at adjacent Ir-CUS sites, anions influenced the free energy of co-adsorbed O and OH species. Due to their high electron affinity, anions create electron-deficient zones near surface atoms, causing charge accumulation when OER intermediates are co-adsorbed, leading to repulsive interactions between negatively charged species.⁶¹ This charge transfer and repulsion ultimately weaken the adsorption of OER intermediates on IrO_x.

In summary, acidic electrolyte anions competitively adsorb on catalyst surfaces, blocking active sites, weakening OER intermediate binding, and modifying the IrO_x surface's electronic properties. For the SA3.5 catalyst, which consists of orthorhombic (*Pbcn*) and monoclinic (*C2/m*) phases, the three-point adsorption of anions on the *Pbcn* (11-1) surface and the notable increase in Bader charge on the *C2/m* (-100) surface lead to pronounced anion poisoning effects, significantly impacting catalytic performance.

5.4 Conclusions

This study provides a profound insight into the electrocatalytic performance and structural dynamics of amorphous SA3.5 and crystalline SA58 IrO_x catalysts. Through *operando* XAS and PDF analysis, we demonstrated that the amorphous SA3.5 exhibits superior OER activity due to its higher density of unsaturated oxygen sites ($\mu_1\text{-O}/\mu_2\text{-O}$), facilitating rapid

deprotonation processes. However, it also showed increased susceptibility to anion poisoning compared to the more stable, but less active, crystalline SA58. DFT calculations results indicate that the most stable adsorption occurring on the *Pbcn* (11-1) surface with three oxygen atoms involved. Furthermore, anion adsorption increases the Bader charge of Ir, raising its oxidation state and weakening its catalytic performance. Particularly for the SA3.5 catalyst, anion adsorption at Ir-CUS sites in the *Pbcn* and *C2/m* structures significantly hindered the adsorption and reaction of OER intermediates. The findings underscore the intricate balance between catalytic activity, crystal structure, and the influence of electrolyte composition on performance, thereby providing critical insights for the development of efficient and durable OER catalysts.

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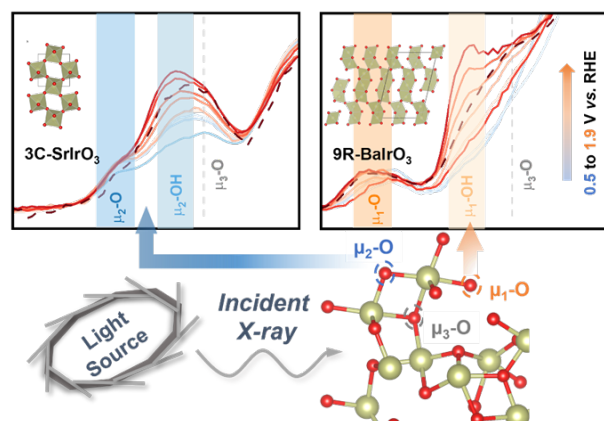
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Chapter 6. Identification of Structure-Activity Correlations in Iridium-Based Perovskite Oxides for Oxygen Evolution by *operando* X-ray absorption spectroscopy



Iridium-based perovskite oxide catalysts show unique activity and stability in oxygen evolution reactions (OER). This exceptional performance is majorly attributed to surface restructuring and the formation of (μ_1/μ_2) active sites). However, the experimental

confirmation of this relationship has been a challenge. Therefore, to examine the structure-activity relation, this study synthesized four iridium-based perovskite oxides (9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, and BCC-SrIrO₃) for application as OER catalysts in polymer electrolyte membrane water electrolysis (PEMWE). Among these, 9R-BaIrO₃ showed the highest OER activity and durability, attributed to its unique face-shared [IrO₆] octahedral trimer structure and significant surface hydroxylation. *Operando* Ir L₃-edge XAS and high-energy-resolution fluorescence-detected XAS (HERFD-XAS) revealed that Ir species in 9R-BaIrO₃ undergo more significant oxidation state changes and Ir-O bond shortening, which enhances the electrophilicity of Ir and facilitates hydroxyl oxidation and proton release. Additionally, *operando* O K-edge XAS analysis provided insights into selective oxygen binding sites influenced by structural distortions in the [IrO₆] octahedra, with less symmetrical structures (6H and 9R) favoring μ_1 sites and more symmetrical structures (3C and BCC) favoring μ_2 sites. The continuous generation of μ_3 sites within the crystal structure also contributes to catalyst stability. This research not only advances the understanding of the operational mechanisms of iridium-based perovskite oxides in OER but also provides guidance for developing innovative, efficient, and durable OER catalysts.

6.1 Introduction

Given the rapidly increasing global energy demand and worsening environmental issues, the development of efficient and eco-friendly energy conversion technologies, such as hydrogen energy, is crucial due to its high energy density and clean by-products.¹⁻⁶ The production of hydrogen via polymer electrolyte membrane water electrolysis (PEMWE) is hindered by the sluggish kinetics of the anodic oxygen evolution reaction (OER) and the scarcity and high cost of state-of-the-art OER catalysts like IrO₂ and RuO₂.^{7, 8} Therefore, it is essential to develop cost-effective, novel iridium-based catalysts that demonstrate high efficiency and durability in acidic conditions.

Iridium-based perovskite oxides have gained attention for their unique A_xIr_yO_z structures and cost-effectiveness, with the structural diversity significantly influencing their catalytic activity.^{9, 10} The geometric arrangement of [IrO₆] octahedra and their interaction with A-site cations are key factors in determining OER performance. Distorted [IrO₆] octahedra often exhibit higher activity due to the closer proximity of π - and π^* orbitals to the Fermi level.¹¹⁻¹³ Additionally, these perovskite oxides undergo surface reconstruction and metal dissolution under electrochemical conditions, indicating a strong connection between structural evolution and catalytic activity.¹⁴⁻¹⁹ This dynamic process highlights changes on the catalyst surface under various external conditions,²⁰ underscoring the importance of *in-situ* and *operando* analytical techniques to track active structures, understand catalytic mechanisms, and guide the design of new catalysts.

X-ray spectroscopy is a pivotal tool for probing the atomic and electronic structures of materials, providing detailed insights at the elemental level.²¹ Understanding the reaction and degradation mechanisms of electrocatalysts requires information about their structural composition under actual *operando* conditions, which can be obtained via techniques such as X-ray absorption spectroscopy (XAS).²² Some recent studies have revealed that reducing the coordination number of Ir-O can lower the energy barrier of the rate-determining step, thus potentially accelerating OER.²³ Additionally Ge et al. found that the coordination number of

Ru–O in SnRuO_x remained around 6, while in RuO_x it decreased from 6.4 to 4.7 during OER, indicating the formation of oxygen vacancies and contributing to catalyst deactivation.²⁴

However, most *in situ/operando* studies of catalysts have primarily utilized bulk-sensitive spectroscopies, especially hard XAS for Ir L-edge.²⁵ Given the fact that OER activity is determined by the surface and electronic structure of the catalyst, making *operando* analysis an essential tool for obtaining information about the catalyst surface during OER. In this context, soft X-ray absorption techniques, particularly *operando* O K-edge measurements, are used to analyze OER catalysts. This method provides insights into reaction mechanisms by highlighting the formation and deprotonation of μ_1 - and μ_2 -OH species, which are crucial intermediary steps in the OER process.²⁶⁻²⁸ Although current research has identified some key components of the OER,²⁹ a detailed discussion on the structure of [IrO₆] and oxygen species, particularly regarding the evolution of the OER catalyst surface under reaction conditions requires further study. Additionally, the significant variability in OER activity among iridium-based perovskite catalysts with different crystal structures necessitates the use of this technique to investigate and explain these discrepancies.³⁰

In this study, four iridium-based perovskite oxides with distinct structures (9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, and BCC-SrIrO₃) were synthesized and compared with conventional rutile-type IrO₂ catalysts to understand their differences in OER performance. The results demonstrated that the synthesized iridium-based perovskites exhibited higher activity than the rutile-type catalysts, wherein 9R-BaIrO₃ showed the lowest overpotential (~ 290 mV *vs.* RHE) and best stability (over 70h) at 10 mA cm⁻². *Operando* O K-edge XAS analysis confirmed dynamic changes in surface oxygen species with increasing OER potential, highlighting the selectivity of μ_1 -O and μ_2 -O species towards different crystal structures, crucial for optimizing OER performance. Further, *operando* Ir L₃-edge XAS and high-energy-resolution fluorescence-detected XAS (HERFD-XAS) analyses revealed that Ir-O bond length and coordination numbers significantly influence OER activity. This comprehensive approach, integrating synthesis, structural analysis, electrochemical testing, and spectroscopic techniques, has deepened the understanding of catalyst behavior, offering valuable insights for the design

of high-performance catalysts.

6.2 Experimental Methods

6.2.1 Chemicals

Barium nitrate ($\text{Ba}(\text{NO}_3)_2$, 99.0%), Hydrogen hexachloroiridate(IV) n-Hydrate ($\text{H}_2\text{IrCl}_6 \cdot \text{H}_2\text{O}$, 36.5%_{Ir}), Ethylene glycol (EG, 99.5%), Ethylenediaminetetraacetic acid (EDTA, 99.5%), Citric acid (98.0%), Ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28.0%), Perchloric acid (HCl, 35.0%), Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, 99.9%), Ethanol (99.5%) were acquired from Fujifilm. All chemical reagents were used as received without further purification. The electrolyte was prepared from ultra-pure water (Milli-Q, 18.2 M Ω) and perchloric acid (ultra-pure, Kanto Chemical Co. Inc.). IrO_2 was procured from Tanaka Kikinzoku (TKK) and used as a standard sample for comparison.

6.2.2 Material Synthesis

All four catalysts were synthesized using the ethylenediaminetetraacetic acid-citric acid (EDTA-CA) complex sol-gel method. For the synthesis of 9R-BaIrO₃, 117.6 mg of $\text{Ba}(\text{NO}_3)_2$ and 77.3 mg of $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ were dissolved in a solution of 20.0 mL of deionized water and 2.0 mL of EG. Then, 292.0 mg of EDTA and 3.6 g of citric acid were added as complexing agents, maintaining a mole ratio of 1:1:3 for total metal ions to EDTA to citric acid. The pH of the solution was adjusted to 6-7 using an NH_3 aqueous solution to ensure complete complexation. The mixture was heated to 200 °C with continuous stirring until gel formation occurred. To obtain the precursor, the drying temperature was raised to 350 °C and maintained for 8 to 9 hours. The precursor was then finely ground and calcined in air at 700 °C for 5 hours. Afterward, the product was immersed in 0.1 M HCl for 3 hours to eliminate any BaCO_3 impurities and achieve the desired surface structure. The excess liquid was removed by filtration, yielding the acid-treated catalyst sample.

The synthesis protocol for the other catalysts followed a similar approach, with

modifications including the substitution of $\text{Ba}(\text{NO}_3)_2$ with $\text{Sr}(\text{NO}_3)_2$ (47.61 mg) and adjustments in the quantity of citric acid used. Specifically, 280 mg of citric acid was used for 6H-SrIrO_3 , while 10.0 g was used for 3C-SrIrO_3 . For the synthesis of BCC-SrIrO_3 , the quantity of $\text{Sr}(\text{NO}_3)_2$ was increased by 1.5 times, along with the addition of 280 mg of citric acid, leading to successful synthesis.

6.2.3 Characterization

X-ray diffraction (XRD) analyses were conducted on a Rigaku Ultima IV (Japan) employing $\text{Cu K}\alpha$ radiation, with a scanning rate of 2° per minute to characterize the crystalline structure of the samples. Transmission Electron Microscopy (TEM) imaging was performed on a JEM-2200FS (JEOL Ltd.) at an operating voltage of 200 kV to observe the microstructural features. Similarly, Scanning Transmission Electron Microscopy (STEM) investigations utilized a JEM-ARM200F (JEOL Ltd.) at the same acceleration voltage, enabling high-resolution examination of the samples. The surface chemical compositions were analyzed using X-ray Photoelectron Spectroscopy (XPS) on a PHI5000 VersaProbe II, utilizing monochromatic $\text{Al K}\alpha$ radiation for high precision.

6.2.4 Electrochemical measurements

For the preparation of the catalyst inks, a certain mass of catalyst powder was blended with 7.5 μL of a 5 wt% Nafion solution (Sigma-Aldrich), 0.4 mL of ethanol, and 1.6 mL of ultra-pure deionized water. This mixture was sonicated for 30 minutes in an ice bath to ensure homogeneity. The resulting ink was then carefully deposited onto a polished gold rotating disk electrode (RDE) with a 5 mm diameter (Hokuto-Denko). The working electrode was dried at room temperature at 400 rpm to obtain a uniform catalyst layer with a loading of $80 \mu\text{g}_{\text{Ir}}/\text{cm}^2$.

Electrochemical measurements were conducted using a standard three-electrode setup connected to an MPG-205-NUC electrochemical workstation (Bio-Logic). This configuration included a platinum mesh counter electrode, a reversible hydrogen electrode (RHE) as the reference, and the catalyst-coated gold RDE as the working electrode. Cyclic Voltammetry (CV)

analyses were performed in nitrogen-saturated 0.1 M HClO₄, scanning from 0.1 V to 1.2 V vs. RHE at a scan rate of 50 mV s⁻¹. Linear Sweep Voltammetry (LSV) measurements were conducted at a rotation speed of 1600 rpm, covering a potential window from 1.1 to 1.6 V vs. RHE at a scan rate of 10 mV s⁻¹. Stability tests were performed at a current density of 10 mA cm⁻².

6.2.5 *Operando* XAS measurement

Operando soft XAS measurements of the O K-edge were performed in Total Electron Yield (TEY) mode at the BL27SU beamline of SPring-8, using a custom-built *operando* cell. This experimental setup employed a platinum wire as the counter electrode and a reversible hydrogen electrode (RHE) as the reference electrode. Catalyst-coated membrane (CCM) samples were prepared by depositing various catalysts onto Nafion 212 membranes, achieving an iridium loading of approximately 0.1 mg cm⁻². The CCM setup was integrated with a glassy carbon (GC) disc featuring a central hole (1 mm diameter) alongside the cell body, as shown in Figure 6-1. Monochromatic X-rays were generated using a line-spacing plane grating monochromator. Electrochemical polarization was applied, ranging from 0.5 V to 1.9 V vs. RHE under vacuum conditions. XAS signals were acquired after maintaining each potential for 10 minutes to ensure equilibrium current conditions were established.

Traditional Ir L₃-edge XAS measurements were conducted at the BL37XU beamline, SPring-8, Japan, using the same *operando* cell as for the soft XAS measurements. HERFD-XANES at the Ir L₃-edge was performed at the BL39XU beamline. The design of the custom *operando* cell was based on previous research.³¹ Measurements were conducted in 0.1 M HClO₄ electrolyte, with potentials ranging from 0.5 V to 1.55 V vs. RHE. X-ray Emission Spectroscopy (XES) was used to monochromatize the fluorescent X-rays before acquiring HERFD-XANES signal. Incident X-ray were generated using a pair of Si (220) monochromators and a total-reflection Rh mirror (4.5 mrad). Data analysis was primarily conducted using the ATHENA and ARTEMIS software packages from the IFEFFIT suite, facilitating a comprehensive examination of the spectral information obtained.

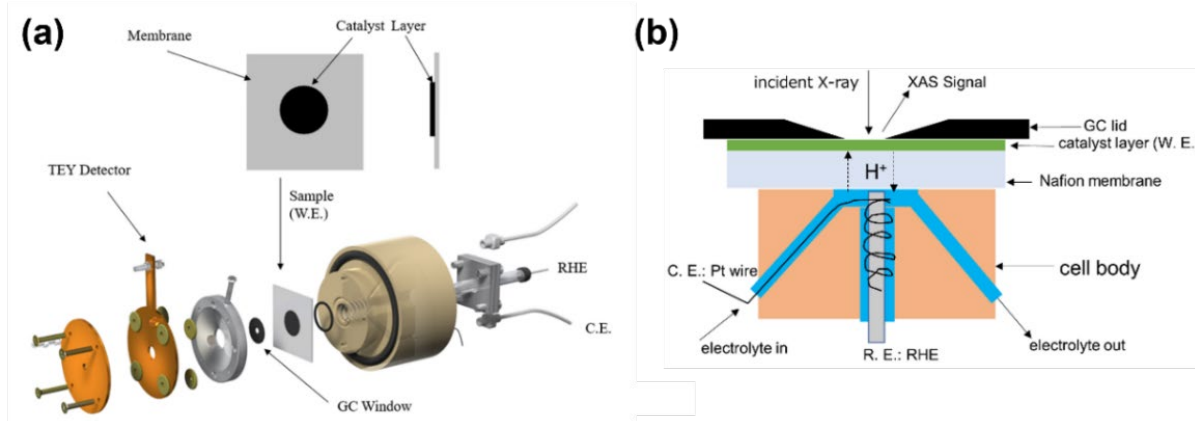


Figure 6-1. (a) Representing components and (b) sectional view of *operando* XAS cell.

6.3 Result and Discussion

6.3.1 Structure characterization

Four iridium-based perovskite oxides—9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, and BCC-SrIrO₃—were synthesized using a solution calcination method, followed by an acid treatment to refine their structures. Critical synthesis parameters, such as the quantity of citric acid and calcination temperature, were identified as pivotal in controlling the process (detailed synthesis steps are provided in the supplementary information).¹⁶

X-ray diffraction (XRD) analyses, detailed in Figure 6-2 and 6-3a, confirmed the effective removal of BaCO₃/SrCO₃ impurities post-acid treatment, with the most substantial diffraction peaks matching those of the standard reference. Based upon the XRD results all catalysts revealed distinct connection modes of the [IrO₆] octahedra within these oxides (Figure 6-4 and Table 6-1): in the 9R-BaIrO₃ structure, [IrO₆] octahedra are arranged in triads ([IrO₆]-[IrO₆]-[IrO₆]) connected via face-shared interactions, forming a three-dimensional network through corner-shared connections.¹⁵ The 6H-SrIrO₃ displays [IrO₆] octahedra organized as face-shared dimers, which function as discrete units linked by corner-sharing with adjacent octahedra.¹⁸ BCC-SrIrO₃ is characterized by a body-centered cubic structure composed of edge-shared [IrO₆] octahedral dimers interconnected alternately through apex oxygen atoms, resulting in a nbo-type topology with circular channels.³² In contrast, 3C-SrIrO₃ features [IrO₆] octahedra

interconnected exclusively through corner-sharing. It is important to note that corner-shared connections generally exhibit lower structural strength compared to edge- or face-sharing geometries.³³

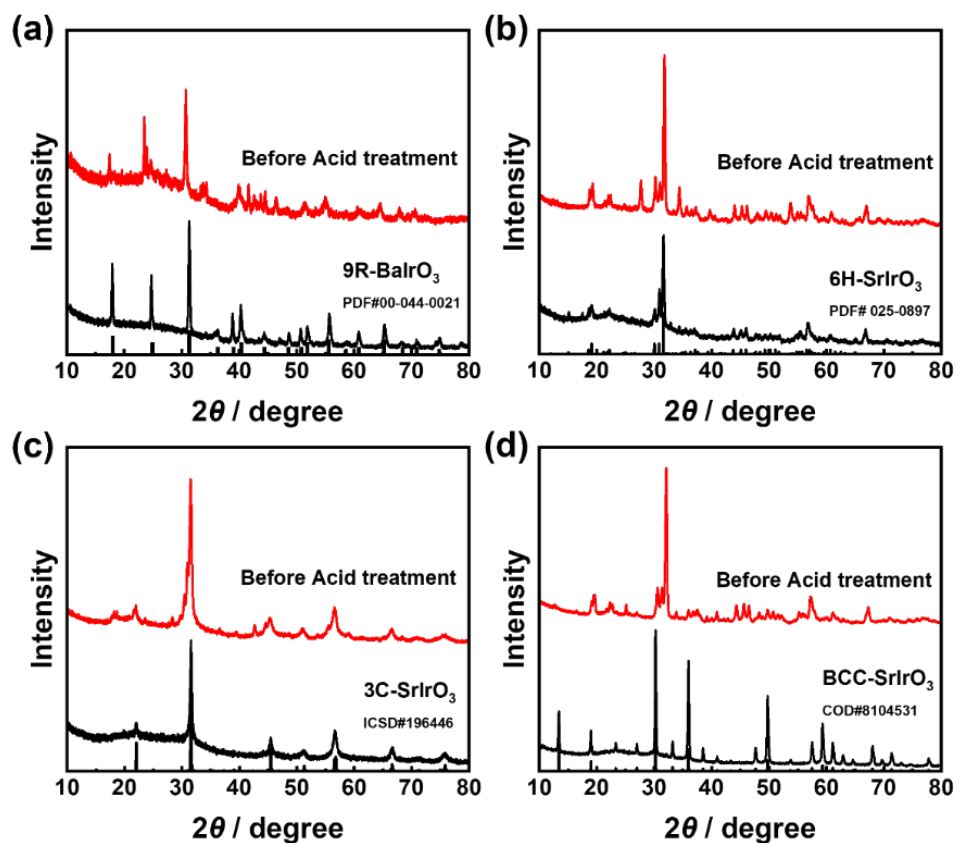


Figure 6-2. XRD patterns of (a) 9R-BaIrO₃, (b) 6H-SrIrO₃, (c) 3C-SrIrO₃ and (d) BCC-SrIrO₃ before and after 0.1 M HCl treatment.

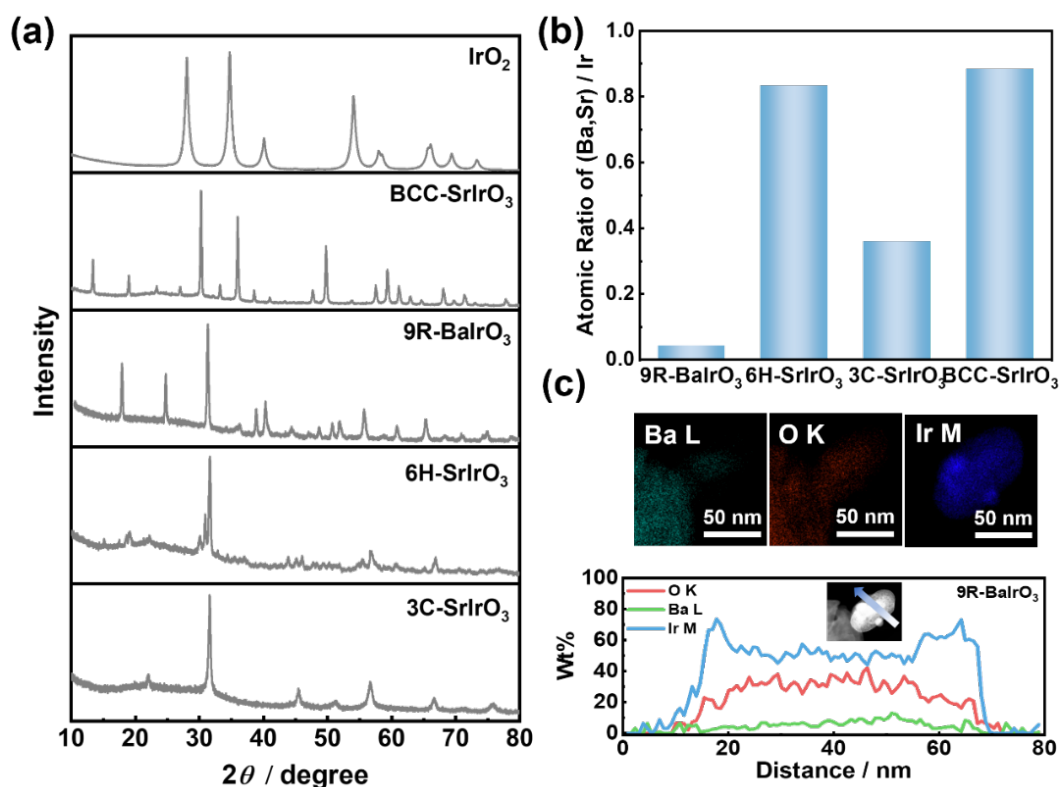


Figure 6-3. (a) XRD pattern of 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃ and BCC-SrIrO₃. (b) Comparison of the atomic ratio between (Ba or Sr)/Ir on 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃ and BCC-SrIrO₃. (c) STEM and EDX analysis of 9R-BaIrO₃. All catalysts were subjected to acid treatment.

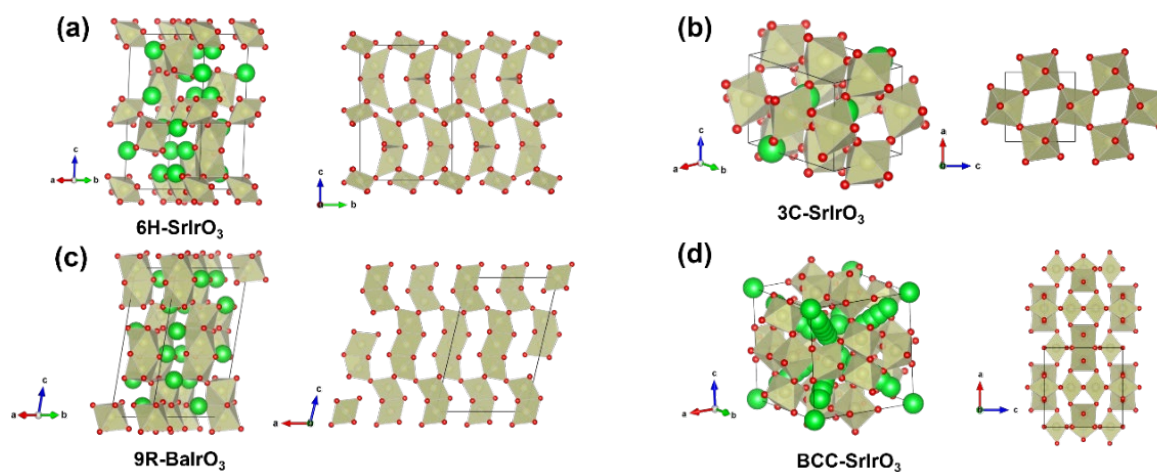


Figure 6-4. Typical crystal structure of (a) 6H-SrIrO₃, (b) 3C-SrIrO₃, (c) 9R-BaIrO₃ and (d) BCC-SrIrO₃.

Table 6-1. Crystallographic information for 9R-BaIrO₃, 6H-SrIrO₃, BCC-SrIrO₃ and 3C-SrIrO₃

Sample	Crystal system	Space group	Cell length a (Å)	Cell length b (Å)	Cell length c (Å)	Cell angle α (°)	Cell angle β (°)	Cell angle γ (°)
9R-BaIrO ₃	Monoclinic	C2/m	10.005	5.753	15.183	90.00	103.27	90.00
BCC-SrIrO ₃	Cubic	Im-3	9.340	9.340	9.340	90.00	90.00	90.00
3C-SrIrO ₃	Orthorhombic	Pnma	5.590	7.882	5.561	90.00	90.00	90.00
6H-SrIrO ₃	Monoclinic	C2/c	5.6113	9.6335	14.186	90.00	93.26	90.00

Acid treatment significantly modified the surface structures of the catalysts by inducing the dissolution of Ba/Sr components and promoting surface amorphization. XPS analysis detailed in Figure 6-3b and Table 6-2 revealed that the atomic ratios of Ba and Sr to Ir in all samples were below 1.0. This was particularly notable in the 3C and 9R samples, where the dissolution of surface Ba and Sr exceeded 80%, leading to the formation of an active surface layer (IrO_x/AlrO_{3- δ}) as documented in previous studies.^{15, 19} STEM images and corresponding STEM-EDS analysis (Figure 6-3c and 6-5) verified the distribution of Ba and Ir atoms in 9R-BaIrO₃, confirming the surface Ir-rich structure. TEM and SEM images presented in Figure 6-6 and 6-7 illustrated varying particle sizes and morphologies, which were influenced by

differing amounts of citric acid used during synthesis. Notably, increased citric acid concentration resulted in a smaller catalyst particle size, connected with the higher A-site solubility found in the 3C and 9R samples, suggesting a relationship between the crystal structure's characteristics and reduced particle size.³⁴

Table 6-2. Atomic concentration of 9R-BaIrO₃, 6H-SrIrO₃, BCC-SrIrO₃ and 3C-SrIrO₃ according to XPS result.

Sample	C 1s	O 1s	Cl 2p	Sr 3d	Ba 3d5	Ir 4f
9R-BaIrO ₃	22.59	53.47	7.44	0.00	0.69	15.82
BCC-SrIrO ₃	9.65	60.63	2.70	10.91	0.00	16.11
3C-SrIrO ₃	19.20	56.16	6.96	2.43	0.00	15.25
6H-SrIrO ₃	7.33	59.05	2.27	14.26	0.00	17.10
IrO ₂	11.33	66.10	0.00	0.00	0.00	22.56

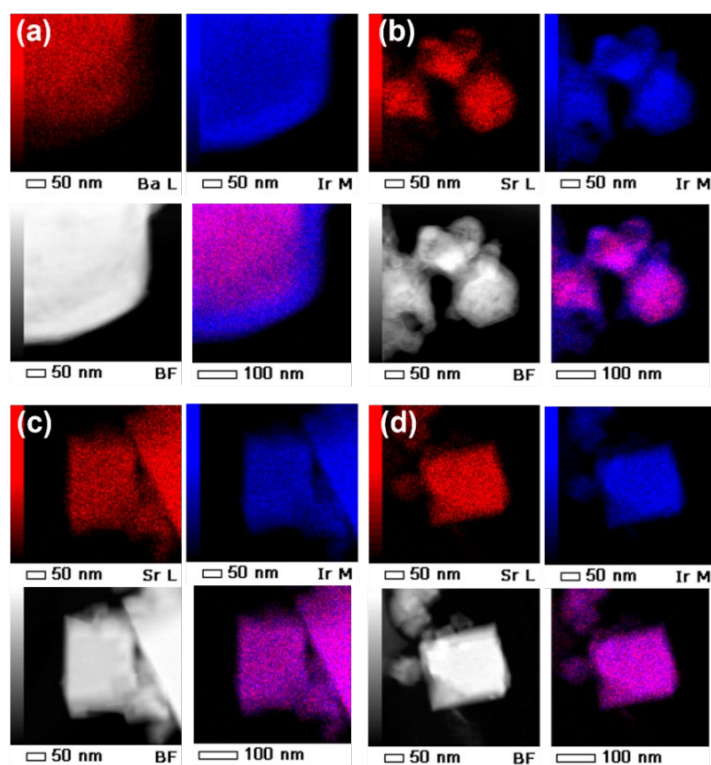


Figure 6-5. (c) STEM and EDX analysis of (a) 9R-BaIrO₃, (b) 3C-SrIrO₃, (c) 6H-SrIrO₃, and (d) BCC-SrIrO₃.

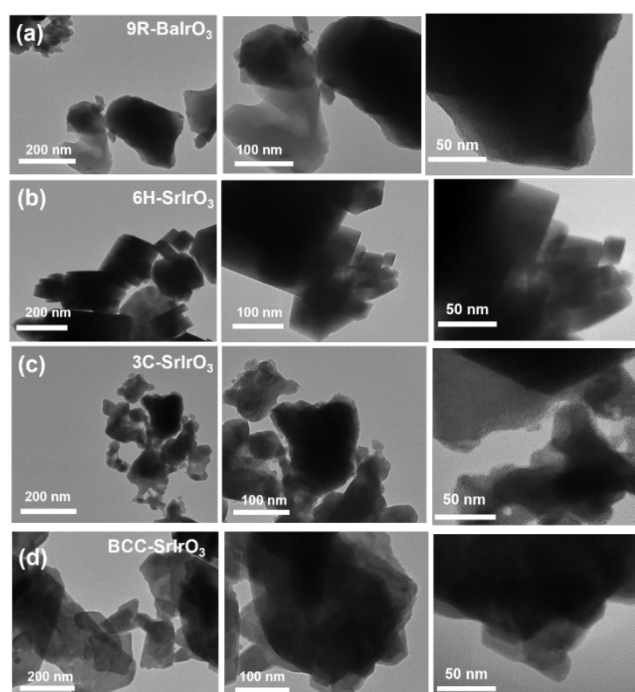


Figure 6-6. (c) TEM images of (a) 9R-BaIrO₃, (b) 6H-SrIrO₃, (c) 3C-SrIrO₃ and (d) BCC-SrIrO₃.

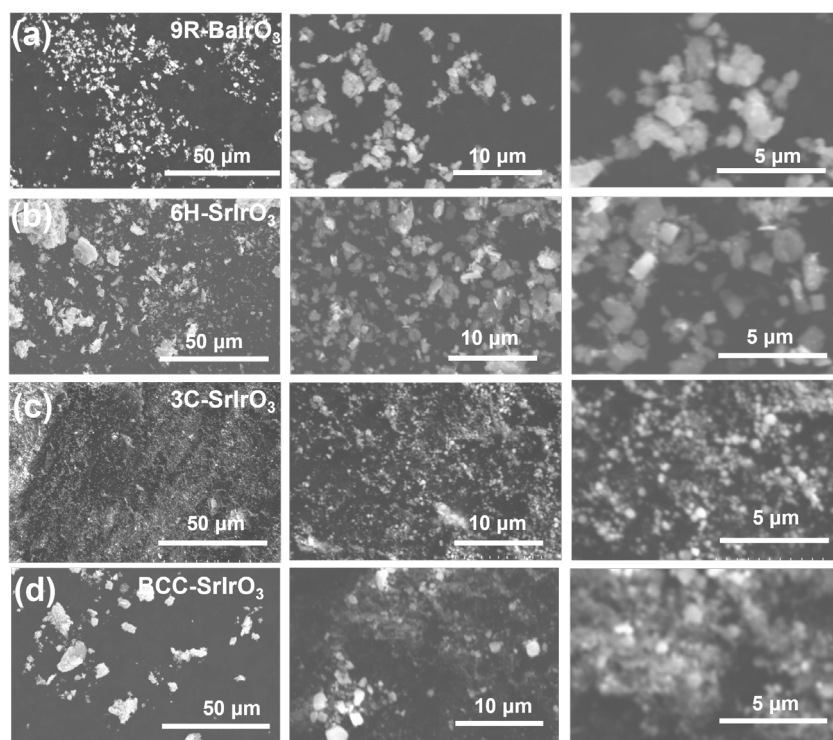


Figure 6-7. (c) SEM images of (a) 9R-BaIrO₃, (b) 6H-SrIrO₃, (c) 3C-SrIrO₃ and (d) BCC-SrIrO₃.

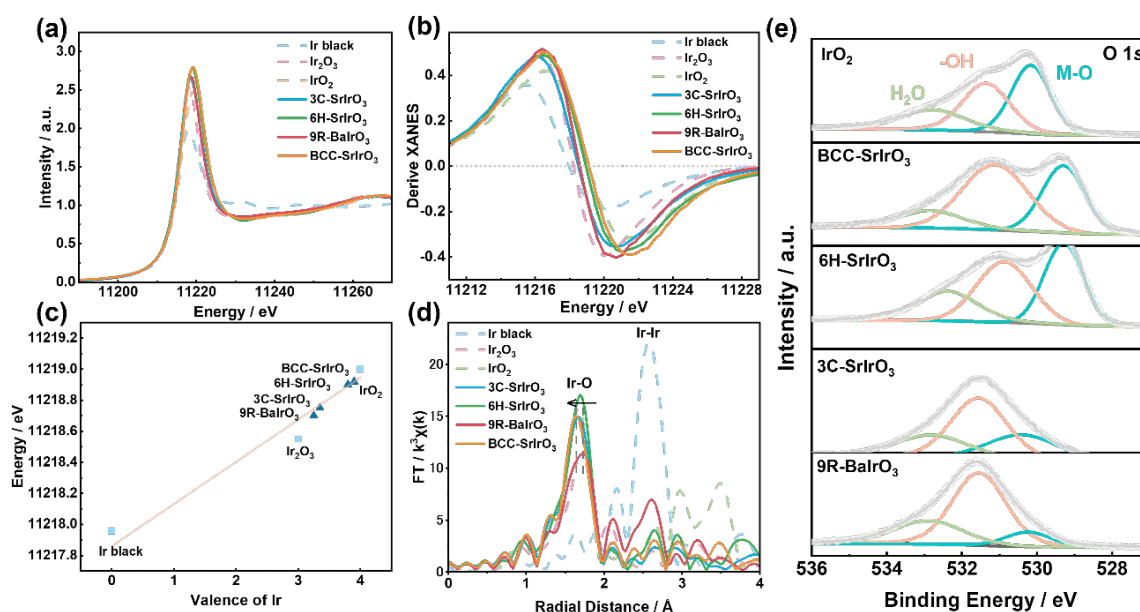


Figure 6-8. (a) Ir L₃-edge XANES spectra, (b) the first derivatives of XANES spectra, (c) the valence states of Ir from XANES spectra, (d) Fourier transform of the Ir L₃-edge EXAFS spectra of 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, BCC-SrIrO₃, Ir black, Ir₂O₃ and IrO₂. (e) O 1s XPS spectra of 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, BCC-SrIrO₃ and IrO₂.

The electronic structure of iridium and its coordination environment were explored using XAS measurement. Ir L₃-edge XANES analysis, as depicted in Figure 6-8a and b, demonstrated a shift of the white line towards lower energy levels relative to traditional rutile-type IrO₂, suggesting that the iridium in the catalysts resides predominantly between the +3 and +4 oxidation states. The observed shift in the white line indicates significant structural changes at the crystal surface, driven by the dissolution of A-site metals and the activation of lattice oxygen, leading to the formation of an amorphous layer and oxygen vacancies.^{14, 35} Subsequently, Iridium transitions into a low-coordination, amorphous Ir^{3+δ} compound, leading to a disordered octahedral network that forms the active sites crucial for OER.^{36, 37} Catalysts such as 9R-BaIrO₃, which have higher A-site solubility, exhibit higher oxygen vacancies and, consequently, lower oxidation states. The FT-EXAFS analysis results, depicted in Figure 6-8d and detailed in Table 6-3, elucidate the coordination number and Ir-O bond lengths, revealing the relationship between these parameters and the crystal structure. Monoclinic 9R-BaIrO₃ exhibits a lower Ir-O coordination number (CN=4.5) compared to rutile IrO₂ (CN=6.0), suggesting that Ba dissolution enhances oxygen vacancy formation and the generation of active IrO_x surface. The formation of Ba-deficient unsaturated IrO_x show an extended Ir-O bond length (~2.05 Å) and surface-active Ir bonding (~2.70 Å).¹⁷ The 3C-SrIrO₃ sample exhibits an Ir-O coordination number of 5.5 with a bond length of 2.0 Å, suggesting the presence of small number of oxygen vacancies than BaIrO₃ alongside a nearly complete Ir-O octahedral structure on the catalyst surface.¹⁹ For BCC-SrIrO₃ and 6H-SrIrO₃, which exhibited minimal surface Sr dissolution, the coordination numbers consistently maintained around 6.0, resulting in fewer surface active sites. To demonstrate the influence of crystal structure on surface IrO_x, wavelet transform analysis of the EXAFS spectra (Figure 6-9) characterizes the coordination in 6H and 9R monoclinic-structured catalysts, revealing longer Ir-O bonds and pronounced Ir-Ir interactions. In contrast, catalysts with higher structural symmetry, such as 3C and BCC, exhibit shorter Ir-O bonds and weaker Ir-Ir coordination. This difference is attributed to the face-shared [IrO₆] octahedra in monoclinic structures, which have shorter Ir-Ir bond length.³⁸

Table 6-3. The corresponding R space curve fitting results of Ir L₃-edge for the catalysts.

Sample	Shell	CN	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R factor
9R-BaIrO ₃	Ir-O	4.5(5)	2.05(3)	0.004	14.7	0.019
	Ir-Ir	1.3(9)	2.70(2)	0.003	10.2	
BCC-SrIrO ₃	Ir-O	6.2(4)	1.99(4)	0.005	25.6	0.072
3C-SrIrO ₃	Ir-O	5.5(4)	2.00(6)	0.004	17.8	0.0057
6H-SrIrO ₃	Ir-O	6.0(2)	2.02(2)	0.003	15.2	0.0079

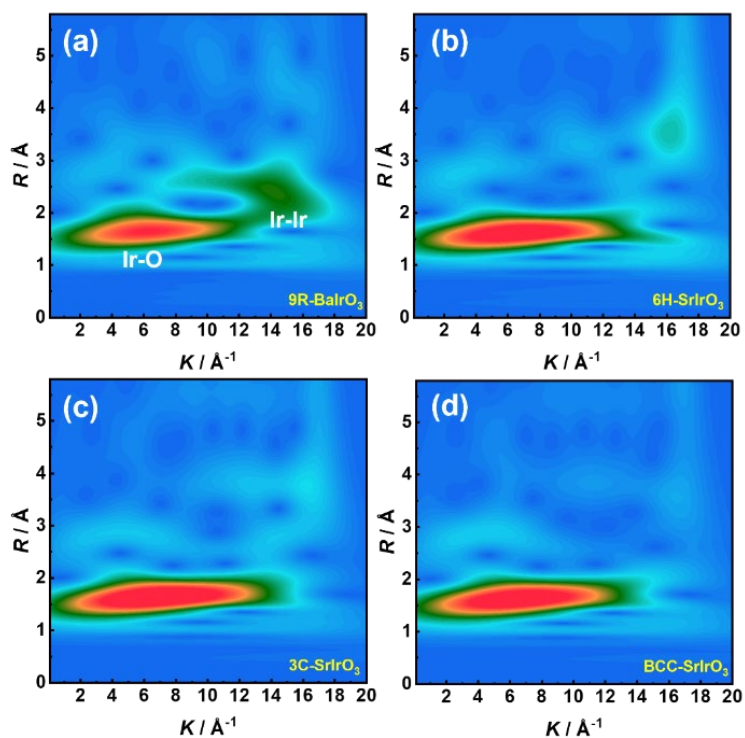


Figure 6-9. Wavelet transforms of EXAFS for (a) 9R-BaIrO₃, (b) 6H-SrIrO₃, (c) 3C-SrIrO₃ and (d) BCC-SrIrO₃.

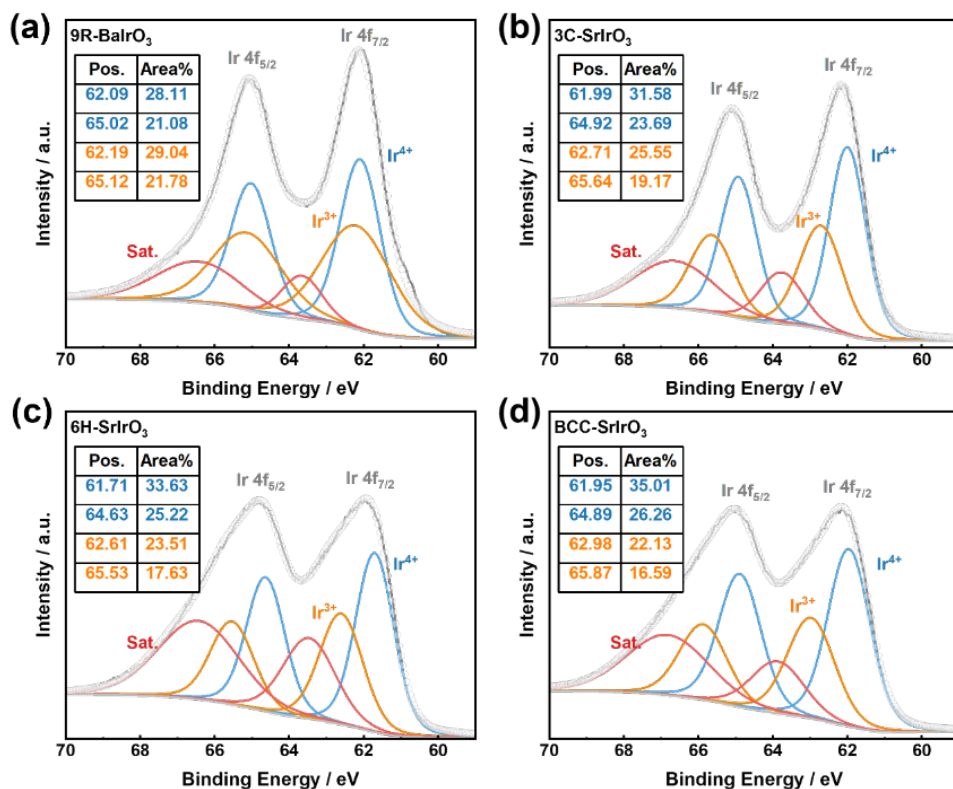


Figure 6-10. Ir 4f XPS spectra of 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃ and BCC-SrIrO₃.

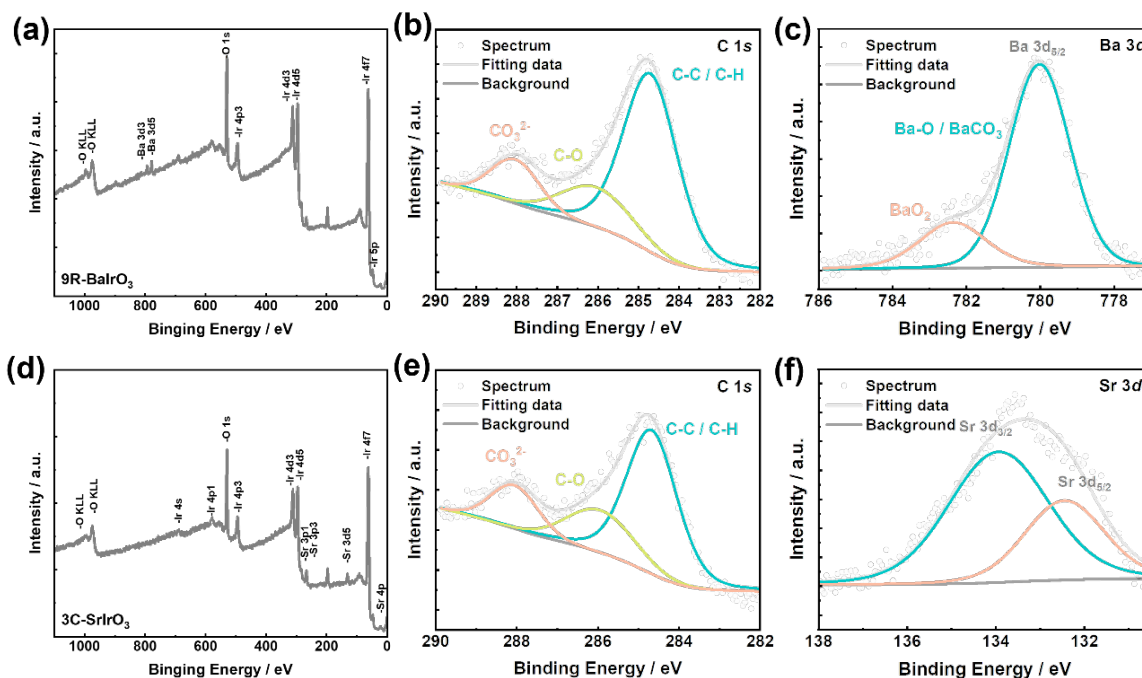


Figure 6-11. (a) XPS total spectra of 9R-BaIrO₃. XPS spectra of (b) C 1s and (c) Ba 3d. (d) XPS total spectra of 3C-SrIrO₃. XPS spectra of (b) C 1s and (c) Sr 3d.

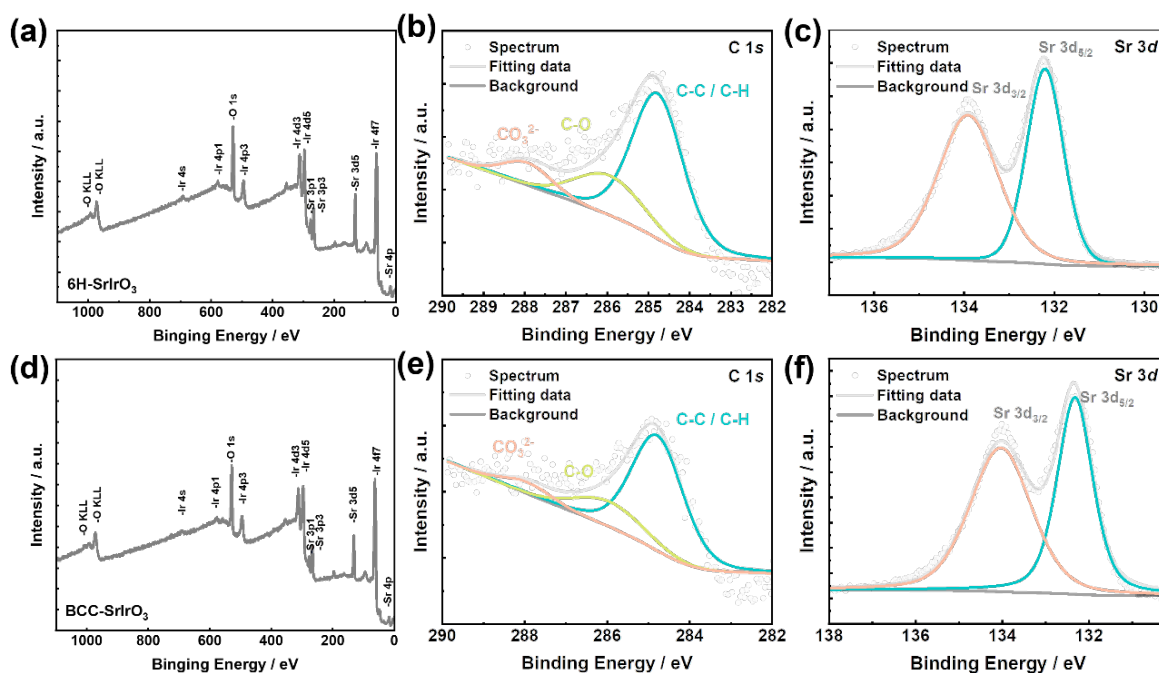


Figure 6-12. (a) XPS total spectra of 6H-SrIrO₃. XPS spectra of (b) C 1s and (c) Sr 3d. (d) XPS total spectra of BCC-SrIrO₃. XPS spectra of (b) C 1s and (c) Sr 3d.

To understand the electronic structure of the catalyst surface, X-ray photoelectron spectroscopy (XPS) was performed (Figure 6-10 to 6-12). As shown in Figure 6-10, the Ir4f spectrum can be deconvoluted into two sets of double peaks centered around 61.9/64.9 eV and 62.7/65.6 eV, corresponding to Ir⁴⁺ and Ir³⁺, respectively. This indicates that the chemical state of Ir species on the catalyst surface is between +3 and +4.^{39, 40} Additionally, 9R-BaIrO₃ and 3C-SrIrO₃ exhibit higher intensity of Ir³⁺ peaks, indicating that their surface oxidation states are lower than those of 6H and BCC catalysts, which is consistent with the XAS results. Furthermore, as shown in Figure 6-8e, the O 1s spectrum of all samples displayed three prominent peaks located at 529.6 eV, 531.2 eV, and 532.8 eV, representing lattice oxygen (O-Ir-O), hydroxyl groups (-OH), and adsorbed water (-H₂O), respectively.¹⁶ Further analysis revealed that in the 3C-SrIrO₃ and 9R-BaIrO₃ samples, the degree of surface hydroxylation increased due to a significant exchange effect of Sr²⁺ or Ba²⁺ with H⁺, enhancing the surface's electrophilic properties. This increased concentration of surface hydroxyl groups aids in accelerating electron transfer efficiency during the OER process.⁴¹

6.3.2 OER performance

The electrocatalytic OER performance of all $\text{IrO}_x/\text{AlrO}_{3-\delta}$ samples with different crystal structures was evaluated in 0.1 M HClO_4 and compared with rutile IrO_2 catalysts for reference. Cyclic voltammetry (CV) was recorded continuously for 50 cycles in the potential range of 0.1 to 1.2 V. Significant changes in the CV curves were observed for the 3C-SrIrO₃ and 9R-BaIrO₃ samples, indicating the formation of the active site on their surfaces (Figure 6-13).⁴² In contrast, the CV curves of the other samples did not show significant changes. By comparing the 100th CV cycle (Figure 6-14), differences in the redox properties of Ir in various samples were observed. Two oxidation peaks representing $\text{Ir}^{3+}/\text{Ir}^{4+}$ transitions were evident in all CV plots.^{18,43}

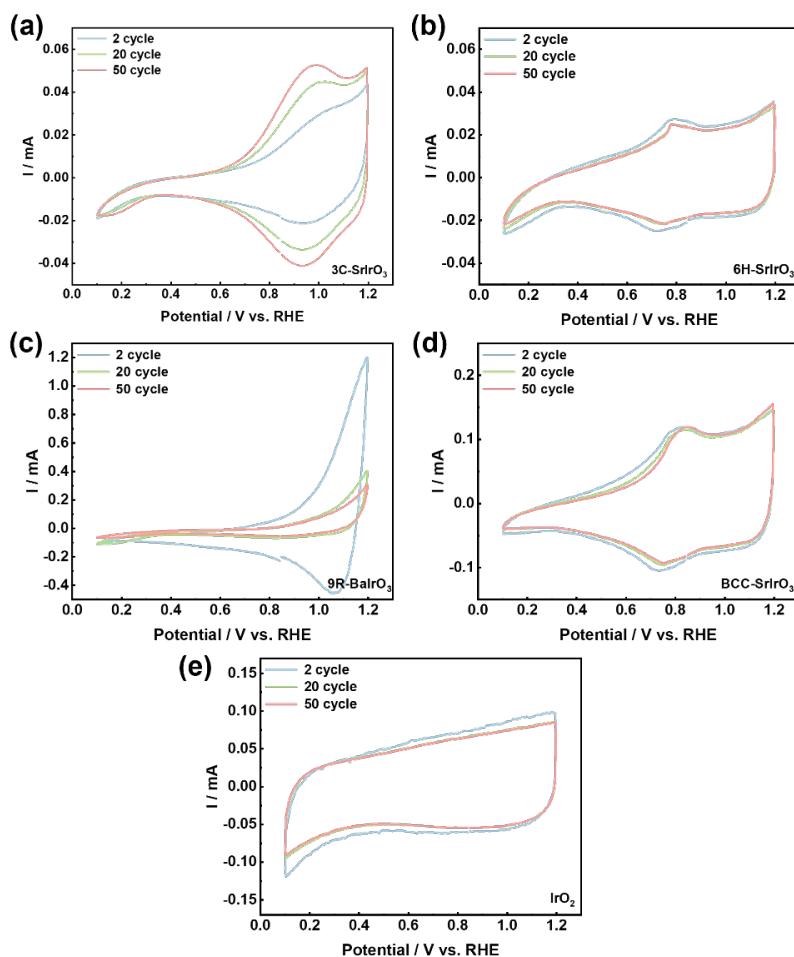


Figure 6-13. The CV recorded at the 2nd, 20th, and 50th cycles for (a) 3C-SrIrO₃, (b) 6H-SrIrO₃, (c) 9R-BaIrO₃, (d) BCC-SrIrO₃, (e) IrO₂.

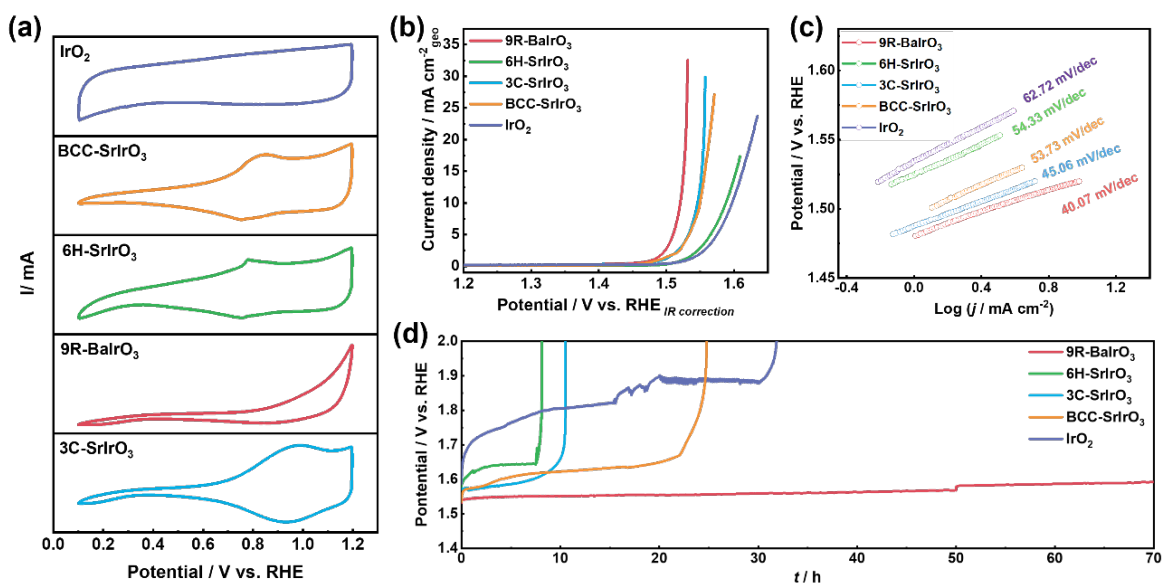


Figure 6-14. (a) CV curves, (b) polarization curves at a scan rate of 10 mV s^{-1} , (c) the corresponding Tafel plots and (d) chronopotentiometric measurements of 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, BCC-SrIrO₃ and IrO₂. All measurements were performed in 0.1 M HClO₄.

The OER polarization curve results in Figure 6-14b, and 6-15a showed that the 9R-BaIrO₃ catalyst exhibited the lowest overpotential ($\sim 290 \text{ mV vs. RHE}$ @ 10 mA cm^{-2}) at a current density of 10 mA m^{-2} while 6H-SrIrO₃ had the highest overpotential ($\sim 358 \text{ mV vs. RHE}$). Additionally, with a Tafel slope of $40.07 \text{ mV dec}^{-1}$, 9R-BaIrO₃ demonstrated superior OER activity compared to BCC-SrIrO₃ ($53.73 \text{ mV dec}^{-1}$), 3C-SrIrO₃ ($45.06 \text{ mV dec}^{-1}$), and 6H-SrIrO₃ ($54.33 \text{ mV dec}^{-1}$), reflecting its faster kinetics and electron transfer process (Figure 6-14c). Figure 6-15b compares the mass activities of various catalysts, expressed as current per unit mass of iridium (A g^{-1}) at an operating potential of 1.5 V vs. RHE . Notably, 9R-BaIrO₃ exhibits a mass activity of 35 A g^{-1} , which is six times higher than that of commercial IrO₂.

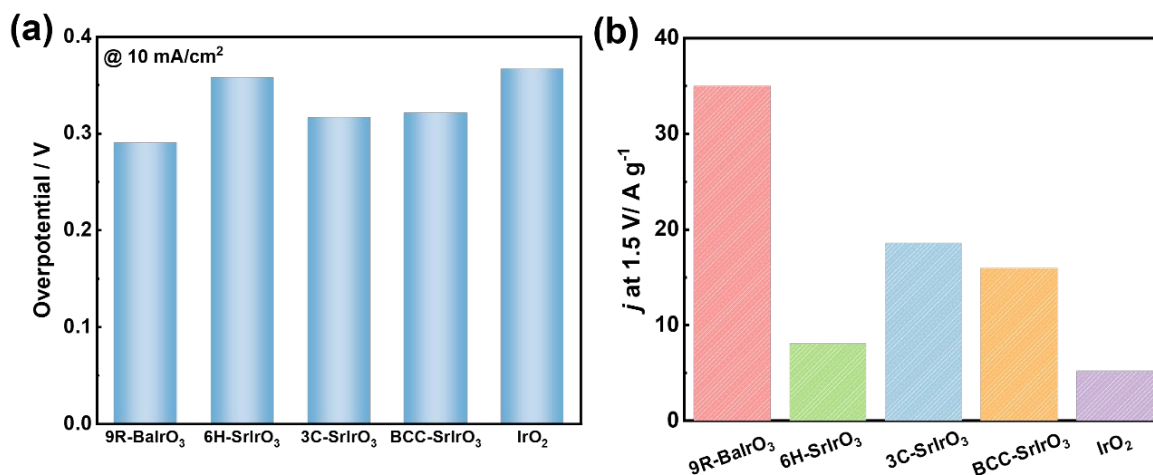


Figure 6-15. (a) Overpotential at 10 mA cm⁻² of 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃ and BCC-SrIrO₃. (b) Comparison of the Ir mass activity at 1.5 V vs. RHE for 9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃ and BCC-SrIrO₃.

The electrochemical stability of different samples was assessed through long-term stability tests conducted at a constant current density of 10 mA cm⁻² (Figure 6-14d). The 3C-SrIrO₃ and 6H-SrIrO₃ samples lost their electrochemical activity after 12 and 8 hours of continuous electrolysis, respectively. In contrast, BCC-SrIrO₃ demonstrated good stability for up to 23 hours of continuous operation, and 9R-BaIrO₃ sustained electrolysis for 70 hours without significant potential change. Additionally, the degradation of OER activity was evaluated after 30, 300, and 3000 CV cycles, revealing that the 9R-BaIrO₃ catalyst exhibited exceptional electrochemical stability, with its overpotential increasing by only 50 mV vs. RHE (Figure 6-16). This outstanding performance is attributed to its unique face-sharing trimer [IrO₆] octahedral structure in 9R-BaIrO₃. Similarly, the edge-sharing [IrO₆] octahedral three-dimensional body-centered cubic structure in BCC-SrIrO₃ ensures that the [IrO₆] octahedra are structurally interconnected, enhancing the catalyst's structural stability.

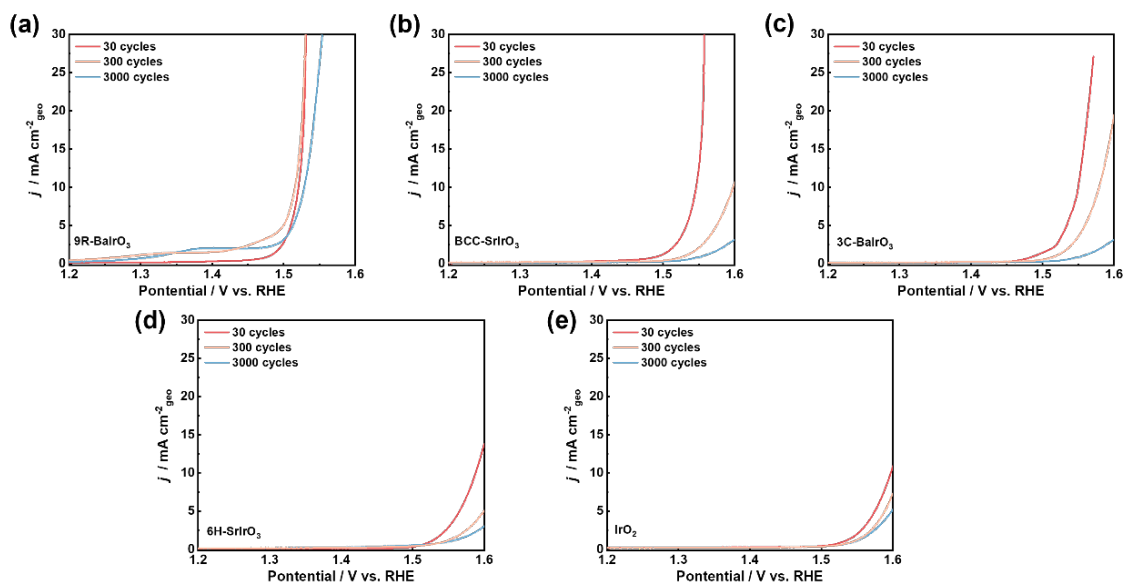


Figure 6-16. The LSV curves recorded after the 30th, 300th, and 3000th cycles CV cycles for (a) 9R-BaIrO₃, (b) BCC-SrIrO₃, (c) 3C-SrIrO₃, (d) 6H-SrIrO₃ and (e) IrO₂.

6.3.3 Operando Ir L₃-edge XAS analysis

Operando Ir L₃-edge XANES analysis was performed on the 3C-SrIrO₃ and 9R-BaIrO₃ catalysts to explore potential mechanisms occurring during their OER processes (Figure 6-17). Experimentally, only the 9R-BaIrO₃ sample, with lower Ir-O coordination, showed a slight shift of the Ir L₃-edge white line towards higher energy regions, while the 3C-SrIrO₃ sample did not exhibit any change. This observation does not fully align with the previously anticipated valence transition from Ir³⁺ to Ir⁴⁺ at high potential.^{25, 44} To further investigate the reaction behaviors of these two catalysts, high-energy-resolution fluorescence-detected XAS (HERFD-XAS) was employed, which can monochromatize fluorescence lines, enhancing the detection of excited core electron X-rays and providing detailed information about the electronic state of the Ir atom.⁴⁵

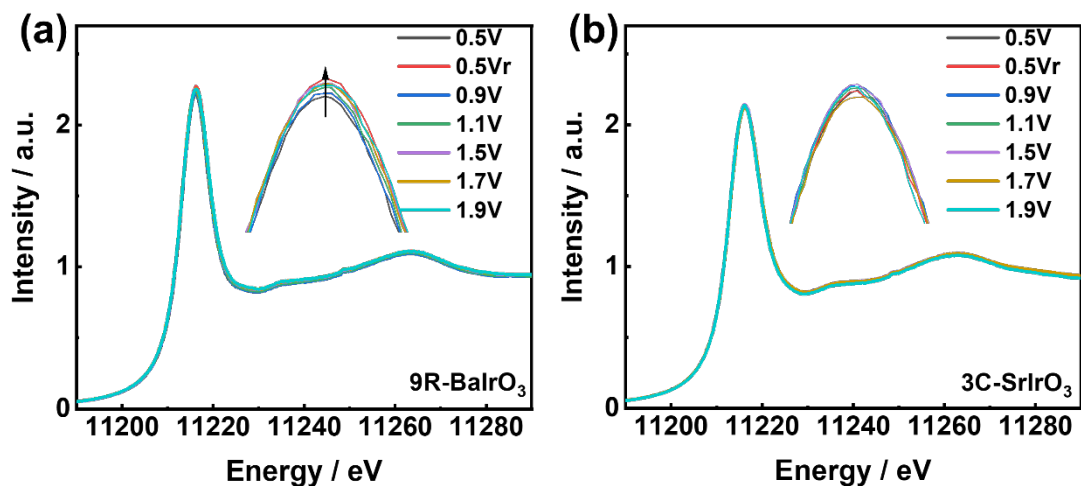


Figure 6-17. *operando* XANES spectra of Ir L_3 -edge for (a) 9R-BaIrO₃ and (b) 3C-SrIrO₃.

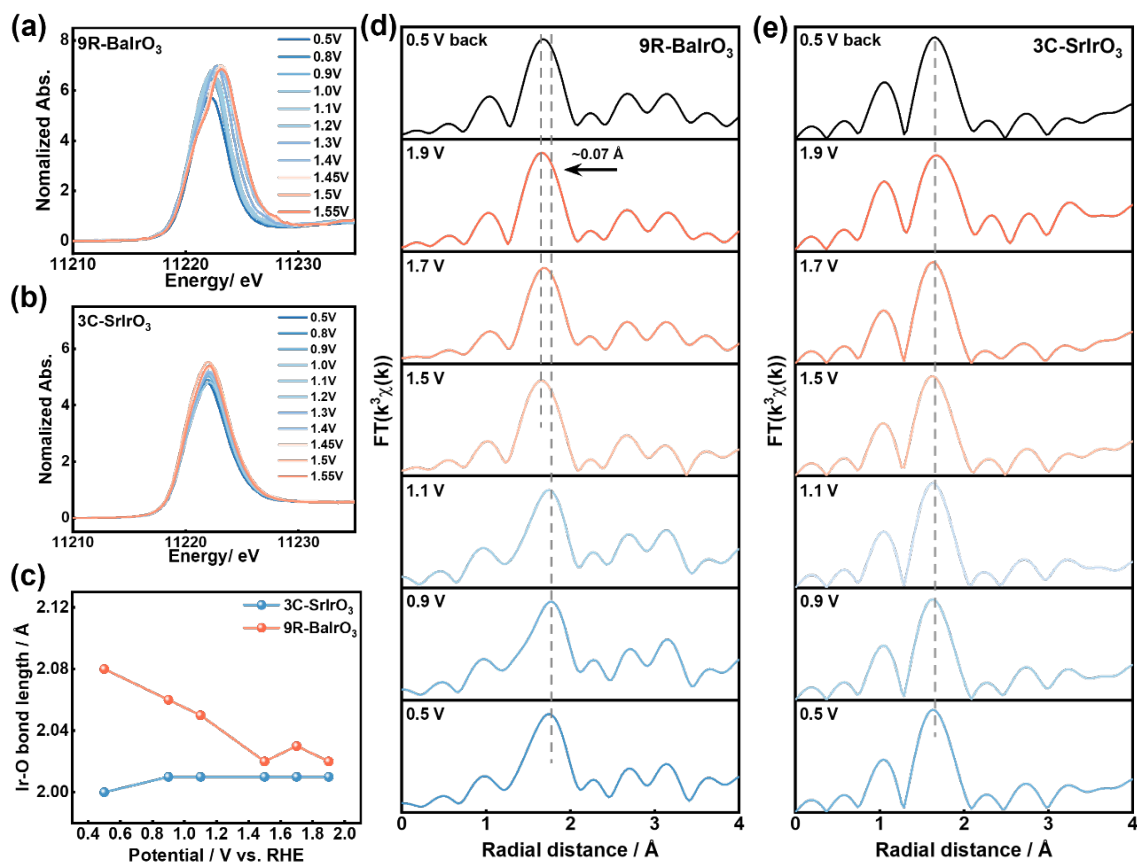


Figure 6-18. *operando* HERFD- Ir L_3 -edge XANES spectra of (a) 9R-BaIrO₃ and (b) 3C-SrIrO₃. (c) The change of Ir-O bond length with the potential for 9R-BaIrO₃ and 3C-SrIrO₃. Corresponding Fourier transform EXAFS spectra of (d) 3C-SrIrO₃ and (e) 9R-BaIrO₃.

Figure 6-18a and b display the changes in the Ir L₃-edge XANES white lines for the two catalysts at different potentials. The $\Delta\mu$ spectra quantify the differences resulting from potential changes (Figure 6-19), indicating variations in oxidation states between the catalysts. The spectral changes in the 9R-BaIrO₃ sample are more pronounced compared to 3C-SrIrO₃, which is related to the lower initial Ir-O coordination in 9R-BaIrO₃. Additionally, *operando* FT-EXAFS analysis (Figure 6-18d and e) shows a significant negative shift in the Ir-O signal for the 9R-BaIrO₃ catalyst with increasing potential, indicating changes in the local bonding environment of Ir. In contrast, the Ir-O coordination peak for 3C-SrIrO₃ remains consistent across different potentials. Fitting results in Figure 6-18c, 6-20, 6-21, Table 6-4, and 6-5 indicate that the Ir-O bond length in 9R-BaIrO₃ decreases from 2.08 Å to 2.03 Å as the potential increases to 1.9 V *vs.* RHE, while the bond length in 3C-SrIrO₃ remains unchanged.

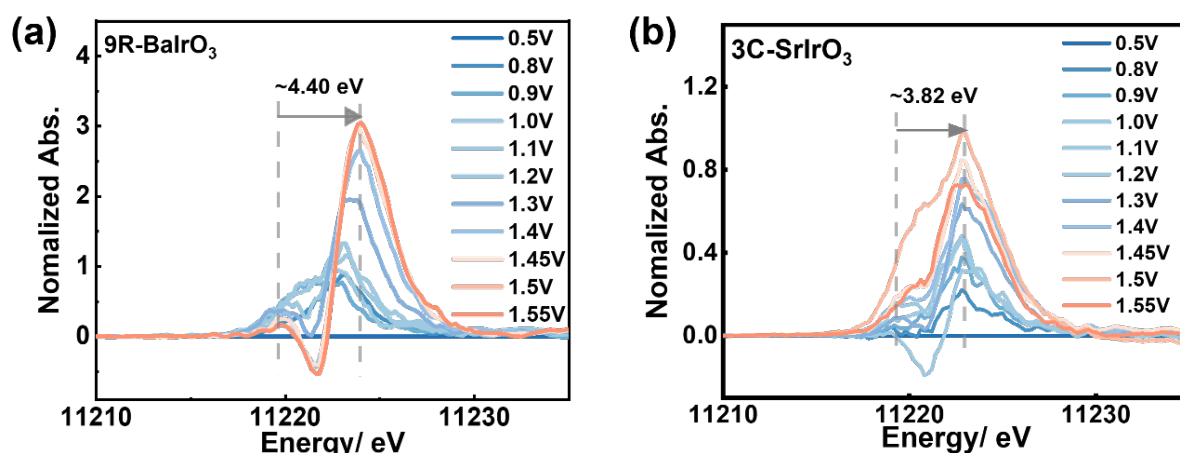


Figure 6-19. $\Delta\mu$ XANES spectra for the catalysts calculated by $\mu p(E) - \mu 0.5V$ according to **Figure 6-18**. $\Delta\mu$ XANES spectra of (a) 9R-BaIrO₃ and (b) 3C-SrIrO₃.

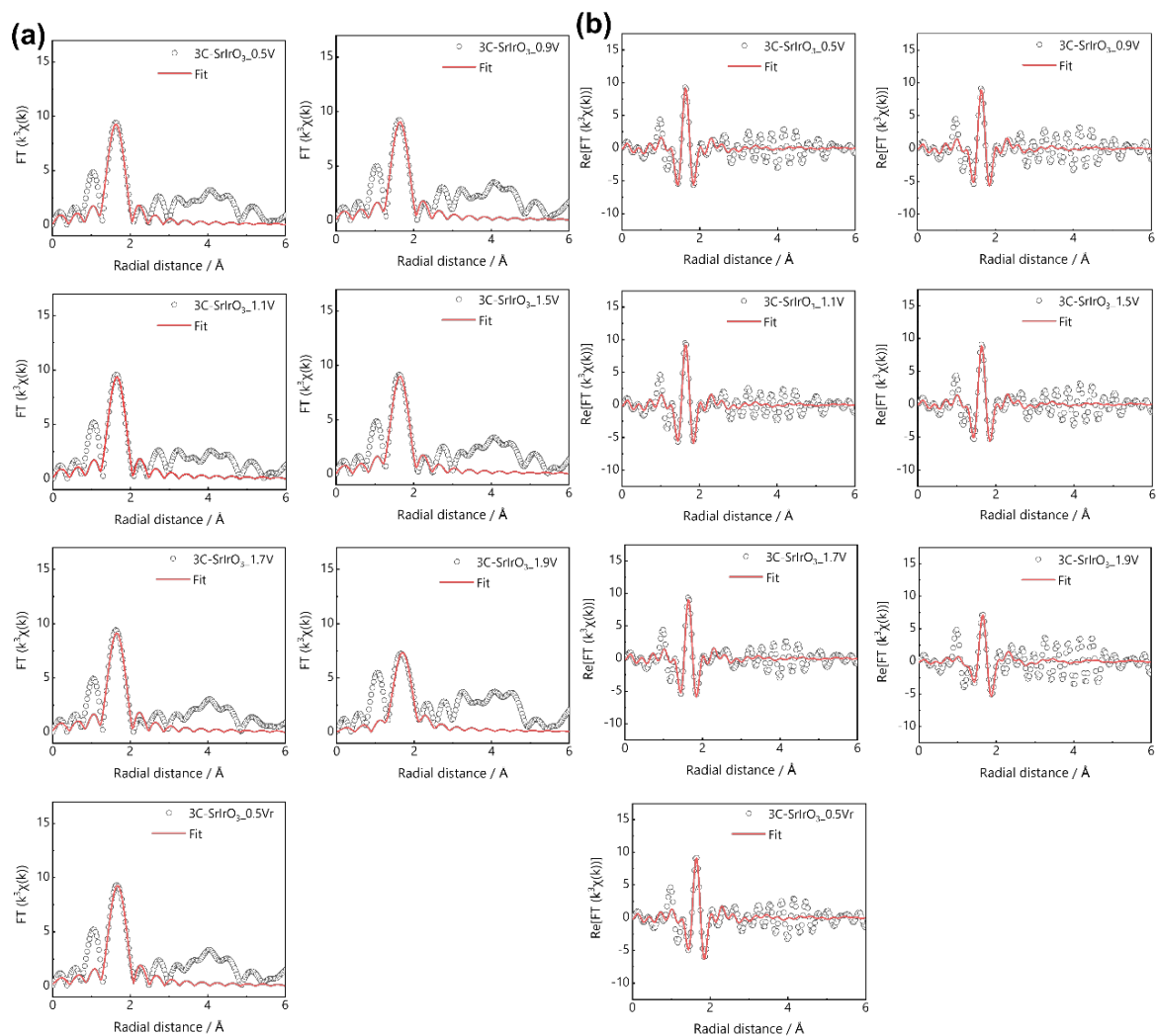


Figure 6-20. Fourier transformed k^3 -weighted Ir L_3 -edge EXAFS spectra of 3C-SrIrO₃ at different potentials. Gray line is the FT-EXAFS spectrum and red line is the fitted spectrum.

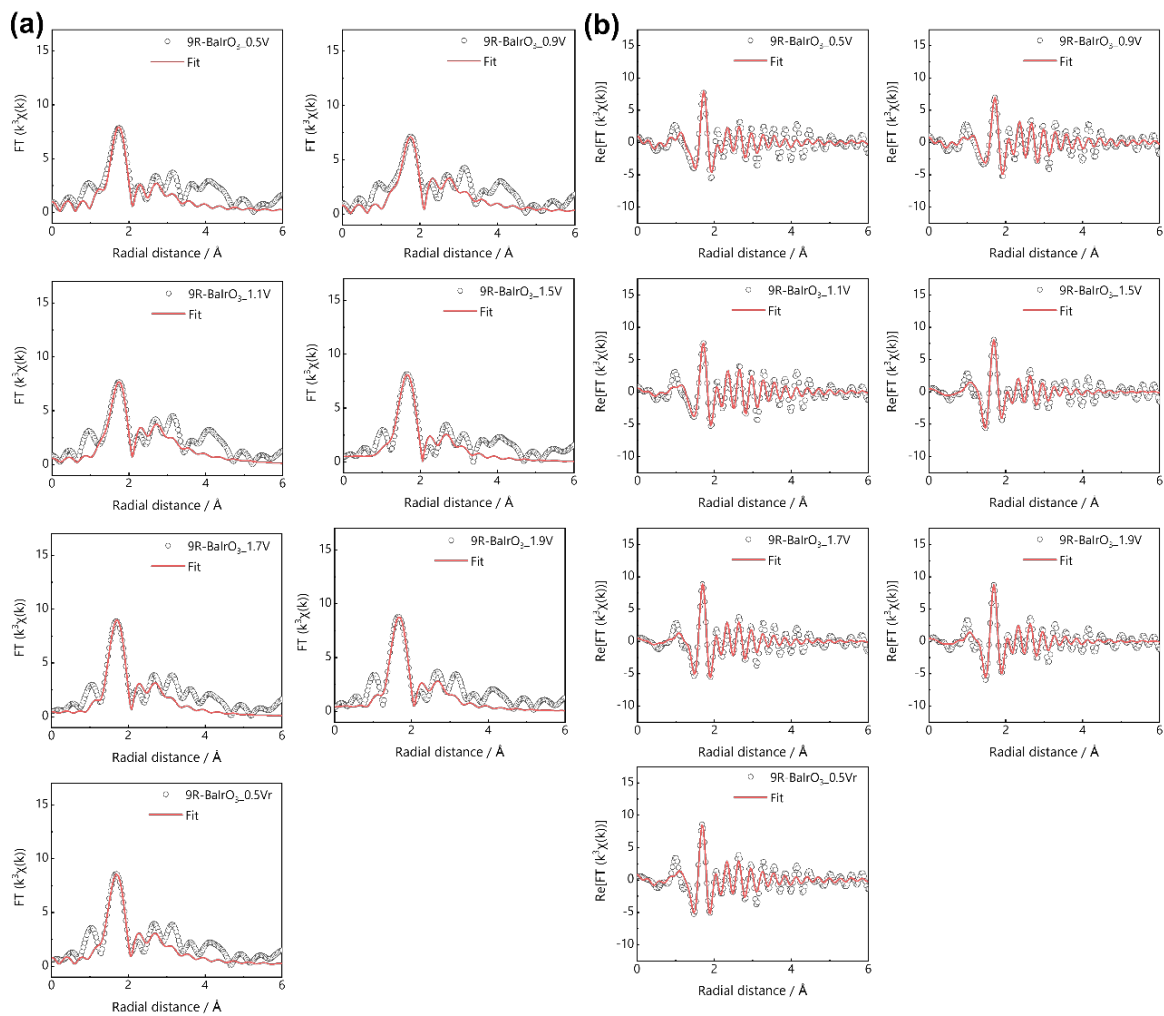


Figure 6-21. Fourier transformed k^3 -weighted Ir L_3 -edge EXAFS spectra of 9R-BaIrO₃ at different potentials. Gray line is the FT-EXAFS spectrum and red line is the fitted spectrum.

Table 6-4. The corresponding R space curve fitting results of Ir L₃-edge for the 3C-SrIrO₃ catalysts varying different potential.

Sample	Shell	CN	R (Å)	$\sigma^2(\text{Å}^2)$	ΔE_0 (eV)	R factor
0.5V	Ir-O	5.6(7)	2.00(4)	0.002	13.9	0.0103
0.5Vr	Ir-O	5.4(4)	2.02(5)	0.002	16.7	0.0105
0.9V	Ir-O	5.6(4)	2.01(4)	0.002	14.9	0.0064
1.1V	Ir-O	5.5(2)	2.01(6)	0.002	14.7	0.0051
1.5V	Ir-O	5.8(6)	2.01(8)	0.003	15.0	0.0099
1.7V	Ir-O	5.4(8)	2.01(3)	0.002	15.2	0.0058
1.9V	Ir-O	5.6(7)	2.01(3)	0.005	18.6	0.0352

Table 6-5. The corresponding R space curve fitting results of Ir L₃-edge for the 9R-BaIrO₃ catalysts varying different potential.

Sample	Shell	CN	R (Å)	$\sigma^2(\text{Å}^2)$	ΔE_0 (eV)	R factor
0.5V	Ir-O	4.5(5)	2.08(7)	0.006	12.54	0.0969
	Ir-Ir	0.5(9)	2.74(2)	0.013	18.06	
0.5Vr	Ir-O	3.7(6)	2.03(7)	0.003	9.93	0.0276

0.9V	Ir-Ir	0.5(8)	2.73(9)	0.013	16.09	0.0757
	Ir-O	3.9(5)	2.06(1)	0.006	12.88	
1.1V	Ir-Ir	0.4(5)	2.74(10)	0.014	11.67	0.0308
	Ir-O	4.0(10)	2.05(5)	0.005	11.60	
1.5V	Ir-Ir	0.3(2)	2.74(4)	0.015	15.72	0.0311
	Ir-O	4.3(6)	2.02(9)	0.005	8.01	
1.7V	Ir-Ir	0.3(9)	2.73(8)	0.009	16.08	0.0347
	Ir-O	3.6(5)	2.04(6)	0.002	11.43	
1.9V	Ir-Ir	0.2(8)	2.73(3)	0.009	15.10	0.0262
	Ir-O	3.7(9)	2.03(7)	0.003	9.94	
	Ir-Ir	0.2(2)	2.74(3)	0.007	17.21	

Typically, further oxidation of Ir leads to shorter Ir-O bonds,²³ but some studies also suggest that during OER, the average bond length in metal oxides is influenced by coordination with lattice oxygen (O^{2-}) and adsorbed OH^- species (M-OH). Since O^{2-} carries more negative charge than OH^- , M-OH bond lengths are relatively longer, increasing the average M-O bond length.⁴⁶ In the highly symmetric 3C-SrIrO₃, the corner-sharing [IrO₆] octahedra are periodically connected, making changes in Ir-O distances difficult during oxidation and influenced by adsorbed OH species, resulting in negligible bond length changes.⁴⁷ The asymmetric, face-sharing [IrO₆] octahedra in 9R-BaIrO₃ are more disordered and prone to

distortion, with weaker interactions, leading to more significant Ir-O bond shortening. Notably, even when the potential returns to 0.5 V vs. RHE, this oxidation state remains stable, indicating that the oxidation and structural changes in Ir are not easily reversible.

The oxidation state transition is closely linked to the activity of iridium-based catalysts during OER.⁴⁸ In 9R-BaIrO₃, Ir species undergo greater oxidation state changes and significant Ir-O bond shortening during OER, making the Ir species more electrophilic and promoting hydroxyl oxidation and proton release.⁴⁹ The resulting oxygen species with shortened Ir-O distances in the [IrO₆] octahedra can act as electrophilic centers for water molecule attacks, facilitating O-O bond formation in the OER and effectively promoting the rapid water oxidation process.^{25, 50} In contrast, 3C-SrIrO₃ exhibits a more rigid structure similar to rutile IrO₂, making Ir oxidation much more difficult and hindering the water oxidation kinetics on its less electrophilic Ir species.²³

6.3.4 *Operando* O K-edge XAS analysis

It is important to note that Ir L₃-edge XAS, while sensitive to bulk properties, reflects the combined characteristics of the electrocatalyst's surface and bulk material.⁵¹ However, given that OER primarily occur at the catalyst surface, changes in oxidation state and coordination number at surface-active sites are likely more pronounced than those detected by *operando* Ir L₃-edge XAS, suggesting that surface changes may exceed the scope of this measurement technique.⁵²

FT-EXAFS result already reveals that distorted [IrO₆] octahedra in these oxides lead to variable Ir-O bond lengths, diverging from the uniformity seen in regular [IrO₆] structures.^{33, 53} Such distortions facilitate electron delocalization near the Fermi level, improving conductivity and reducing the energy barrier for oxygen binding, which in turn diversifies oxygen binding modes.¹¹ At elevated OER potentials, these changes promote the formation of electron-deficient oxygen species (O^{I-}), considered crucial intermediates or promoters in the OER pathway.^{54, 55} Therefore, capturing the binding states of oxygen species in different [IrO₆] octahedra is crucial.

To better understand the evolution of catalytic activity, TEY mode *operando* O K-edge XAS measurements were conducted within a custom-built electrochemical cell, effectively capturing intermediates in the catalytic process. The consistency of CV curves, as shown in Figure 6-22 and obtained via the *operando* setup with a RDE, confirmed the accuracy of OER potentials and the reliability of current-potential relationships. Detailed analysis of *operando* O K-edge XAS spectra recorded during OER, focusing on the white line resonance between 528-531 eV, elucidated the characteristics of adjacent oxygen (hydrogen) species on the catalytic surface.^{56, 57}

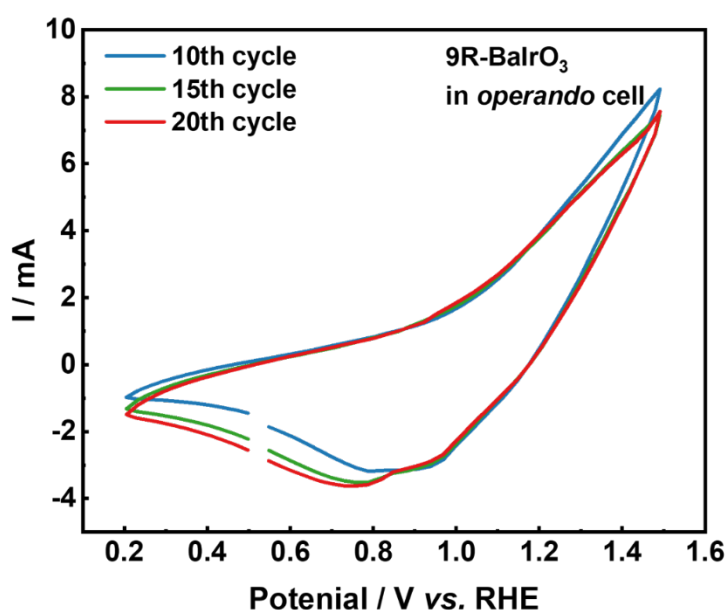


Figure 6-22. CV of 9R-BaIrO₃ in *operando* O K-edge cell.

To categorize oxygen species, this study uses the established μ notation.²⁶ Specifically, μ_1 -O at around 528.5 eV indicates oxygen at coordination unsaturated sites (CUS), μ_2 -O at 529.5 eV signifies bridging oxygen, and μ_3 -O at approximately 531.0 eV typically corresponds to bulk oxygen, which may also surface (Figure 6-23). Hydroxyl groups (OH) at these sites, labeled as μ_1 -OH and μ_2 -OH, are situated around 530.0 eV and 530.5 eV, respectively. Normally, the deprotonation of OH species results in hole transfer to oxygen by iridium defects, which depresses the white line's energy and enhances its intensity (μ -OH $\rightarrow$ μ -O + H⁺ + e⁻).⁵⁸ Consequently, the white line position of μ -O is lower compared to that of μ -OH. Among all oxygen binding site, the μ_1 and μ_2 types are of particular interest because their deprotonated

forms are electron-deficient and are prone to forming O-O bonds via a peroxo-mechanism.⁵⁹ Specifically, the electron deficiency on μ_1 -O makes it susceptible to nucleophilic attack, indicating that the high catalytic activity is closely related to the electron hole accumulation on μ_1 -O.^{60, 61}

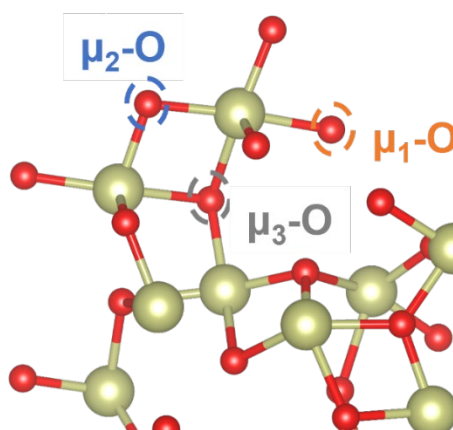


Figure 6-23. Schematic representation of the proposed μ_1 , μ_2 and μ_3 site.

The analysis of four catalysts in Figure 6-24 demonstrates that the active sites for oxygen species are intricately linked to their respective crystal structures. To enhance spectral clarity and differentiate peaks corresponding to various oxygen species, baseline subtraction was applied to the data, and a split-peak fitting technique was used for precise spectral analysis (Figure 6-25 and 6-26).⁵⁸ In catalysts with monoclinic structures like 6H and 9R, oxygen species predominantly bind at μ_1 sites, while in higher symmetry catalysts, such as those with tetragonal or cubic structures (3C and BCC), binding occurs mainly at μ_2 sites. Notably, μ_3 binding is observed across all catalysts. Some research on DFT calculations has shown that Ir atoms in face-shared octahedra exhibit better catalytic activity for OER than those in isolated corner-shared $[\text{IrO}_6]$ octahedra.¹⁷ Our results support this conclusion, as the Ir atoms in the face-shared octahedra trimers of 9R-BaIrO₃ provide more active μ_1 sites, resulting in higher catalytic activity.

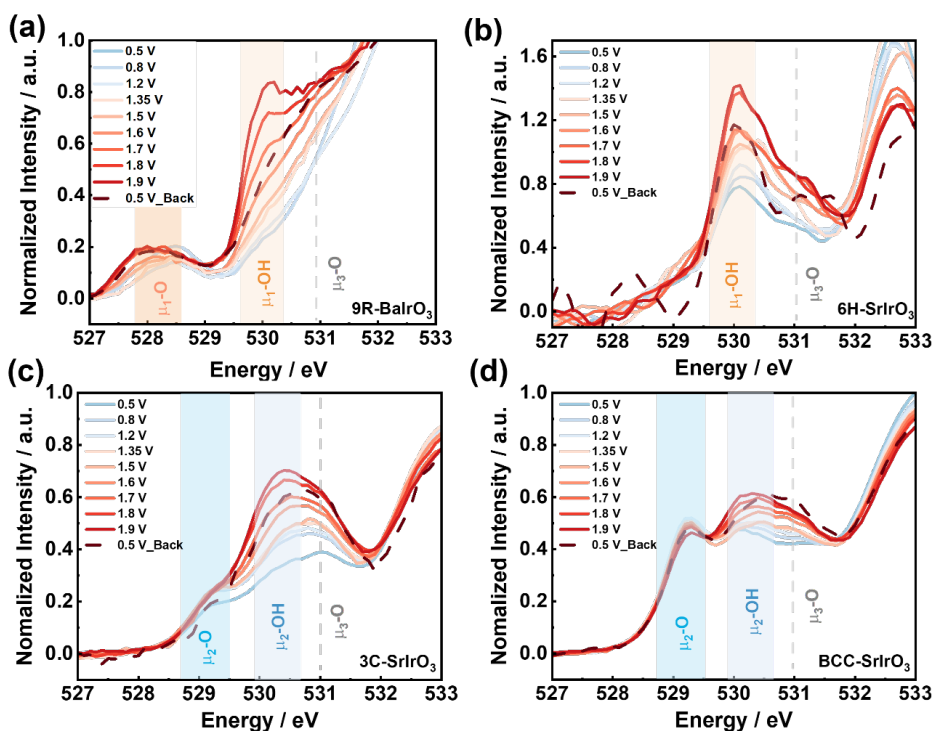


Figure 6-24. Operando O K-edge XAS spectra of (a) 9R-BaIrO₃, (b) 6H-SrIrO₃, (c) 3C-SrIrO₃ and (d) BCC-SrIrO₃. The spectra were recorded using the TEY detection mode.

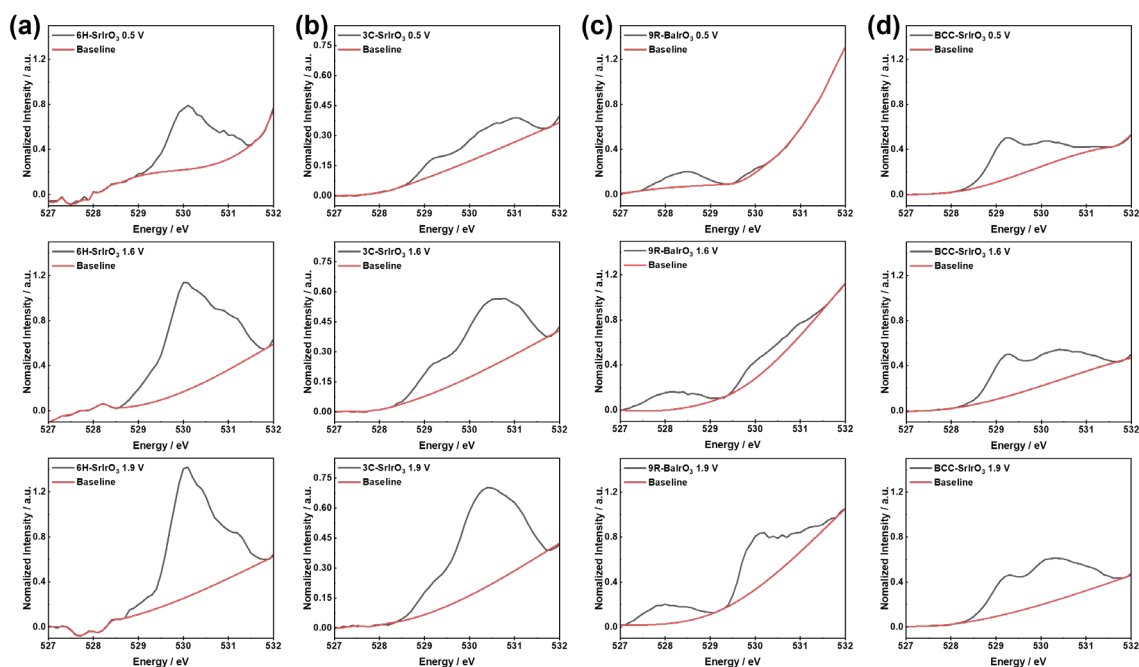


Figure 6-25. operando O K-edge spectra and corresponding baseline at different potentials for (a) 6H-SrIrO₃, (b) 3C-SrIrO₃, (c) 9R-BaIrO₃ and (d) BCC-SrIrO₃.

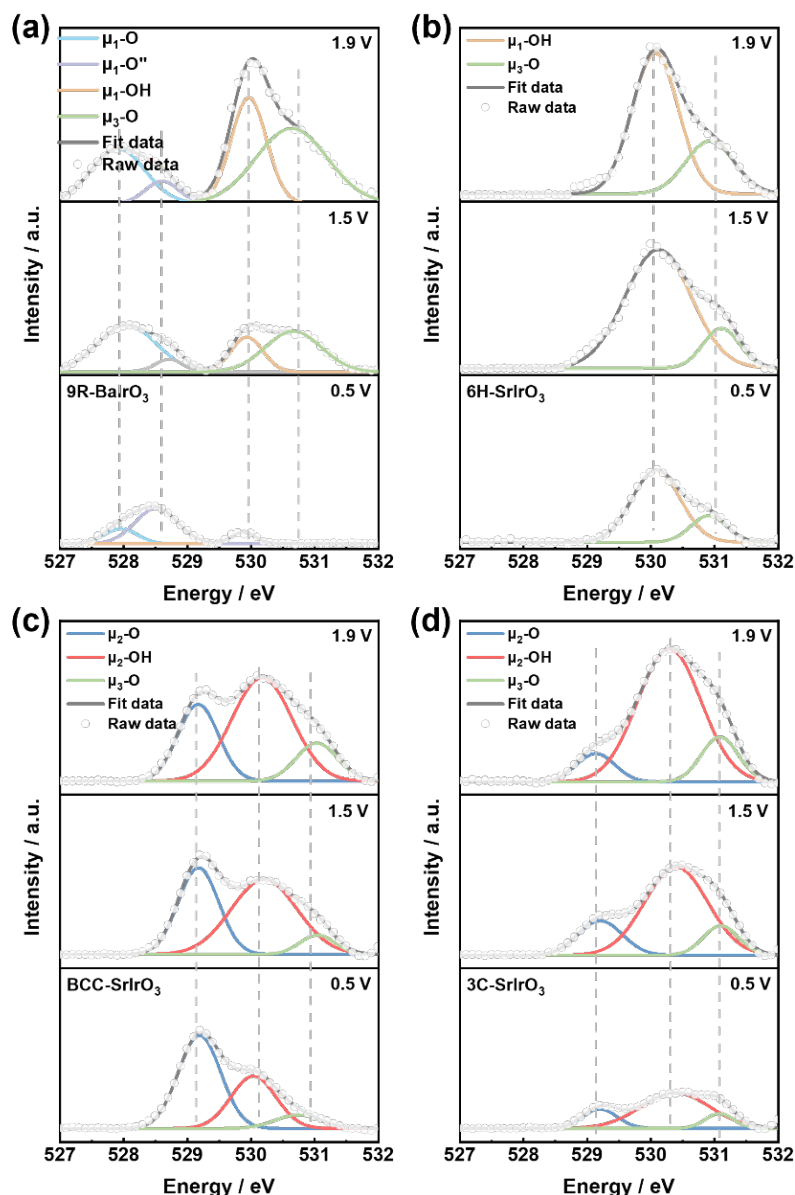


Figure 6-26. Peak fitting of (a) 9R-BaIrO₃, (b) 6H-SrIrO₃, (c) BCC-SrIrO₃ and (d) 3C-SrIrO₃ were performed to **Figure 6-25** after subtracting the baseline.

An increase in potential significantly boosts the peak intensity across all catalysts, indicating extensive hydroxylation and deprotonation at the surface. For 9R-BaIrO₃, this potential increase shifts the μ_1 -O signal to a lower energy range, suggesting structural changes in the oxide surface. This shift could be attributed to variations in the exposed crystal faces of the catalyst at elevated potentials, as theoretical studies on RuO_x single crystal faces ((110), (100), and (101)) during OER.⁶² Although 6H-SrIrO₃ provides more μ_1 sites and was expected to exhibit higher OER activity, it actually showed the lowest activity among all catalysts. This

is likely due to the consistent absence of its μ_1 -O peak, even at higher potentials. The dense electrophilic μ_1 -O groups near the active sites facilitate deprotonation of adjacent μ_1 -OH groups, significantly reducing the energy barrier for the rate-limiting O-O coupling step, thus enhancing OER activity.^{26, 63} Thus, the slow deprotonation process at the μ_1 site on the 6H-SrIrO₃ catalyst is a crucial factor for its lower activity. This difference may stem from the distinct dissolution mechanisms and crystal structures. In 9R-BaIrO₃, the robust face-shared [IrO₆] octahedra trimer are better preserved during Ba leaching compared to the weaker connections of octahedra in the 6H-SrIrO₃ structure, where [IrO₆] octahedra are more prone to dissolution during Sr leaching. As a result, no clear amorphous layer forms on the surface of 6H-SrIrO₃ during acidic OER, leading to the suppression of the deprotonation process.¹⁵

For catalysts like 3C-SrIrO₃ and BCC-SrIrO₃, where μ_2 -O/OH serves as the active site, an increase in potential also elevates the μ_2 -O/OH absorption peaks. Notably, the surface of 3C-SrIrO₃ shows further hydroxylation at high potential, evident from the peak around ~530.5 eV, which promotes the deprotonation process and enhances OER performance.

All catalysts exhibit inert μ_3 -O species around 531.0 eV, aligning with studies showing that rutile IrO₂ predominantly contains these oxygen species.⁶⁴ *Operando* O K-edge analysis of rutile IrO₂ reveals minimal fluctuation in the μ_3 -O peak near 531.1 eV (Figure 6-27), underscoring its negligible role in the OER process due to its stability and inactivity in O-O bond formation. Conversely, an increase in the μ_3 -O peak is noted in perovskite-structured catalysts, suggesting an enhanced presence of the μ_3 site. This change is related to the continuous dissolution of Ba and Sr from the A-site, leading to the exposure of more stable internal IrO_x structures and the slight crystallization of surface amorphous structures at high potentials.

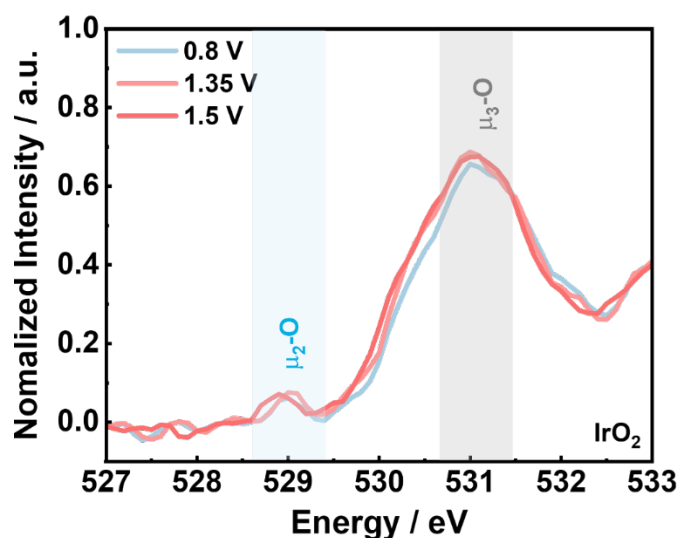


Figure 6-27. *operando* O K-edge XAS spectra of IrO₂.

The dashed line in Figure 6-24 (0.5 V_{re}) demonstrates that the deprotonation of iridium oxide is reversible, with the material returning to a protonated state as the potential decreases, consistent with previous findings.²⁶ This finding contradicts the previous conclusion of irreversibility reached by *operando* Ir L-edge XAS and underscores the superiority of the surface-sensitive O K-edge technique. However, there is no notable decrease in the intensity of the μ_3 -O signal, underscoring its inert nature and structural stability. Research has shown that increases in μ_1 -O and μ_2 -O sites enhance catalytic activity but compromise stability. In contrast, μ_3 -O sites, while not contributing to activity, significantly enhance structural stability and, thus, the durability of the catalyst.^{26, 54} Therefore, perovskite-structured catalysts exhibit higher stability during the OER process by continuously reconstructing μ_3 sites, compared to typical amorphous IrO_x catalysts.

6.4 Conclusion

In conclusion, this study offers a comprehensive investigation into the synthesis and characterization of iridium-based perovskites as OER catalysts, highlighting the crucial role of *operando* analytical techniques in elucidating catalytic mechanisms. By using a solution calcination method to synthesize four distinct iridium-based perovskite oxides—9R-BaIrO₃, 6H-SrIrO₃, 3C-SrIrO₃, and BCC-SrIrO₃—the study highlights the critical influence of crystal

structure on OER performance. Among these, 9R-BaIrO₃ emerges as the most effective catalyst, owing to its superior activity and durability, which are attributed to its unique face-shared [IrO₆] octahedral trimer structure, extensive surface hydroxylation, and optimized Ir-O coordination environment.

The integration of *operando* XAS analysis, including Ir L₃-edge and O K-edge XAS, provides new insights into the oxidation state changes of iridium and the selective binding of oxygen species during OER. Ir species in 9R-BaIrO₃ experience more significant oxidation state changes and Ir-O bond shortening, enhancing the electrophilicity of Ir and facilitating hydroxyl oxidation and proton release. Additionally, the study reveals the impact of structural distortion on catalytic performance, with oxygen species showing a preference for binding at μ_1 sites in less symmetrical monoclinic structures, as opposed to μ_2 sites in more symmetrical tetragonal or cubic structures. Furthermore, in perovskite-structured catalysts, activation at μ_3 sites involves lattice oxygen, promoting structural stabilization and contributing to the high activity and stability of the 9R-BaIrO₃ catalyst. This research advances the understanding of the operational dynamics of iridium-based perovskite oxides in OER and paves the way for developing more efficient and stable catalysts.

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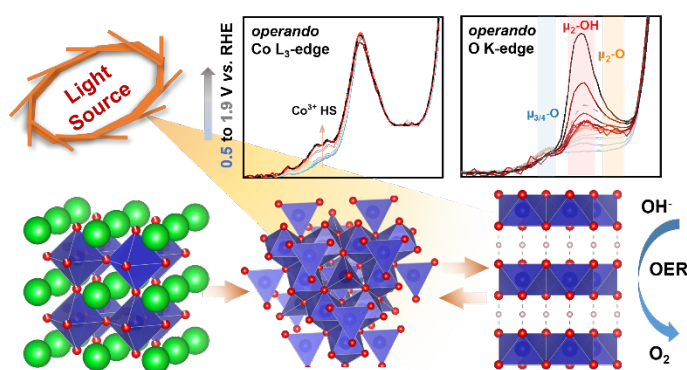
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Chapter 7. Elucidation of the Factors Governing the Oxygen Evolution Reaction in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ Catalysts via *operando* Hard and Soft X-ray Absorption Spectroscopy



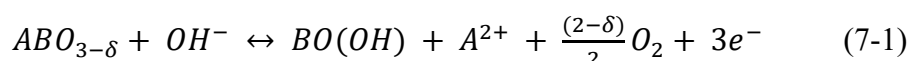
Despite the significant attention given to $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ (BSCF) as a promising alkaline oxygen evolution reaction (OER) catalyst, the intrinsic role of Co and Fe at active sites during the OER process remains largely unclear.

This study provides a comprehensive investigation of the OER performance of BSCF catalysts with varying Fe concentrations ($x = 0, 0.2, 0.8, 1$) using both rotating disk electrode (RDE) and a newly proposed forced-flow cell method. *operando* X-ray absorption spectroscopy (XAS), including Co/Fe K-edge, Co/Fe L-edge, and surface-sensitive O K-edge measurements, was used to assess the structural and electronic changes during OER. The superior OER activity of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582) is attributed to the interplay between its crystal structure and spin states. Minor Fe doping ($x = 0.2$) preferentially occupies octahedral sites, altering the electronic state of Co. As the potential increases, tetrahedral sites $\text{Co}^{2+}(\text{T}_d)$ transitions to octahedral sites $\text{Co}^{3+}(\text{O}_h)$, facilitating the formation of the active CoOOH phase. Fe further promotes the formation of high-spin Co^{3+} , enhancing electron transfer and OH/OOH intermediate adsorption. In contrast, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCF5528), with higher Fe doping, stabilizes Co^{3+} in octahedral sites without significant oxidation state changes, leading to FeOOH as the main active site and reduced activity. According to *operando* O K-edge results, the formation of reducible $\text{Fe}^{3+}/\text{Co}^{3+}-\text{O}$ sites, particularly $\mu_2\text{-O}(\text{H})$ bridges, significantly boosts OER performance, emphasizing the important role of Fe doping in optimizing catalytic activity.

7.1 Introduction

Hydrogen energy, as a clean and sustainable fuel, is essential for reducing our global reliance on fossil fuels.¹⁻³ Among the various methods of hydrogen production, large-scale alkaline water electrolysis is emerging as a promising method from the perspectives of environmental compatibility and cost-effectiveness.⁴⁻⁷ In this context, perovskite oxide $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582) has garnered significant attention due to its remarkable oxygen evolution reaction (OER) performance in alkaline media.⁸⁻¹² This superior catalytic activity is attributed to its unique electronic structure and high surface reactivity, making it a focal point of ongoing research.¹¹⁻¹³

Shao-Horn et al. discovered a volcano-shaped relationship between the intrinsic catalytic activity of perovskite oxides and the occupancy of the e_g orbital of 3d transition metal ions.^{10,}
¹⁴ In the case of BSCF, with its optimal e_g filling, it provided a balanced oxygen binding strength, thereby significantly enhancing its OER activity. Additionally, they proposed that the formation of dynamic, self-assembled oxide (hydroxide) layers on the surface of B-site cations (Co/Fe in BSCF) is a critical feature for achieving high OER activity.¹¹ This self-assembled Co/Fe oxide (hydroxide) layer is generated via the lattice oxygen evolution reaction shown below, benefiting from the perovskite structure's flexibility and high oxygen vacancy content.^{8,}
¹⁵



Moreover, Bae-Jung Kim et al. suggested that slight Fe doping in cobalt-based perovskite oxides can alter their inherent properties, stabilizing Co in a lower oxidation state and enhancing OER activity and stability, which provides valuable insights into the specific role of Fe.¹⁶

Despite extensive studies on BSCF, significant uncertainties remain regarding the exact structure of the active Co/FeOOH layer, the potential synergistic effect between Co and Fe, and the involvement of Co and/or Fe at active sites in BSCF catalysts with different Co/Fe ratios,¹⁷

particularly those with high Fe content, such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCF5528). Clarifying this issue is essential for further improving the activity of this widely researched BSCF, and for this purpose, there is a strong desire to apply *operando* measurement techniques that clarify the active sites of the catalysts during the reaction. X-ray absorption spectroscopy (XAS) has been widely used to investigate the local electronic and geometric structures of BSCF and to determine the active Co/FeOOH layer based on oxidation states and coordination environments.^{8, 13, 16, 18} However, most *in situ/operando* studies of catalysts preliminary rely on bulk-sensitive spectroscopies, such as *operando* hard X-rays XAS.¹⁹⁻²² Since OER is predominantly governed by the surface/electronic structure of the catalyst, surface-sensitive *operando* analysis methods are essential to acquire information about the catalyst surface during OER. Recently, techniques such as *operando* O K-edge XAS have been reported for gaining insights into the catalytic interface of Ir-based catalysts during acid OER.^{22, 23} Still, further study of the intrinsic mechanism of BSCF catalysts in alkaline OER processes remains inadequately understood. Additional studies utilizing the combination of various bulk and surface-sensitive advanced *operando* techniques are necessary to resolve these ambiguities and gain a clearer understanding of surface phenomena in BSCF catalysts during OER.

In this study, we synthesized four different catalysts: $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (BSC), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (BSF), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582), and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCF5528). To mitigate the influence of bubbles during OER activity testing using the three-electrode method, a new electrochemical measurement technique, the "time-zero method", was introduced. This approach allows us to estimate kinetic currents under conditions of no supersaturation or bubbles on the catalyst surface. Additionally, *operando* XAS was employed, including Co/Fe K-edge, Co/Fe L-edge, and O K-edge, to examine the surface structure dynamics of BSCF during OER. The high OER activity of BSCF5582 is attributed to the formation of high-spin Co^{3+} states, geometric site confinement through minor Fe doping, and dynamic structural transformation ($\text{Co}^{3+}(T_d)$ to $\text{Co}^{3+}(O_h)$) that facilitates active site formation. Fe^{3+} in BSCF5582 undergoes slight oxidation during OER, forming FeOOH active sites that contribute to the reaction. In contrast, BSCF5528, with higher Fe doping, stabilizes Co^{3+} in octahedral sites

without significant oxidation state changes, leading to lower activity due to an unfavorable electronic structure and reduced Co content. *operando* O K-edge measurements identified reducible $\text{Fe}^{3+}/\text{Co}^{3+}\text{-O}$ sites, associated with $\mu_2\text{-O(H)}$ bridges, which are favorable for fast OER catalysis. This analysis highlights the critical role of minor Fe doping in optimizing BSCF's surface structure and enhancing OER performance, offering valuable insights for future catalyst development.

7.2 Experimental Methods

7.2.1 Chemicals

Barium nitrate ($\text{Ba(NO}_3)_2$, 99.0%), iron(III) nitrate enneahydrate ($\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.0%), cobalt(II) nitrate hexahydrate ($\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.0%), citric acid (98.0%), ethylenediaminetetraacetic acid (EDTA, 99.5%), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28.0%), perchloric acid (HCl, 35.0%), strontium nitrate ($\text{Sr(NO}_3)_2$, 99.9%), ethanol (99.5%) were acquired from Fujifilm. All chemical reagents were used as received without further purification. The electrolyte was prepared from ultra-pure water (Milli-Q, 18.2 M Ω) and perchloric acid (ultra-pure, Kanto Chemical Co. Inc.).

7.2.2 Synthesis of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.5, 0.8, 1$)

The four catalysts, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.8, 1$), were synthesized using an ethylenediaminetetraacetic acid-citric acid (EDTA-CA) complexation sol-gel method. For $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ as an example, stoichiometric amounts of 0.26g $\text{Ba(NO}_3)_2$, 0.21g $\text{Sr(NO}_3)_2$, 0.46g $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.16g $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 20 mL deionized water. 1.17g EDTA and 1.54g citric acid were then added sequentially as complexing agents in a mole ratio of 1:1:2 for total metal ions: EDTA: citric acid. The pH of the solution was adjusted to 6-7 using $\text{NH}_3 \cdot \text{H}_2\text{O}$ to ensure complete complexation. The solution was heated to 90 °C and stirred continuously until a gel formed. This gel was dried in a furnace at 250 °C for 5 hours to produce a solid precursor. The solid precursor was milled and sintered at 1000 °C for 5 hours in an air atmosphere to form the BSCF powder.

The synthesis of the other catalysts followed the same procedure as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, with the only difference being the molar amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ used.

7.2.3 Characterization

X-ray diffraction (XRD) analyses were performed using a Rigaku Ultima IV with $\text{Cu K}\alpha$ radiation at a scanning rate of 2° per minute to characterize the crystalline structure of the samples. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were conducted using a Hitachi S-3400N microscope at an accelerating voltage of 20 kV. For these analyses, a 0.2 mg sample was dispersed in anhydrous ethanol, dropped onto tape attached to the sample holder, and allowed to dry before observation. Sample morphologies were examined using a JEM-2200FS transmission electron microscope (JEOL, Ltd.) at an accelerating voltage of 200 kV. Surface chemical compositions were analyzed using X-ray Photoelectron Spectroscopy (XPS) on a PHI5000 VersaProbe II, utilizing monochromatic $\text{Al K}\alpha$ radiation for high precision. Ex-situ Fe and Co K-edge XAS was conducted in transmission mode using a Si (111) monochromator on BL14B2 at SPring-8, Japan. The surface area of the nanosized material was calculated using the Brunauer–Emmett–Teller (BET) method. N_2 adsorption–desorption experiments were conducted at 77.00 K using an ASAP 2020 physisorption analyzer (Micromeritics Instrument Corporation).

7.2.4 RDE measurement

The synthesized $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0, 0.2, 0.8, 1$) catalysts were evaluated for OER activity using electrochemical measurements in rotating disk electrode (RDE) mode. Catalyst inks were prepared by dispersing 11.76 mg of catalyst powder in 973 μL of ethanol and 26 μL of 5 wt% Nafion solution (Sigma-Aldrich), followed by sonication in an ice bath for 20 minutes. A total of 5 μL of the ink was then dropped onto a polished glassy carbon (GC) electrode (Hokuto Denko, 5 mm diameter, 0.196 cm^2).

OER performance in a 0.1 M KOH solution was assessed using a standard three-electrode electrochemical cell (Naito Rika) controlled by an HZ-7000 electrochemistry workstation

(Hokuto Denko Ltd.). The GC cast with the catalyst served as the working electrode, with Pt mesh as the counter electrode and a reversible hydrogen electrode (RHE) as the reference electrode.

Cyclic voltammetry (CV) was performed at 50 mV s^{-1} from 1.0 V to 1.6 V vs. RHE for 50 cycles for pre-treatment, followed by 5 cycles from 0 V to 1.6 V vs. RHE. Linear sweep voltammetry (LSV) was conducted at 10 mV s^{-1} from 1.0 V to 1.8 V vs. RHE, with the RDE rotating at 1600 rpm.

7.2.5 Forced-flow cell measurement

The anode catalysts and cathode catalyst used were $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.8, 1$) and Pt/C (Pt 28.4%, Tanaka Kikinzoku Kogyo, Japan) respectively. The Pt/C was dispersed in ethanol uniformly sprayed onto a $1 \times 1 \text{ cm}^2$ carbon paper (SGL Carbon Japan Ltd.) with a loading amount of approximately $0.5\text{--}0.6 \text{ mg cm}_{\text{Pt}}^{-2}$ and served as the cathode material. The BSCF catalyst ink (ethanol: $\text{H}_2\text{O} = 1:2$) was ultrasonically homogenized for less than 5 minutes, then applied to Zirfon® (Perl UTP 500, Agfa, Belgium) using a masking tape with five rectangular holes ($1 \times 8 \text{ mm}^2$ each), resulting in an approximate catalyst loading of 1.2 mg cm^{-2} , and was dried before electrochemical testing.

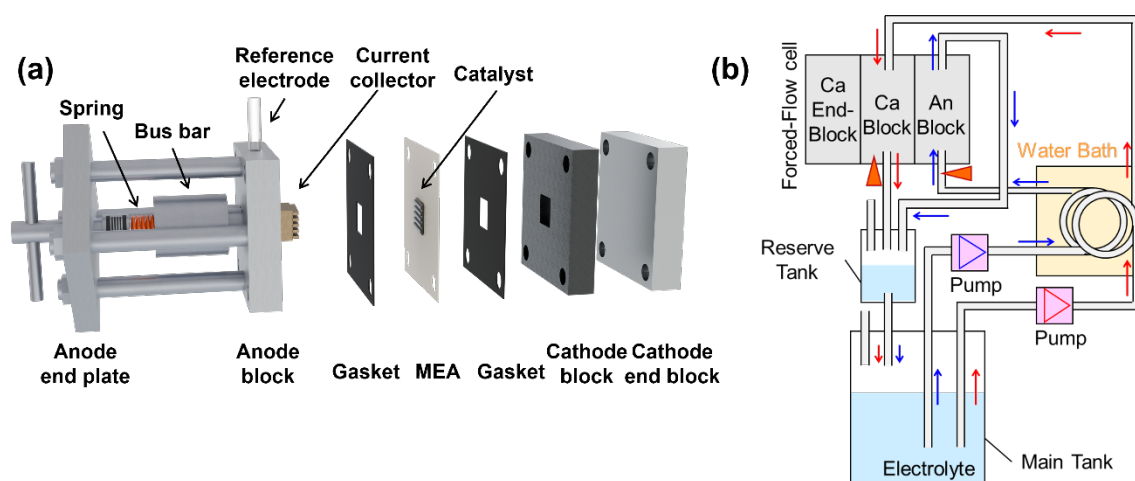


Figure 7-1. Schematic representation of (a) side view of forced-flow cell and (b) experimental conditions.

In the cell setup (Figure 7-1), interdigitated and parallel flow fields were applied to the anode and cathode, respectively. The membrane pressure was set at 4 MPa, with both the anode and cathode chambers circulating 7 M KOH solution at 30 °C. The anode flow rate was 50 mL min⁻¹, while the cathode flow rate was 30 mL min⁻¹.

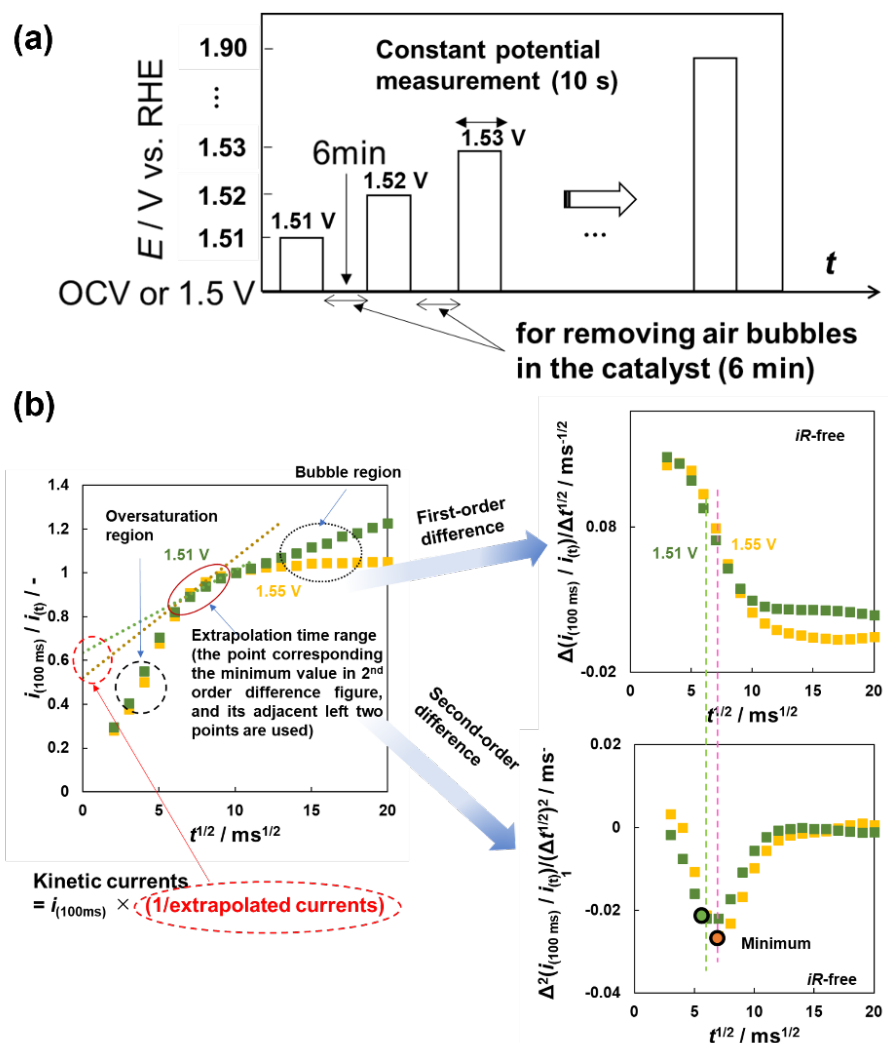


Figure 7-2. (a) Pulsed potential step measurements. (b) Determination of extrapolation region.

OER performance in 7 M KOH solution was evaluated using a forced-flow cell controlled by a Bio-Logic MPG-205 electrochemistry workstation. The electrochemical measurement protocol included pre-treatment with chronopotentiometry (CP) at 1 A cm⁻² for 2 hours, followed by electrochemical impedance spectroscopy (EIS) with an AC amplitude of 10 mV and frequencies from 100 kHz to 0.1 Hz at 1.5 V, 1.6 V, and 1.7 V vs. REH. Pulsed potential

step measurements were performed with a constant increasing potential step applied for 10 seconds per 0.01 V from 1.5 V to 1.7 V vs. RHE. Chronoamperometry (CA) intervals of 360 s were set to remove bubbles generated within the catalyst layer, applying a lower potential during these intervals to avoid phase transitions in the catalyst (Figure 7-2a).

Time-zero analysis details are provided in the Supporting Information (Figure 7-2b).

7.2.6 *operando* XAS measurement

operando soft XAS was conducted at BL27 in SPring-8 using total electron yield (TEY) mode. The working electrode material was prepared by spraying the ink onto an anion exchange membrane (Sustainion® X37-50 Grade RT), achieving a catalyst loading of approximately 0.1 mg/cm². The flow cell, assembled as shown in the Figure 7-3, utilized a Pt wire wrapped around the RHE as the counter electrode, a handmade RHE (H₂ 100% purity) as the reference electrode, and a glassy carbon with the catalyst membrane as the working electrode. The electrolyte was 7M KOH, flowing at 10 mL min⁻¹ during the *operando* soft XAS tests. Monochromatic X-rays were generated using a line-spacing plane grating monochromator. Electrode polarization ranged from 0.5 V to 1.9 V vs. RHE in a vacuum environment. XAS signals were recorded after stabilizing each potential for 10 minutes to ensure steady current conditions.

operando hard XAS was performed at BL37XU in SPring-8 using partial fluorescence yield (PFY) mode. During the test, a pair of Si (111) monochromators and a 4 mrad total-reflection Rh mirror were used to obtain collimated and monochromatic X-rays. The electrode was polarized from 0.5 V to 1.9 V vs. RHE in an air atmosphere. The XAS signal was collected after maintaining polarization at each potential for 10 minutes to achieve stable current conditions.

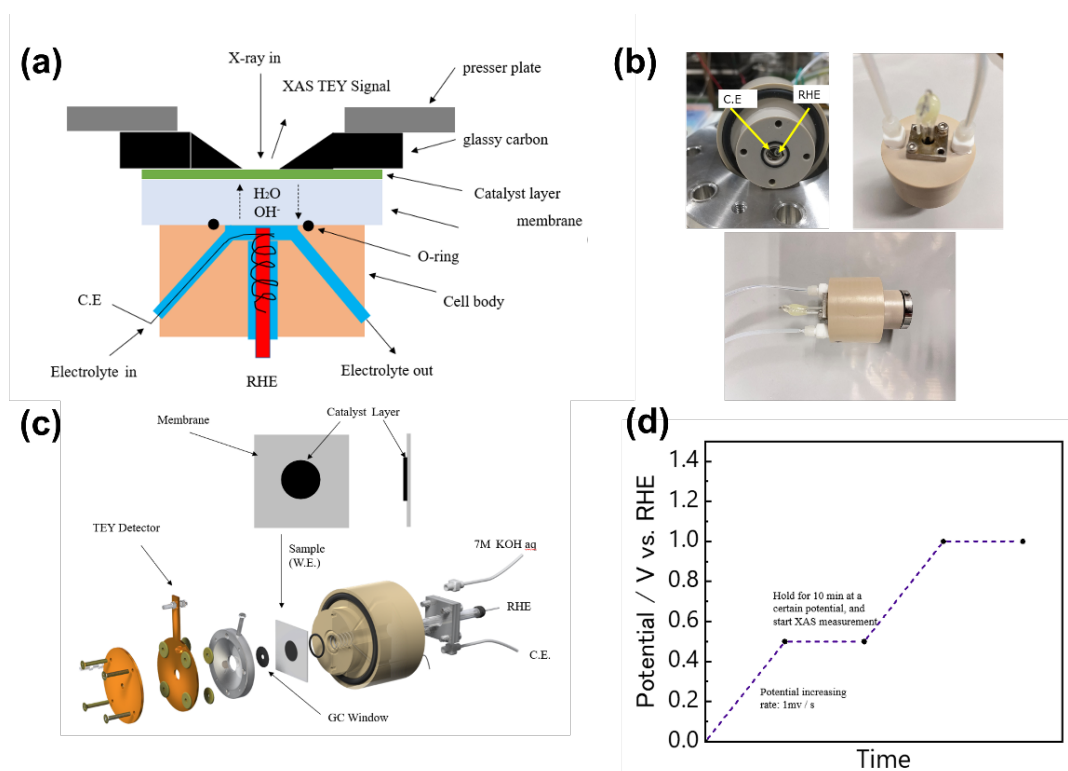


Figure 7-3. (a) Sectional view, (b) practicality images and (c) decomposition chart of *operando* soft XAS cell. (d) *operando* XAS measurement procedure.

7.3 Result and Discussion

7.3.1 Characterization

Various Fe-doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.8, 1$) catalysts were synthesized using the ethylenediaminetetraacetic acid-citric acid (EDTA-CA) complex sol-gel method. The XRD patterns of these catalysts, shown in Figure 7-4a, reveal several characteristic peaks for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.8$) at approximately 23° , 32° , 39° , 46° , 52° , 58° , and 68° , corresponding to the 100, 110, 111, 200, 210, 220, and 300 planes of BSCF, respectively. These peaks align with previously reported XRD results, confirming the cubic perovskite structure.^{9, 24} As the Co/Fe atomic ratio decreases from BSCF5582 to BSF, the peaks systematically shift to lower d-values, indicating lattice contraction (Figure 7-5).²⁵ The XRD pattern of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ shows distinct characteristic peaks, indicating a hexagonal structure (space group P63/mmc). This phenomenon has also been confirmed in previous studies, where

increasing the Co content ($X=0.9, 0.95, 1$) induces a phase transition, attributed to the additional effects of the A-site Ba/Sr.^{26, 27}

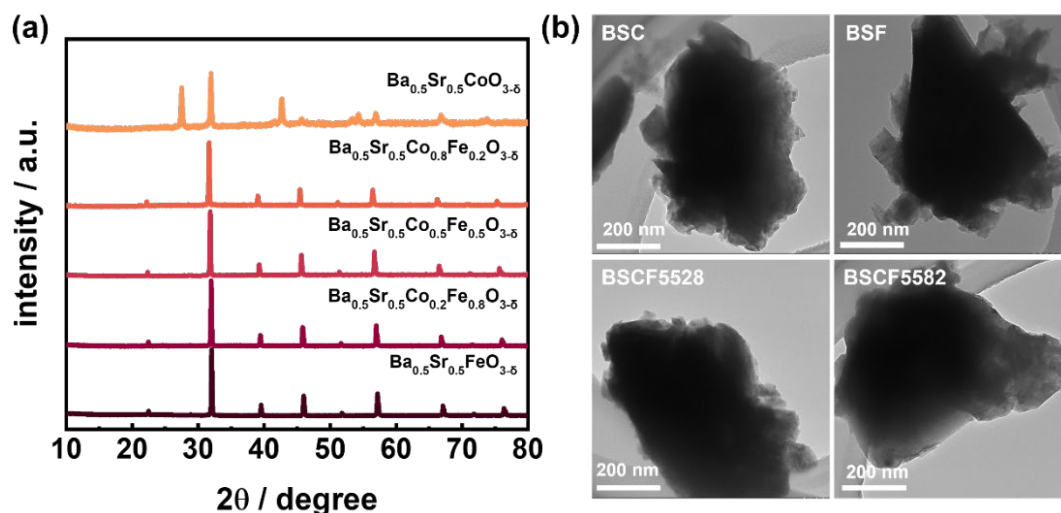


Figure 7-4. (a) XRD patterns and (b) TEM images of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.5, 0.8, 1$).

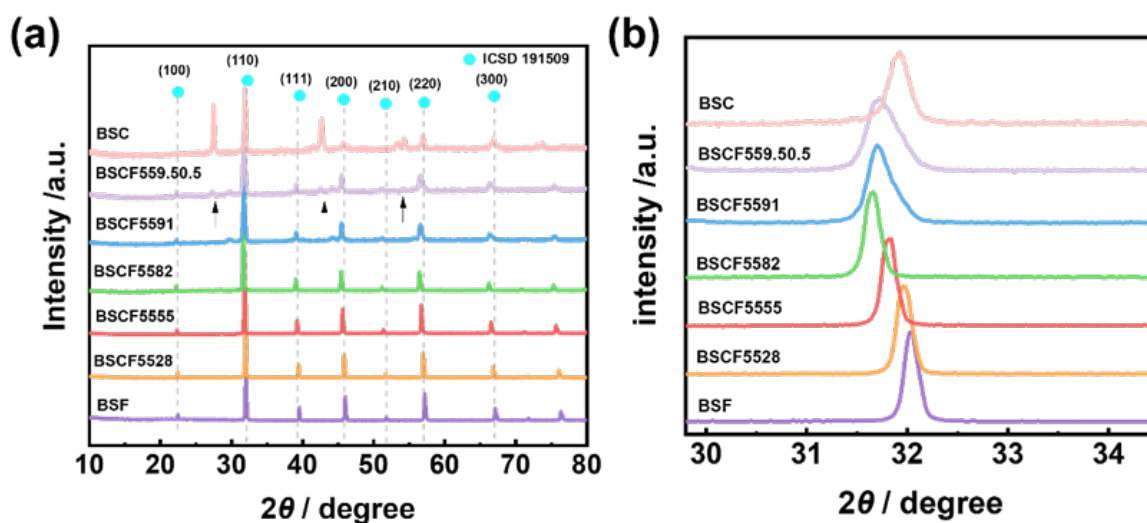


Figure 7-5. (a) XRD patterns of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.5, 0.8, 0.9, 0.95, 1.0$). (b) Partial enlargement of (a).

The particle distribution and surface morphology of the synthesized samples were analyzed using SEM and TEM (as illustrated in Figure 7-4b and Figure 7-6). The results show that the average particle size of the four catalysts ranges from 200 nm to 400 nm, with BSC and BSF having smaller average particle sizes around 200 nm. Figure 7-7 presents the EDS spectrum

and corresponding elemental mapping images of as prepared BSCF5582. The metal atom ratios in the catalysts are roughly consistent with the calculated values.

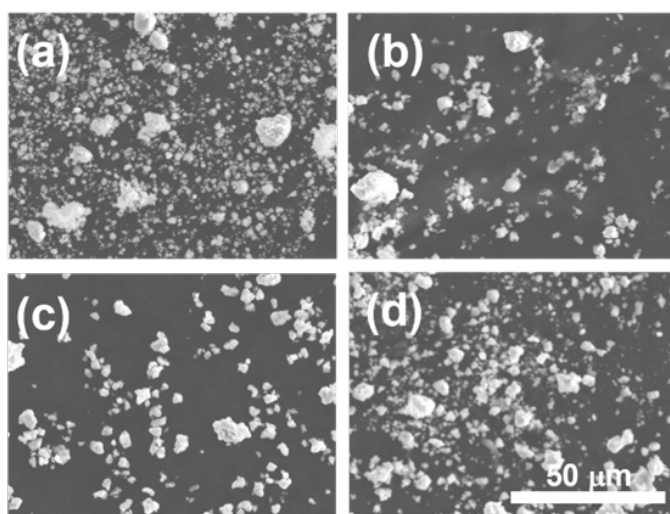


Figure 7-6. SEM images of (a) BSC, (b) BSCF5582, (c) BSCF5528, and (d) BSF.

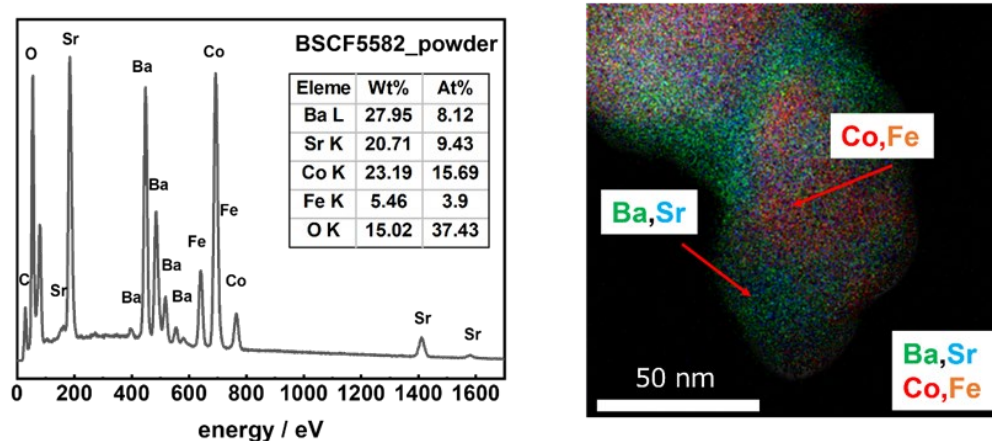


Figure 7-7. EDS spectra of BSCF5582 powder.

The BET specific surface areas of the catalysts were determined from N₂ adsorption-desorption isotherms (Figure 7-8 and Table 7-1). Compared to pure BSC (0.73 m² g⁻¹) and BSF (0.56 m² g⁻¹), the BET specific surface areas of BSCF catalysts are slightly smaller, corresponding to the larger nanoparticle sizes observed in SEM and TEM images. Among the BSCF catalysts, BSCF5582 has a BET surface area of 0.41 m² g⁻¹, similar to BSCF5528 (0.49 m² g⁻¹) and BSCF5555 (0.49 m² g⁻¹). This indicates that the B-site metal ratio does not significantly affect the BET surface area of perovskite oxide catalysts.

Table 7-1. BET specific surface area of each sample.

Sample	$a_{S,BET} (m^2 g^{-1})$
$Ba_{0.5}Sr_{0.5}CoO_{3-\delta}$	0.72
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	0.41
$Ba_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_{3-\delta}$	0.49
$Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$	0.49
$Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$	0.56

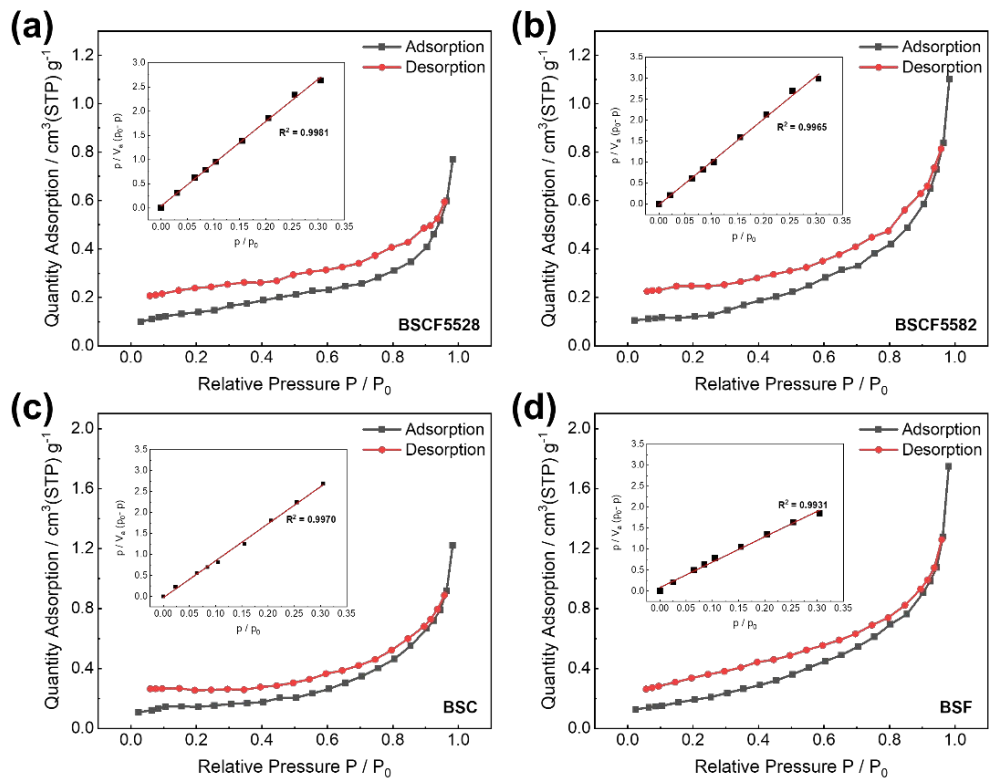


Figure 7-8. Nitrogen adsorption/desorption isotherm patterns of (a) BSCF5528, (b) BSCF5582, (c) BSC, and (d) BSF.

To better understand the real structural characteristics of the catalysts in the alkaline electrolyte environment, the catalysts were surface-treated by immersion in 0.1 M KOH for

two hours prior to the XAS measurement.¹¹ The normalized Co K-edge XANES spectra of the prepared perovskite catalysts, shown in Figure 7-9a, reveal Co oxidation states between +2 and +3 for all samples. Notably, BSCF5582 displays the lowest energy position among the catalysts, suggesting a lower average oxidation state. The Co oxidation states follow the order: BSC > BSCF5528 > BSCF5582. The above phenomenon shows that Fe doping effectively lowers the oxidation state of Co and increases oxygen vacancy concentration, consistent with previous studies.^{16, 28} However, excessive Fe doping in BSCF5528 leads to further oxidation of Co.

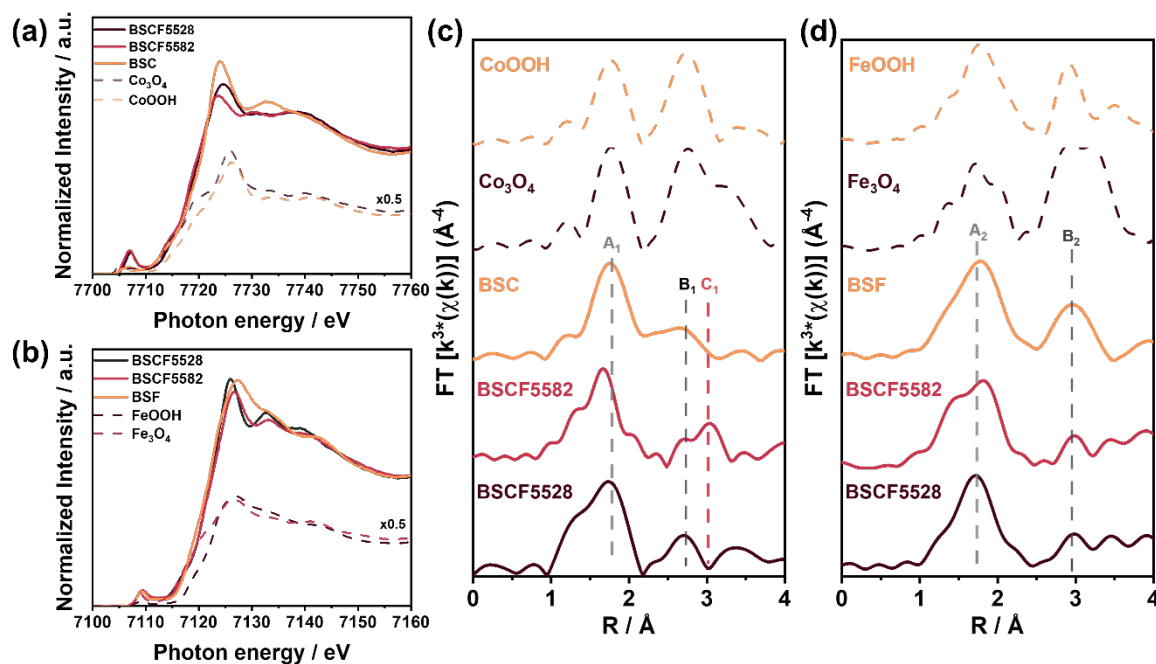


Figure 7-9. (a) The normalized Co K-edge XANES spectra and (c) the R-space Fourier-transformed of the Co K-edge EXAFS spectra for Co_3O_4 , $\text{Co}(\text{OH})_2$, CoOOH, BSC, BSCF5528 and BSCF558. (b) The normalized Fe K-edge XANES spectra and (d) Fourier-transformed of the Fe K-edge EXAFS spectra for Fe_3O_4 , FeOOH, BSF, BSCF5528 and BSCF558.

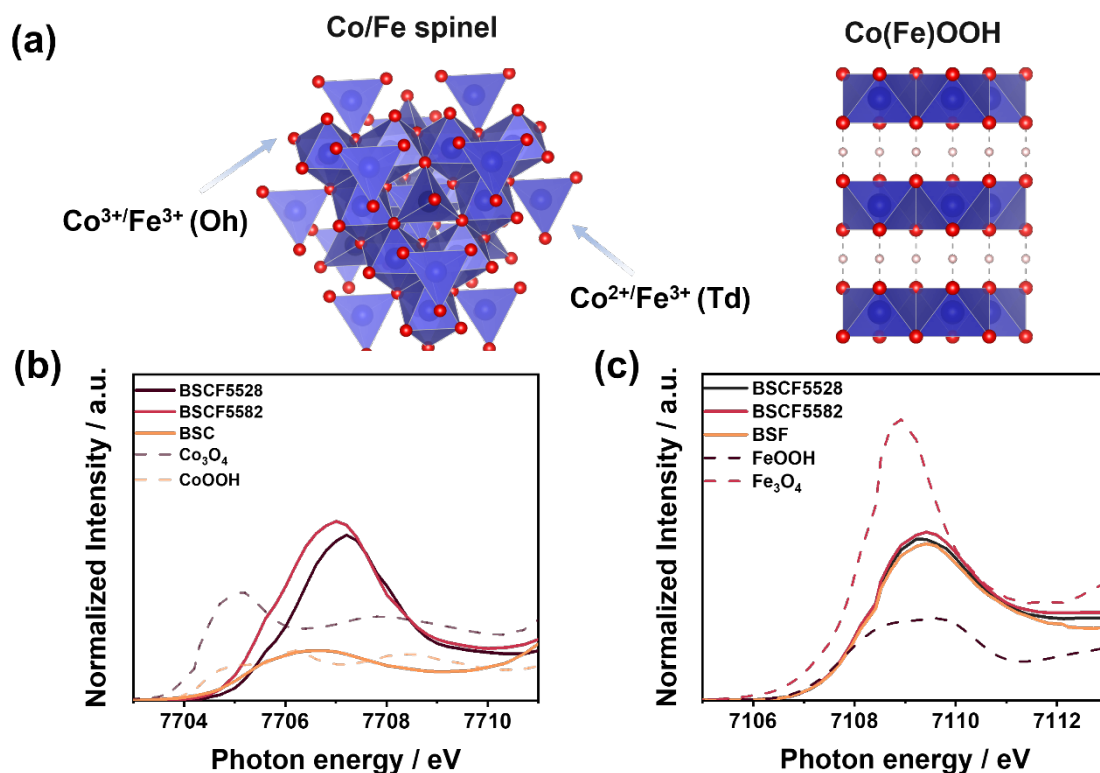


Figure 7-10. (a) Presentation of T_d and O_h site. An expanded view of the pre-edge part of the (b) Co and (c) Fe K-edge XANES.

BSCF5582 exhibits the highest pre-edge (1s to 3d) intensity in the Co K-edge XANES spectra and the lowest oxidation state among all samples (Figure 7-10b). This is due to the sensitivity of the pre-edge peak to the metal's oxidation state and coordination symmetry, with tetrahedral (T_d) sites showing more intense pre-edge features than octahedral (O_h) sites (Figure 7-10a).^{29, 30}

Comparing BSC, it is observed that with a Fe doping of 0.2 (BSCF5582), Co^{2+} (T_d) occupancy increases, leading to the reduction in an average oxidation state of Co as Fe ions preferentially occupy O_h sites.¹¹ However, when Fe doping is increased to 0.8 (BSCF5528), there is a noticeable decrease in normalized intensity in the pre-edge region, and the spectral energy shifts positively due to Fe^{3+} increasingly occupying T_d sites, reducing the presence of Co^{2+} (T_d).²⁸ Comparison of the normalized XANES spectra at the Fe K-edge of the BSCF series catalysts (Figure 7-9b) reveals that the electronic structure of Fe remains consistent, despite variations in the occupancy positions of Fe. This consistency is attributed to the half-filled

configuration in the high-spin $\text{Fe}^{3+}(\text{O}_h)/\text{Fe}^{3+}(\text{T}_d)$ crystal field and the similar energy levels of Δ_{oct} and Δ_{tet} .^{28, 31} The pre-edge peak intensity and position of BSCF resemble those of Fe_3O_4 (Figure 7-10c), which includes Fe^{3+} ions in T_d sites and both Fe^{3+} and Fe^{2+} ions in O_h sites, leading to complex Fe K-edge XANES features.³²⁻³⁶

FT-EXAFS analysis validated the distances and structural deformations within the crystals. As shown in Figures 7-9c and d, the first peak at position A corresponds to the single-scattering path from metal ions to the nearest oxygen atoms (Co-O and Fe-O). The second and third peaks at positions B1 ($\text{Co-Co}(\text{O}_h)$)/B2 ($\text{Fe-Fe}(\text{O}_h)$) and C1 ($\text{Co-Co}(\text{T}_d)$)/Co-Fe(T_d)) represent the scattering from adjacent metal ions in octahedral or tetrahedral sites, depending on the initial position of the metal ions.³⁷ In the Co K-edge FT-EXAFS spectra (Figure 7-9c), a small amount of Fe doping (BSCF5582) leads to Co ions preferentially occupying tetrahedral sites, resulting in higher signal intensity at position C1. Under heavy doping conditions (BSCF5528), the majority of Co ions occupy octahedral sites, consistent with XANES observations. Additionally, since the $\text{Co}^{3+}(\text{O}_h)\text{-O}$ distance is greater than the $\text{Co}^{2+}(\text{T}_d)\text{-O}$ distance, the signal at position A1 in BSCF5582 shifts to a shorter scattering path. From the Fe K-edge FT-EXAFS spectra (Figure 7-9d), it is evident that in all catalysts, most Fe ions reside in octahedral sites. Despite the presence of tetrahedral coordination of $\text{Fe}^{3+}(\text{T}_d)$ in BSCF5528, it still primarily occupies octahedral positions due to its lower formation energy, consistent with previous studies.³⁷ The tetrahedral coordination of $\text{Co}^{2+}(\text{T}_d)$ promotes the formation of the highly active $\text{Co}(\text{Fe})\text{OOH}$ phase, enhancing OER catalytic activity and making BSCF5582 a promising OER catalyst.¹¹

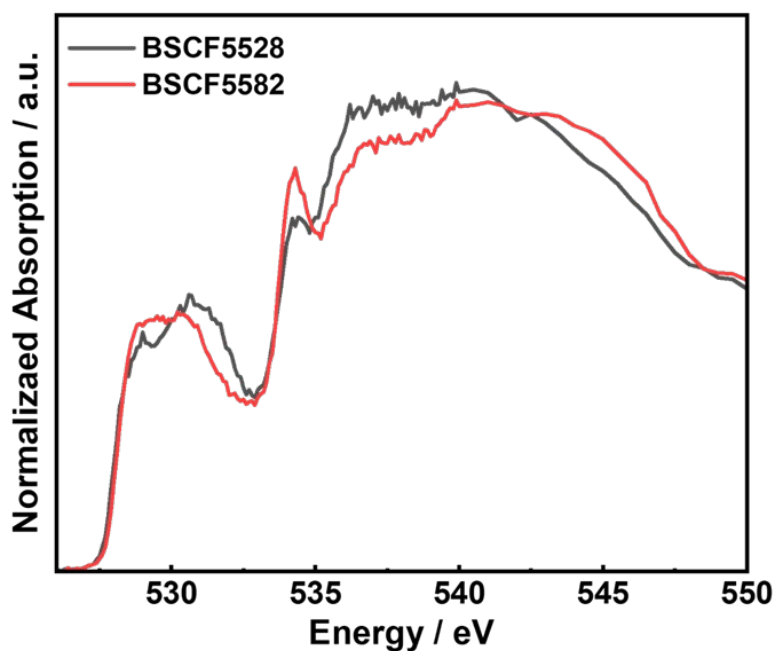


Figure 7-11. O K-edge XAS spectra of BSCF5528 and BSCF5582.

O K-edge XAS provides critical insights into the density of occupied and unoccupied states around the Fermi level of transition metals.³⁸ As shown in Figure 7-11, the peaks at 529.1 eV and 530.5 eV correspond to the hybridization of O 2p with the transition metal 3d t_{2g} and e_g orbitals, respectively. The lower intensity at approximately 529.1 eV in the BSCF5528 sample indicates more occupied states in the e_g orbitals, suggesting a higher spin state because of the heavy Fe doping.^{22, 39}

XPS spectra further confirm the surface oxygen states in the BSCF catalysts. Figure 7-12 shows the O 1s XPS spectra of BSCF5528 and BSCF5582, deconvoluted into three peaks: lattice oxygen (O^{2-}) at 528.6 eV, highly oxidative species (O_2^{2-}/O^-) at 529.9 eV, and hydroxyl groups or surface-absorbed oxygen (OH^- or O_2) at 531.2 eV.⁴⁰ BSCF5582 has a significantly higher O^{2-} content than BSCF5528, enhancing lattice oxygen oxidation during the OER process.^{41, 42}

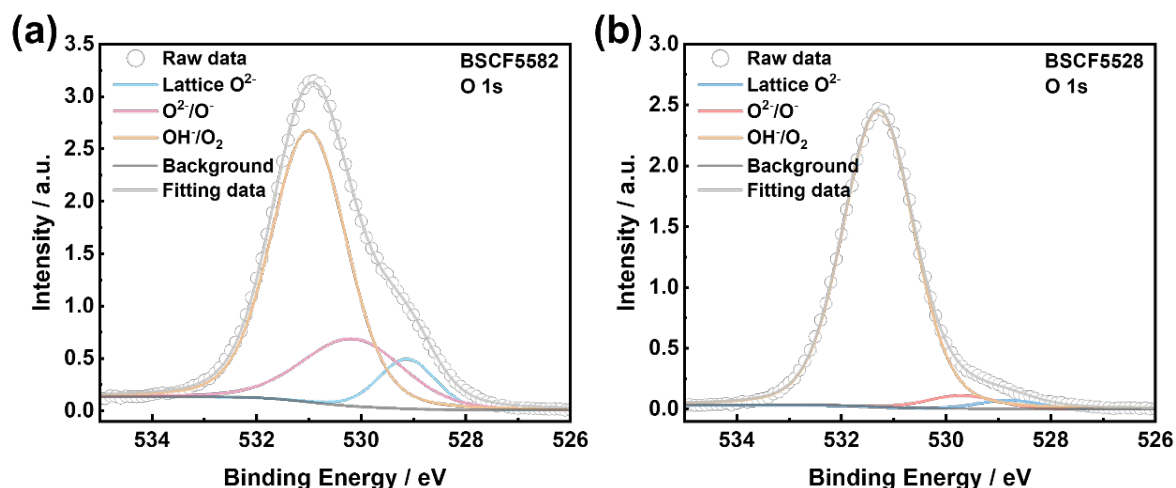


Figure 7-12. XPS spectra of O 1s for (a) BSCF5582 and (b) BSCF5528.

7.3.2 Electrochemical measurement

The OER performance of the synthesized catalysts in 0.1 M KOH solution was evaluated using a standard three-electrode electrochemical cell. Figure 7-13b presents the LSV polarization curves for BSC, BSF, BSCF5582, and BSCF5528. Among these BSCF5582 catalyst demonstrates a lower overpotential (η) at each current density compared to the other catalysts, indicating superior OER electrocatalytic activity. The Tafel plot in Figure 7-13c further reveals that BSCF5582 has the lowest Tafel slope ($111.0 \text{ mV dec}^{-1}$), suggesting faster OER kinetics.

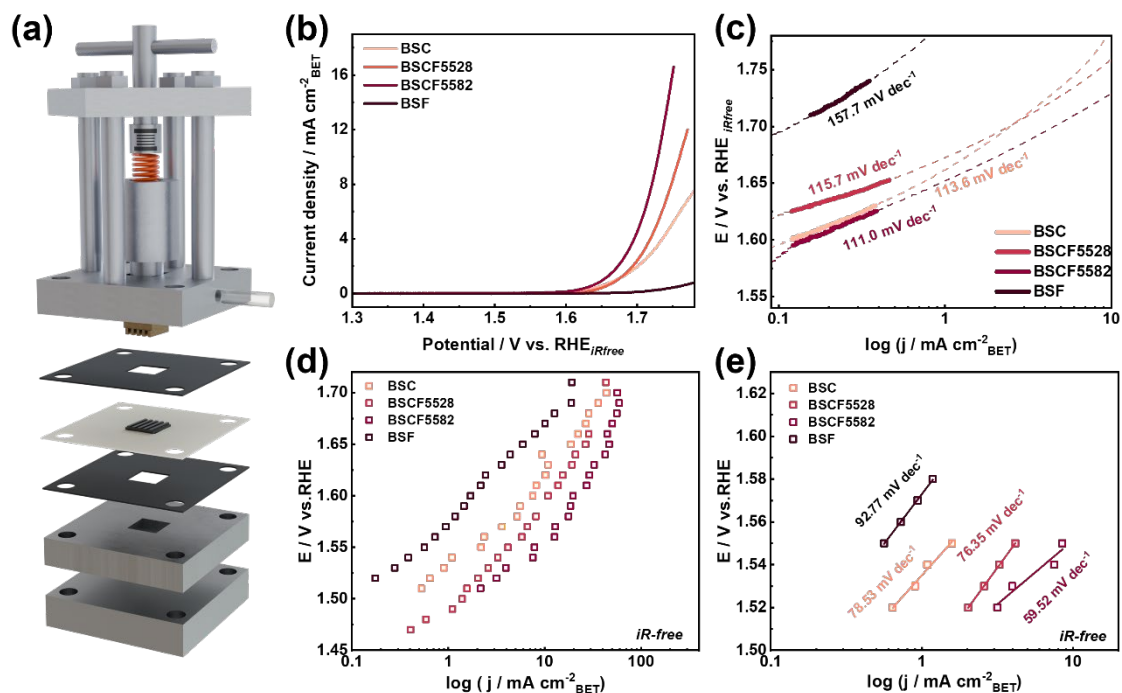


Figure 7-13. (a) Schematic illustration of the forced-flow cell. (b) LSVs curves and (c) tafel slope of BSC, BSF, BSCF5582 and BSCF5528 by RDE method. (d) *i*-*E* curves and (c) tafel slope of BSC, BSF, BSCF5582 and BSCF5528 using the forced-flow cell method and time zero analysis. All results were corrected for ohmic electrolyte resistance (*i*R).

To more precise OER activity measurement, a new "time-zero method" using a forced-flow cell was introduced to address limitations of standard electrochemical cells, allowing for accurate OER activity measurements by preventing catalyst detachment and eliminating bubble interference (Figure 7-13a).^{43, 44} CA tests using a forced-flow cell were performed to precondition and activate the catalysts by maintaining a current density of 400 mA cm⁻² for two hours. This process accelerated the dissolution of surface Ba/Sr and structural transformation, resulting in the formation of a Co/Fe-rich surface layer, which lowered the overpotential and enhanced OER activity (Figures 7-14 and 7-15). EIS was also conducted under the operating conditions for OER, with BSCF5582 exhibiting the lowest charge transfer resistance (0.7 Ω at 1.7 V vs. RHE), signifying excellent conductivity and rapid charge transfer rates (Figure 7-16).

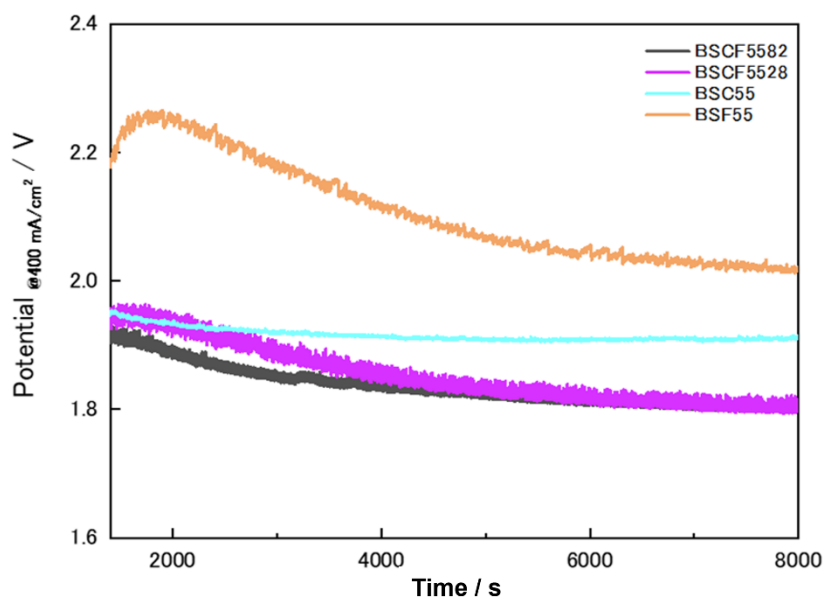


Figure 7-14. Pre-treatment and activation of BSCF5582, BSCF5528, BSC and BSF by chronopotentiometry (CP) at 400 mA cm^{-2} .

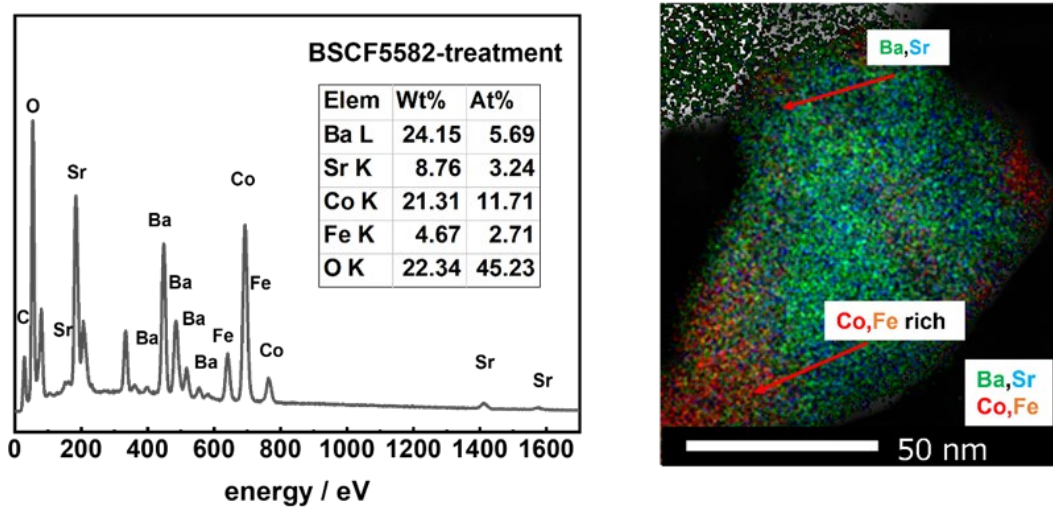


Figure 7-15. EDS spectra of BSCF5582 after pre-treatment.

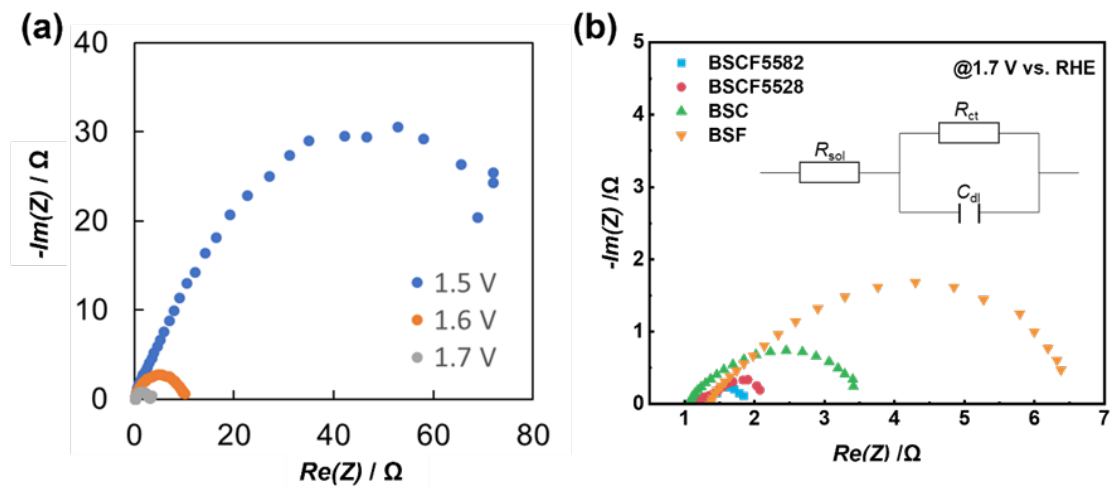


Figure 7-16. (a) EIS plot of BSCF5582 at 1.5 V, 1.6 V and 1.7 V vs. RHE. (b) EIS plot of BSCF5582, BSCF5528, BSC and BSF at 1.7 V vs. RHE.

CV measurements further confirmed the impact of the Co/Fe-rich surface on the OER activity of BSCF catalysts. Figure 7-17 shows the CV curves for the four catalysts at different cycle numbers, with BSCF5582 exhibiting significant surface reconstruction, resulting in increased activity. The redox peak observed around 1.4 V vs. RHE is associated with the Co^{2+} to Co^{3+} transition in Co_3O_4 spinel and the formation of surface hydroxide $Co^{3+}-OH_{ad}$.^{45, 46} Compared to BSC, the anodic shift of BSCF catalysts indicates that Fe doping suppresses Co oxidation and promotes its transition to hydroxides, confirming the presence of a Co/Fe-rich surface.^{11, 28} For the BSF catalyst, the peak around 1.3 V vs. RHE corresponds to the Fe^{2+}/Fe^{3+} transition, contributing minimally to OER activity.⁴⁷

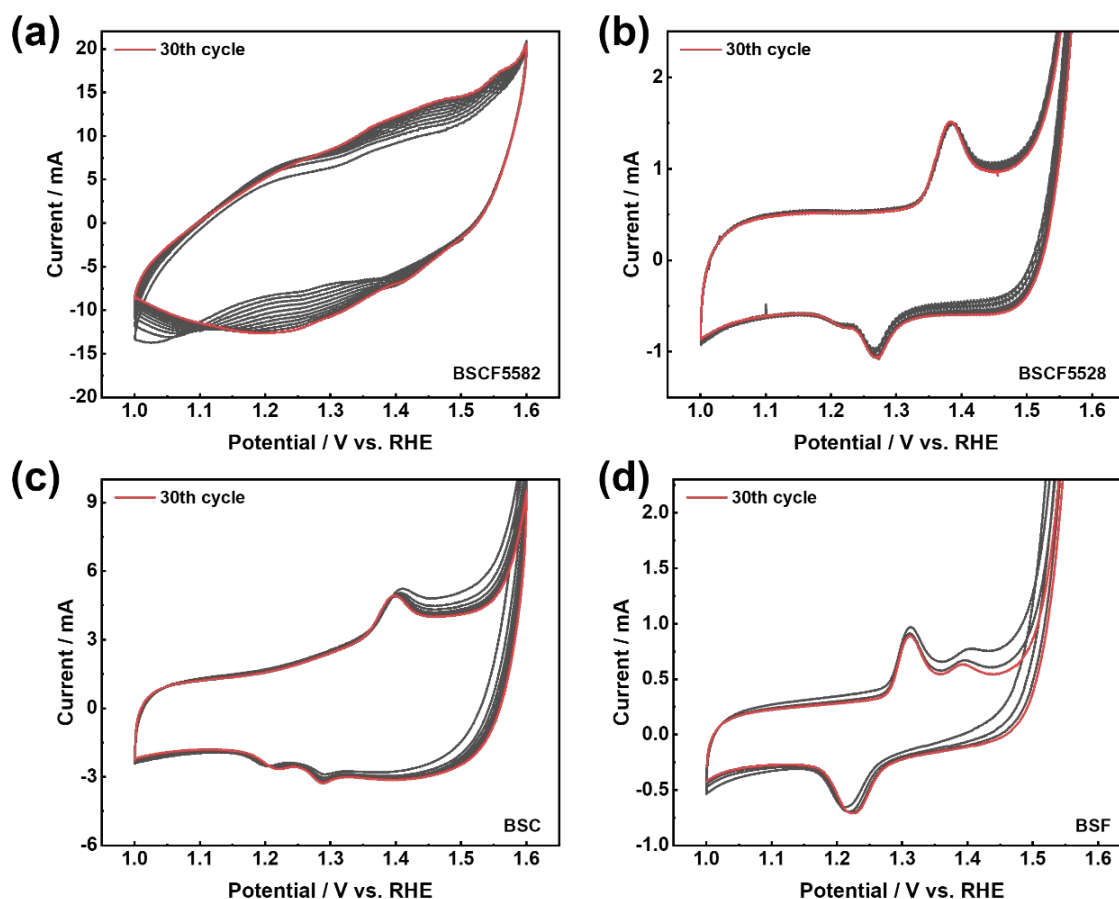


Figure 7-17. CV curves for (a) BSCF5582, (b) BSCF5528, (c) BSC and (d) BSF catalysts during 1st to 30th cycles.

Figures 7-13d and e present the OER activity for all four BSCF catalysts measured using the forced-flow cell and time-zero method, normalized by BET surface area. Within the potential range of 1.45 V to 1.75 V vs. RHE, BSCF5582 demonstrated the highest current density and the lowest Tafel slope among the catalysts. The OER catalytic activity of the BSCF series catalysts follows the order: BSCF5582 > BSCF5528 > BSC > BSF, consistent with results from the RDE method. Under accelerated degradation conditions, the OER durability of BSCF5528 and BSCF5582 was evaluated at 100 mA cm⁻² over different cycle numbers (Figure 7-18). After 600 cycles, BSCF5528 exhibited a significant decrease in OER activity (~81 mV), while BSCF5582 showed excellent stability with only a ~58 mV increase. This superior stability of BSCF5582 is attributed to the reversible surface reconstruction between Co/Fe spinel and Co/Fe oxyhydroxide under accelerated degradation conditions.¹¹

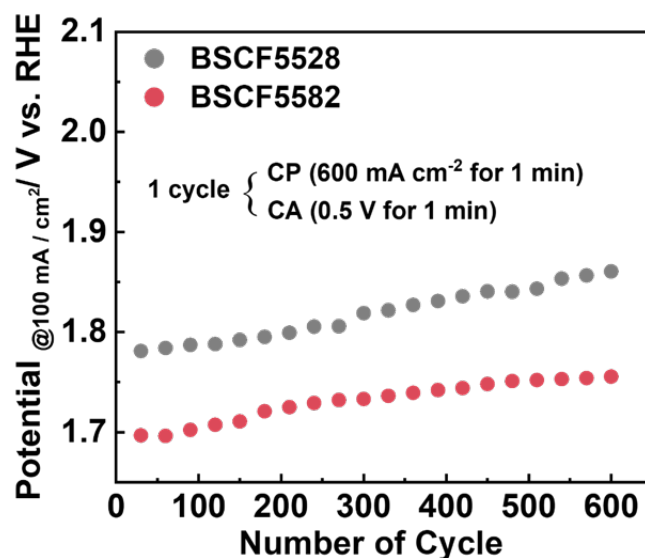
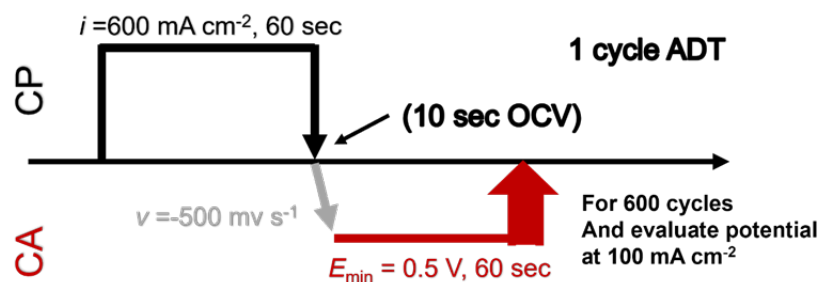


Figure 7-18. The anode potentials corresponding to current density of 100 mA cm^{-2} vs. ADT cycles of BSCF5528 and BSCF5582.

At the same applied potential, the current densities measured using the time-zero method were higher for all four samples compared to those obtained using the RDE method. This indicates that the time-zero method accurately assesses the intrinsic OER activity at the initial time of bubble generation, demonstrating its superiority in electrochemical measurement. The catalytic OER activity measured by both the RDE and time-zero methods exhibits a volcano-type relationship with the Fe doping level (denoted as $1-X$), as illustrated in Figure 7-19. This suggests that slight Fe doping ($1-X = 0.2$) enhances OER activity to an optimal level, beyond which the activity decreases. Thus, varying Fe doping levels result in different surface structures and electronic states, affecting the catalytic activity.

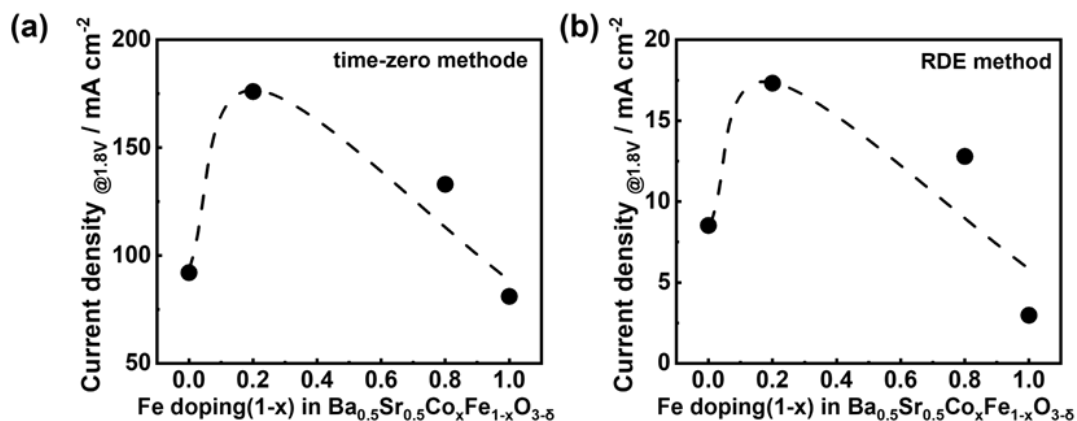


Figure 7-19. Volcano-like relationship of Fe-doping and OER activity measured by (a) *time-zero* method and (b) RDE method.

7.3.3 *operando* Co/Fe K and L-edge XAS measurement

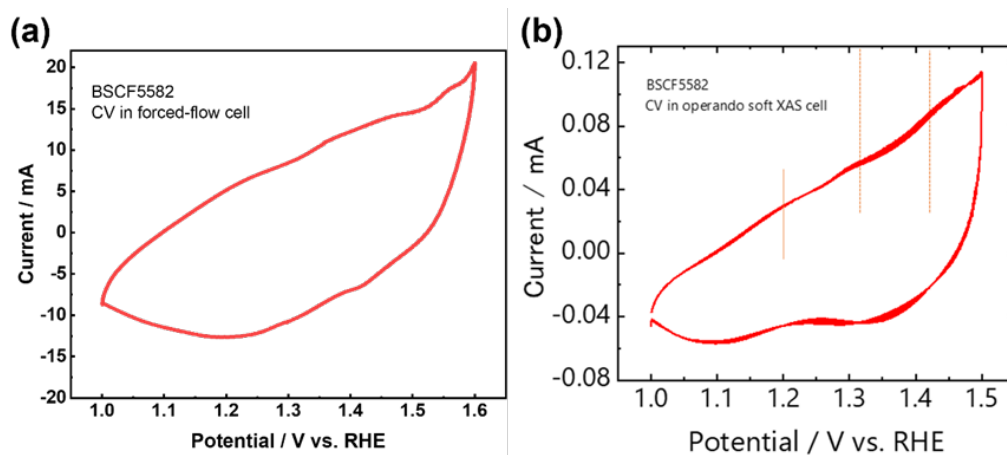


Figure 7-20. CV comparison of BSCF5582 in (a) forced-flow cell and (b) *operando* soft XAS cell

To elucidate the superior performance of BSCF5582 and the relationship between Fe substitution and OER activity, *operando* XAS measurements with a custom-built electrochemical cell were used, highlighting the essential role of *in situ/operando* techniques in identifying actual active sites due to changes in the electronic structure of Fe/Co surface under OER conditions.^{8, 9, 20} The CV curves of BSCF5582 obtained with the *operando* cell and a three-electrode RDE setup demonstrate consistent redox potentials and reliable current-potential relationships, confirming the *operando* method's effectiveness (Figure 7-20).

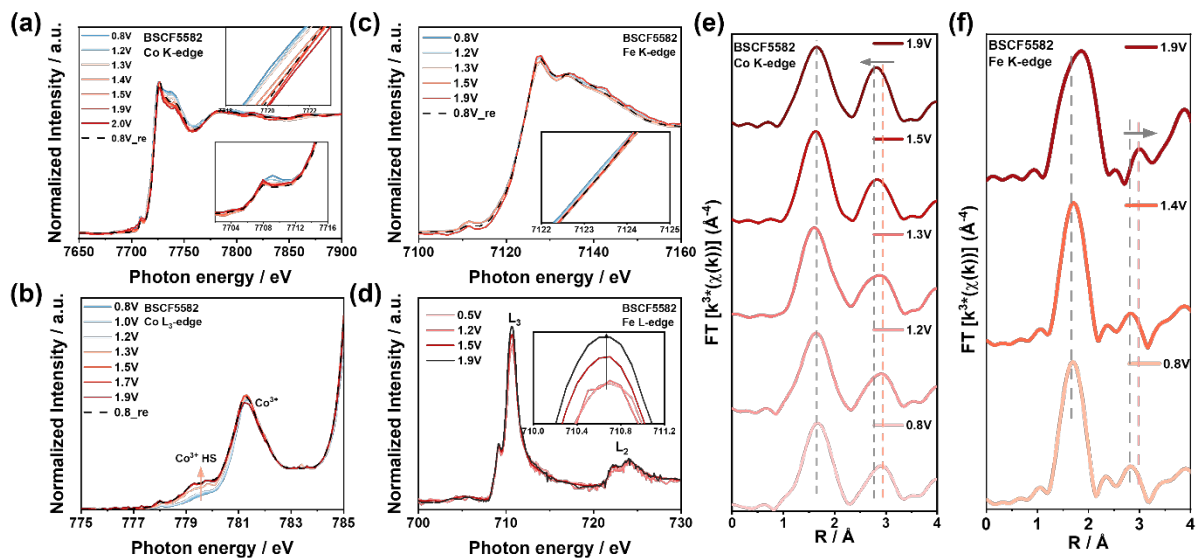


Figure 7-21. *operando* XAS for investigating the origin of OER activity of BSCF5582 under application of catalytic potential from 0.8 V to 1.9 V vs. RHE. (a) Co K-edge XANES and (b) Co L₃-edge XANES spectra. (c) Fe K-edge XANES and (d) Fe L-edge XANES spectra. (e) Fourier-transformed of the Co K-edge EXAFS spectra and (f) Fe K-edge EXAFS spectra.

The *operando* Co K-edge spectra of BSCF5582, shown in Figure 7-21a, indicate a consistent shift to higher energy levels with increasing OER potential, suggesting a continuous increase in the average oxidation state of Co.⁴⁸ This shift is more pronounced in BSCF5582 than in BSC (Figure 7-22a), correlating with higher OER activity attributed to minor Fe doping. The pre-edge peaks of BSCF5582 show a slight decrease, implying a transition of Co ions from T_d to O_h sites, further supported by FT-EXAFS spectra. Figure 7-21e reveals two overlapping peaks at ~ 2.8 Å and ~ 3.0 Å in the Co–Co/Fe coordination shells of BSCF5582, corresponding to $\text{Co}^{3+}(O_h)$ in Co/Fe oxyhydroxide and $\text{Co}^{2+}(T_d)$ in Co/Fe spinel-like structures.¹¹ During anodic polarization, a transition from $\text{Co}^{2+}(T_d)$ to $\text{Co}^{3+}(O_h)$ peaks was observed, indicating the growth of a self-assembled Co hydroxide layer, forming the actual active surface.⁸ This conclusion is further supported by the FT-EXAFS fitting results in Table S2. In contrast, BSC showed minimal growth at the ~ 2.8 Å scattering peak due to side oxide phase formation, inhibiting surface layer reconstruction (Figure 7-22c).¹⁶ Therefore, minor Fe doping promotes structural transformation of Co ions, and enhances the OER process with the formation of the active CoOOH surface layer.^{49, 50}

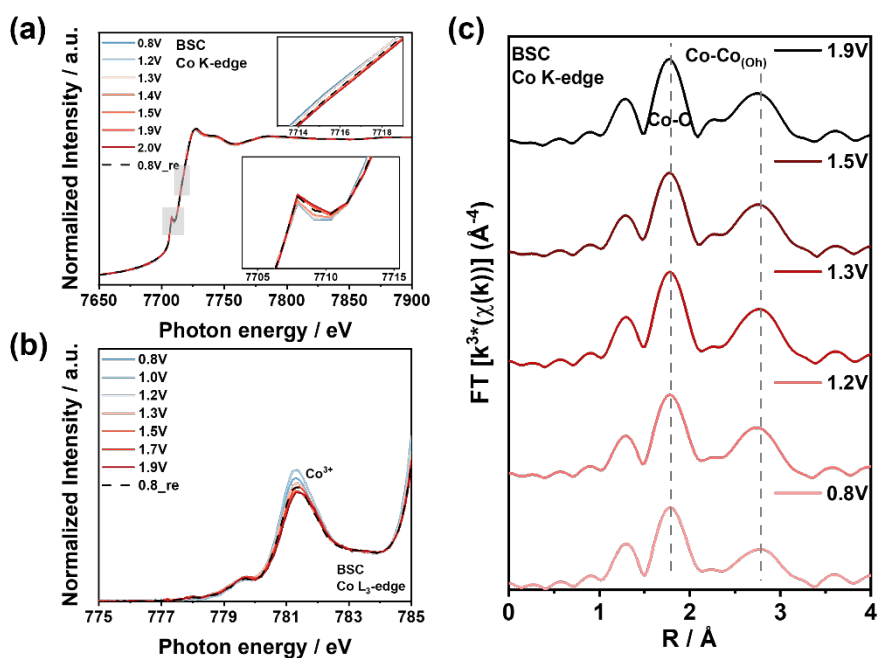


Figure 7-22. *operando* XAS for investigating the origin of OER activity of BSC under application of catalytic potential from 0.8 V to 1.9 V vs. RHE. (a) Co K-edge XANES and (b) Co L-edge XANES spectra. (c) Fourier-transformed of the Co K-edge EXAFS spectra.

Operando Fe K-edge measurements on BSCF5582 revealed a slight positive shift in the XANES energy position during increasing potential step, indicating a minor increase in the average oxidation state of Fe (Figure 7-21c). While many studies suggest that Fe enhances the activity of other transition metals without inherent changes,^{13, 28, 51} research by Boettcher et al. demonstrated that Fe can act as an active site in $\text{Co(Fe)O}_x\text{H}_y$ catalysts during OER.⁵² Therefore, further investigation is required to understand Fe's role in BSCF catalysts during the OER process. The FT-EXAFS spectra of BSCF5582 at different potentials showed a positive shift in the scattering paths at ~ 1.8 Å (Fe-O) and ~ 2.8 Å (Fe-Fe(O_h)) at 1.9 V vs. RHE, indicating an increase in average Fe-O bond length and structural transformation (Figure 7-21f). Studies have shown that average bond lengths in metal oxides during OER consist of metal sites coordinated with lattice oxygen (O^{2-}) and adsorbed OH^- species (M-OH).^{9, 53} When Fe participates in the reaction, it forms Fe-OH intermediates. Since O^{2-} carries more negative charge than OH^- , the Fe-OH bond length is relatively longer, leading to an increase in the average Fe-O bond length. Additionally, changes in the position of the Fe-Fe(O_h) scattering

peak were observed by comparing the FT-EXAFS spectra of FeOOH and Fe₃O₄ (Figure 7-23a). At high OER potentials, Fe undergoes a configuration change, resulting in the formation of FeOOH active sites. This suggests that while Fe serves an auxiliary role, it also actively participates in the reaction. However, due to the dominant role of Co sites, Fe's contribution is less pronounced at lower OER potentials.

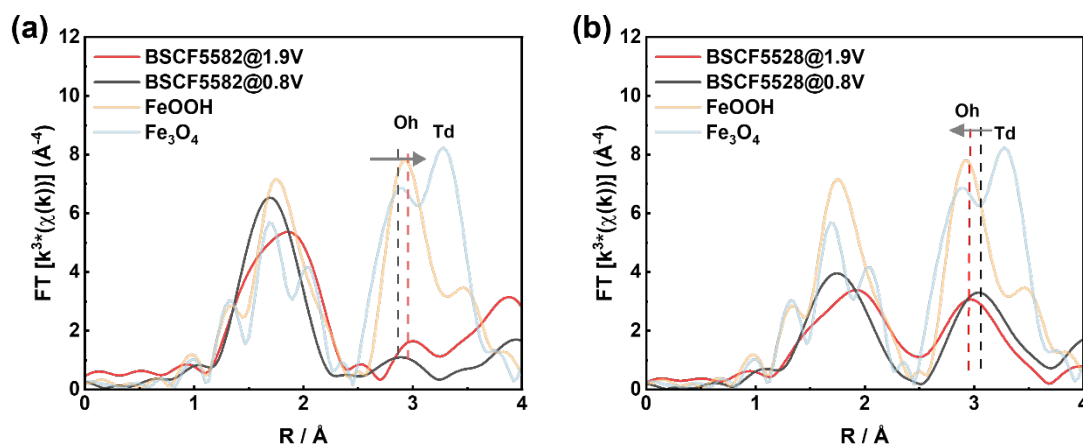


Figure 7-23. (a) Fourier-transformed of the *operando* Fe K-edge EXAFS spectra of FeOOH, Fe₃O₄, BSCF5582 at 0.8 V and 1.9 V vs. RHE. (b) Fourier-transformed of the *operando* Fe K-edge EXAFS spectra of FeOOH, Fe₃O₄, BSCF5528 at 0.8 V and 1.9 V vs. RHE.

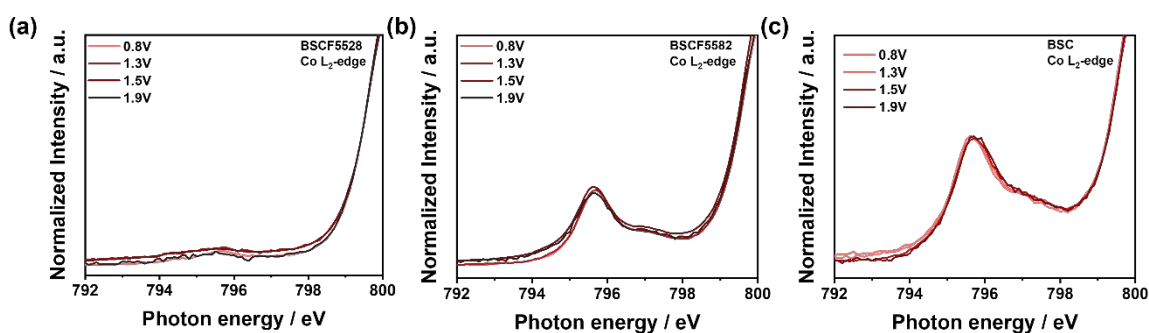


Figure 7-24. *operando* Co L₂-edge XANES spectra of (a) BSCF5528, (b) BSCF5582, and (c) BSC.

To gain deeper insights into the exceptional OER performance of BSCF5582, *operando* soft XAS was conducted using the surface-sensitive total electron yield (TEY) mode (~ 5 nm), which enabled a detailed characterization of the catalyst's surface electronic structure

evolution.^{22, 54} As shown in Figure 7-21b and 7-24, the Co L-edge spectra, dominated by the Co 2p to 3d transition, split into L₃ and L₂ edges due to spin-orbit coupling. The shape and normalized intensity of the L₃ edge depend on the Co 3d-3d interaction and the hybridization of Co 3d orbitals with O 2p orbitals, reflecting the symmetry and spin state.⁵⁵ Compared to the reference CoO, Co₃O₄, and CoOOH L₃ edges, the absorption peaks of BSCF5582 and BSC are attributed to the spin-orbit splitting of Co³⁺ 2p states (Figure 7-25a). In Figure 7-21b, the decreasing intensity of the low-spin (HS, $t_{2g}^6 e_g^0$, S = 0) Co³⁺ (*Oh*) peak (781.5 eV) with increasing potential indicates partial filling of the e_g orbitals, associated with the formation of Co³⁺ in high spin (HS, $t_{2g}^4 e_g^2$, S = 2) states.^{39, 55-57} Additionally, the increasing intensity of the Co³⁺ HS peak at approximately 780.0 eV with increasing potential confirms the formation of the high spin state,³⁹ a change not observed in BSC (Figure 7-22b). It has also been reported that the peak around 780.0 eV can be attributed to twofold metal-coordinated oxygen atoms (μ_2 -OH) bridging pairs of oxygen-coordinated high-spin Co³⁺ and Co²⁺ ions,⁵⁸ which will be further discussed in the *operando* O K-edge results.

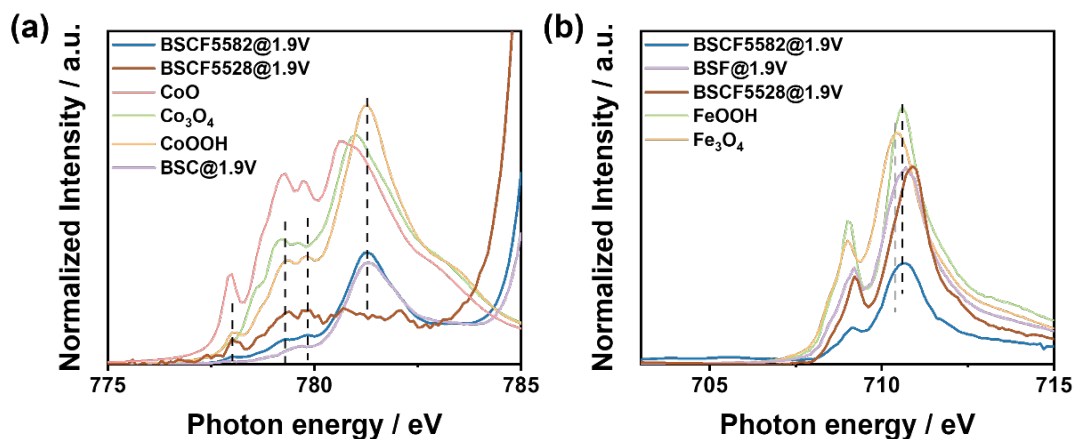


Figure 7-25. (a) *operando* Co L₃-edge XANES spectra at 1.9 V vs. RHE of BSCF5582, BSCF5582, BSC, Co₃O₄, CoO and CoOOH. (b) *operando* Fe L₃-edge XANES spectra at 1.9 V vs. RHE of BSCF5582, BSCF5582, BSC, Fe₃O₄, and FeOOH.

Some research indicates that the apex-to-apex e_g orbital electron transfer in high spin Co³⁺ is faster,⁵⁹ facilitating OH and OOH adsorption, thus reducing overpotential and enhancing OER activity.⁵⁵ Zhang et al. showed that Fe heterojunction doping adjusts Co materials to the

HS state,⁶⁰ and Lee et al. reported an increase in Co spin state during the OER process in Fe-CoOOH.⁶¹ Consequently, Fe doping in BSCF5582 promotes more Co³⁺ HS formation during OER, leading to superior OER activity compared to BSC.

Figure 7-21d displays the Fe L_{3,2}-edge spectra of BSCF5582 at different potentials. The two split peaks near ~710 eV correspond to the transitions of 2p electrons to 3d *t*_{2g} orbitals (~709 eV, A peak) and 3d *e*_g orbitals (~711 eV, B peak) in an octahedral site.⁶² The dominance of the B peak in all spectra, compared to the reference Fe₃O₄ and FeOOH, indicates the typical Fe³⁺ oxidation state (Figure 7-25b). According to Cramer's research, an L₃ / (L₃ + L₂) value above 0.75 indicates a high spin state for iron.⁶³ All calculated L₃ / (L₃ + L₂) values exceeding 0.8 suggest that Fe³⁺ is in a high spin state (*t*_{2g}³ *e*_g²) in the catalyst. Although no significant energy shift in the Fe L-edge was observed, the B/A peak intensity ratio varied with different potentials, reflecting the number of holes in the *t*_{2g} and *e*_g orbitals.⁶⁴ In high spin Fe³⁺, electrons are preferentially removed from the *e*_g state during oxidation, leading to a stronger B peak transition.²² The increasing B/A intensity ratio with potential indicates minor oxidation of Fe during OER, further confirming that Fe not only aids in enhancing Co activity but also directly participates in the reaction.

The exceptional OER activity of BSCF5582 can be attributed to several key factors related to its crystal configuration and spin states: (1) Minor Fe doping preferentially occupies octahedral sites, forming Co²⁺(*T_d*)–O–Fe³⁺(*O_h*), which modulates the electronic state of Co³⁺(*O_h*).³⁷ As the potential increases, Co²⁺(*T_d*) transitions to Co³⁺(*O_h*) with forming CoOOH, serving as active sites during the OER process. (2) High-spin Co³⁺ forms with increasing potential, enhancing electron transfer and facilitating the adsorption of OH and OOH intermediates. (3) Fe in BSCF5582 is in a high-spin state and undergoes slight oxidation during the OER process. This high-spin state of Fe supports the catalytic process by forming FeOOH active sites and enhancing the reactivity of Co sites.

operando XAS analysis on BSCF5528 revealed a distinct OER reaction mechanism compared to BSCF5582. *operando* Co K-edge and FT-EXAFS analysis indicated that Co³⁺ in BSCF5528 did not experience significant changes in oxidation state or configuration (Figures

7-26a, e and Table 7-3). This stability is due to heavy Fe doping, where Fe^{3+} occupies both tetrahedral and octahedral sites, keeping Co^{3+} primarily in octahedral sites.³⁷ Additionally, the lower electron density of $\text{Fe}^{3+}(\text{O}_h)$ in the t_{2g} orbitals reduces electron-electron repulsion between $\text{Fe}^{3+}(\text{O}_h)$ and O 2p πu orbitals, lowering the energy level and inhibiting further oxidation of Co^{3+} .²⁸ *operando* Co L-edge results showed that Co^{3+} in BSCF5528 consistently exhibited a high spin state, with the proportion of high-spin Co^{3+} increasing with potential, thus providing more active sites for OER (Figure 7-26b and Figure 7-25a).

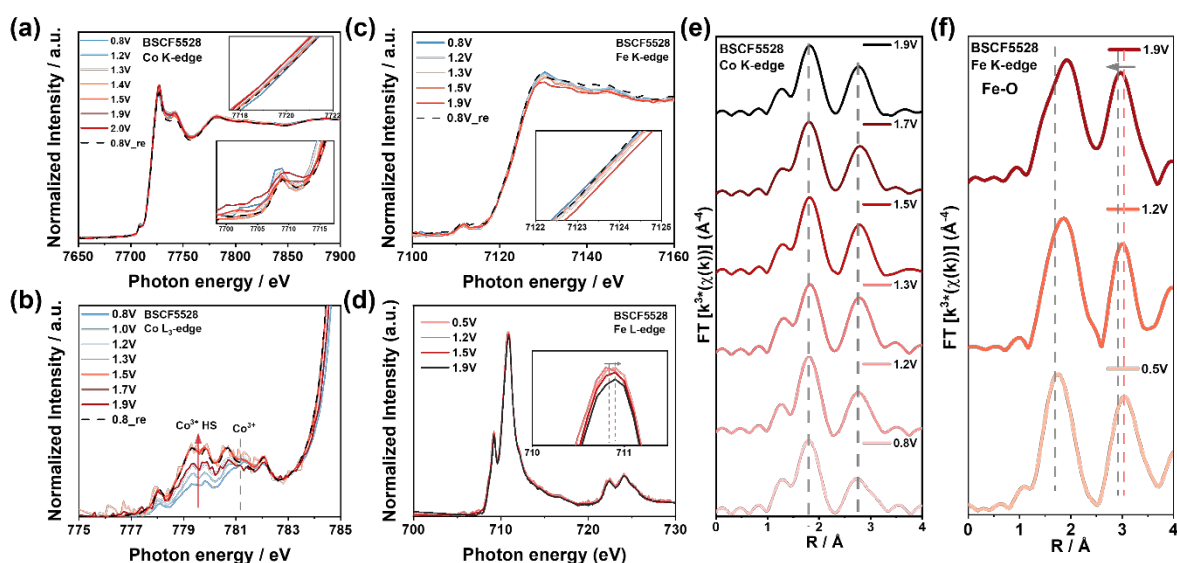


Figure 7-26. *operando* XAS for investigating the origin of OER activity of BSCF5528 under application of catalytic potential from 0.8 V to 1.9 V vs. RHE. (a) Co K-edge XANES and (b) Co L₃-edge XANES spectra. (c) Fe K-edge XANES and (d) Fe L-edge XANES spectra. (e) Fourier-transformed of the Co K-edge EXAFS spectra and (f) Fe K-edge EXAFS spectra.

Fe serves as a critical reaction site in BSCF5528. *operando* Fe K-edge and L-edge analysis revealed that Fe^{3+} undergoes further oxidation at high potentials, forming a $\text{Fe}^{3+\delta}$ oxidation state as indicated by standard FeOOH spectra (Figures 7-26c, d and Figure 7-25b). FT-EXAFS spectra showed that Fe^{3+} also experiences configuration changes during OER (Figure 7-26f), with initial $\text{Fe}^{3+}(\text{T}_d)$ transitioning to $\text{Fe}^{3+}(\text{O}_h)$ at high potentials, contributing to FeOOH formation and causing a slight negative shift in the scattering peak around ~ 3.0 Å (Figure 7-23b). Additionally, the Fe-O peak (~ 1.8 Å) shifts positively at lower potentials (1.2V vs. RHE),

indicating the formation of Fe-OH intermediates, a phenomenon observed only near 1.9V vs. RHE in BSCF5582 (Figure 7-26f). Thus, Fe in BSCF5528 acts as a significant reaction site, actively participating in the OER process alongside high-spin Co^{3+} .

During the OER process in BSCF5528, Co^{3+} remains primarily in octahedral sites without significant oxidation state or configuration changes due to heavy Fe doping, stabilizing Co^{3+} in a high-spin state and increasing the number of active sites as the potential rises. Meanwhile, Fe^{3+} transitions from tetrahedral to octahedral sites at high potentials, forming FeOOH and further oxidizing to $\text{Fe}^{3+\delta}$. These changes enhance electron transfer and the formation of reactive intermediates, significantly promoting OER activity. However, BSCF5528 exhibits lower activity compared to BSCF5582, as Co(Fe)OOH in BSCF5582 generally has higher OER activity than Fe(Co)OOH in BSCF5528. CoOOH has better electronic conductivity and a more favorable electronic structure, facilitating the adsorption and evolution of oxygen intermediates during OER.⁶⁵ Additionally, although BSCF5528 has more high spin Co^{3+} activity sites ratio, the overall lower Co content limits the number of active sites, reducing its effectiveness compared to BSCF5582.

7.3.4 *operando* O K-edge XAS measurement

Most OER reaction mechanisms involve the formation of O-O bonds through bulk water nucleophilic attack (BWNA), occurring at the terminal or bridging oxygen (marked $\mu\text{-O}$) sites.^{66, 67} Arno Bergman et al. identified a unified chemical structure where $\mu_2\text{-OH}$ bridged $\text{Co}^{2+/3+}$ ion clusters form on three-dimensional cross-linked and layered $\text{CoO}_x(\text{OH})_y$ precursors.⁵⁸ Therefore, *operando* O K-edge spectroscopy is essential for understanding the reaction mechanisms, identifying active sites, and examining the structural response of the catalyst during the OER process.

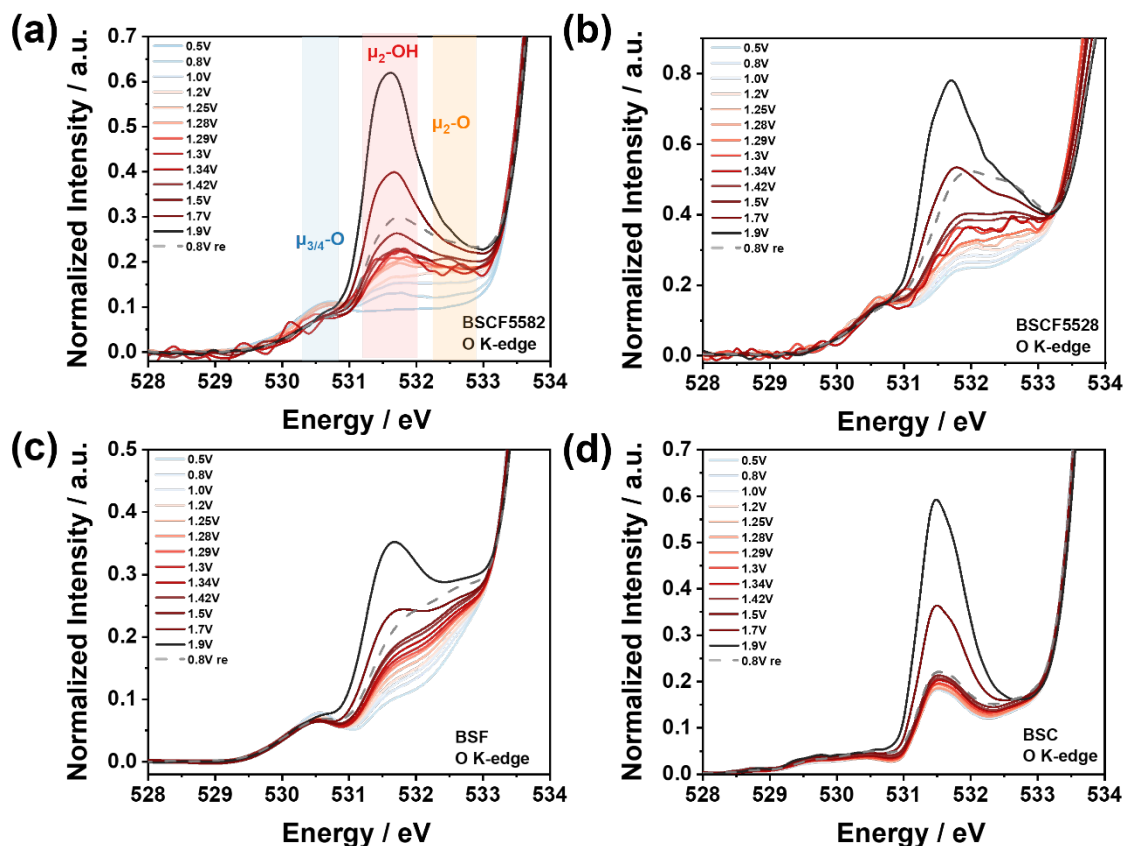
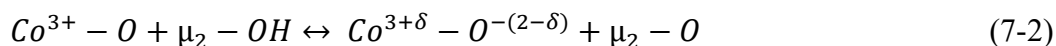


Figure 7-27. *operando* O K-edge XAS spectra of (a) BSCF5582, (b) BSCF5528, (c) BSF and (d) BSC. The spectra were recorded using the TEY detection mode.

Under OER conditions, hybridization between O 2p and TM 3d orbitals is observed in the pre-edge of the O K-edge XANES spectra below 534.0 eV (Figure 7-27). The experimental O K-edge XANES spectra of BSCF catalysts, recorded in TEY mode at different OER potentials, show energy resonance around 530.5 eV attributed to $\text{Fe}^{3+}/\text{Co}^{3+}\text{-O}$ hybridized states with oxygen ions three- or fourfold metal-coordinated (blue: $\mu_{3/4}\text{-O}$). The resonance around 531.5 eV corresponds to protonated, double metal-coordinated oxygen atoms ($\mu_2\text{-OH}$) bridging oxygen-coordinated high-spin Fe^{3+} , Co^{3+} , or Co^{2+} ions, typically found at edges, corners, and metal vacancies in the $\text{Co}(\text{Fe})\text{O}_x(\text{OH})_y$ domains.^{68, 69 70} The resonance around 532.5 eV is associated with $\mu_2\text{-O}$ (orange) formed after $\mu_2\text{-OH}$ deprotonation.⁵⁸



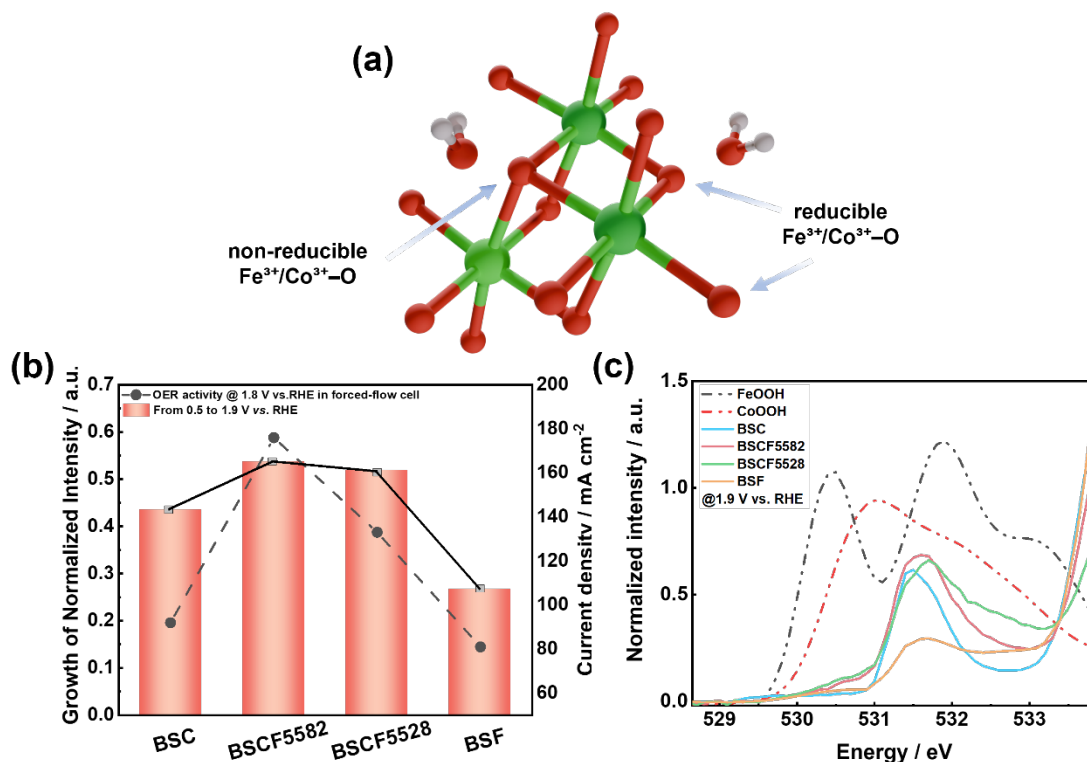


Figure 7-28. (a) Structure model of Co(Fe)OOH . The Co/Fe atoms, O atoms and H atoms are shown in green, red and gray. (b) The relationship between growth of normalized intensity and OER activity in forced-flow cell. (c) Pre-edge of ex-situ O K-edge XAS spectra of CoOOH and FeOOH , as well as pre-edge of *operando* O K-edge XAS spectra of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x=0, 0.2, 0.8, 1$) at 1.9V vs. RHE.

As the OER potential increases, the peak intensity at 530.5 eV remains relatively unchanged, indicating that these electrochemically non-reducible $\text{Fe}^{3+}/\text{Co}^{3+}-\text{O}$ sites have a limited contribution to OER activity (Figure 7-28a). However, a slight decrease in peak intensity was observed in BSCF5582 and BSCF5528 (Figure 7-27a and b), which is associated with a reduction in low-spin Co^{3+} ,⁵⁸ consistent with *operando* Co L-edge results. During the formation of O–O bonds and the eventual generation of molecular oxygen, both terminal oxygen sites and $\mu_2\text{-O(H)}$ ligands are crucial for catalytic activity, enabling the deprotonation of water molecules during BWNA. As the potential increases, the peak intensities at 531.5 eV and 533.0 eV increase significantly. Integrating the peak areas reveals a volcano-shaped trend from 0.5 V

to 1.9 V vs. RHE (BSCF5582 > BSCF5528 > BSC > BSF), consistent with OER activity trends (Figure 7-28b and 7-29). These reducible $\text{Fe}^{3+}/\text{Co}^{3+}\text{-O}$ sites, attributed to $\mu_2\text{-OH}$ bridges between two electronically coupled high-spin metal ions, are highly favorable for fast OER process. Additionally, comparing the O K-edge XANES spectra of the four BSCF catalysts at 1.9 V vs. RHE shows that Fe doping effectively regulates the coordination environment and bonding state of Co/Fe-O, causing a slight shift in the $\mu_2\text{-OH}$ peak position, thereby impacting OER activity (Figure 7-28c).

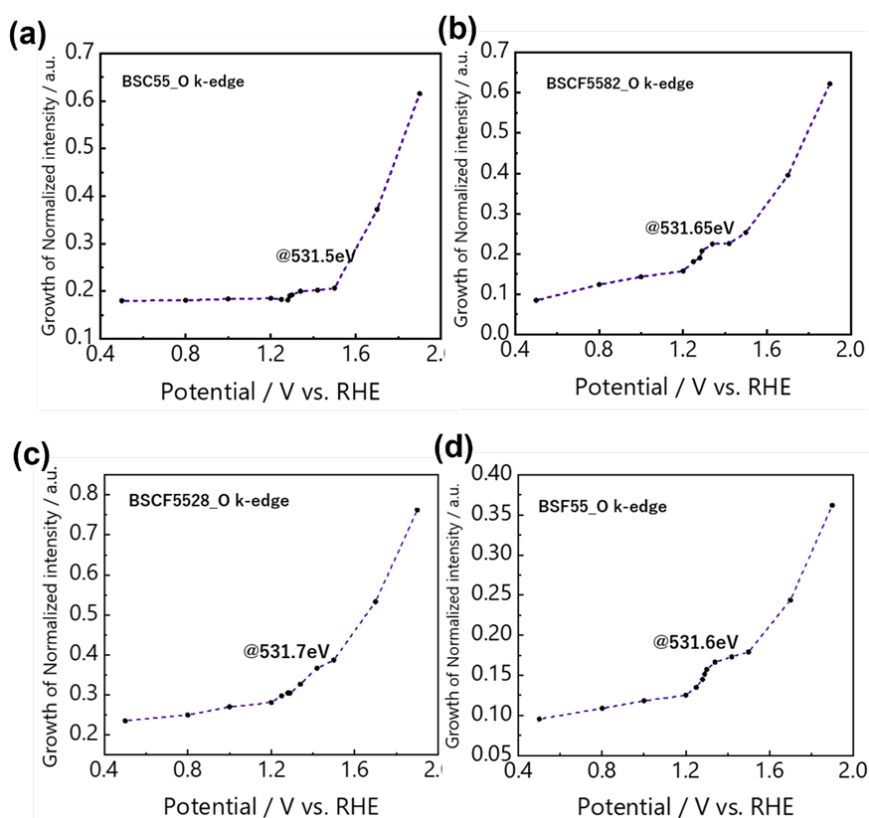


Figure 7-29. Normalized *operando* O K-edge intensity growth with applied potential for (a) BSC, (b) BSCF5582, (c) BSCF5528 and (d) BSF.

Many research has investigated the reversible structural transformation between spinel and oxyhydroxide phases in BSCF catalysts during the OER process.^{8, 11} Chen et al. observed that the ratio of coordination numbers between octahedral and tetrahedral sites increases in the oxidation region and decreases during reduction. This indicates that $\text{Co}^{3+}(\text{Oh})$ in the oxyhydroxide phase can revert to either $\text{Co}^{2+}(\text{Td})$ (active site) or $\text{Co}^{3+}(\text{Oh})$ (inactive site) in the

initial cobalt oxides.²⁸ This multipath conversion can interfere with the overall activation process, as the random migration of Co ions may render the original active sites inactive. *operando* Co/Fe K-edge, L-edge, and O K-edge measurement (dash line of 0.8 V_{re} in Figures 7-21, 7-26 and 7-27) further verified that only a portion of Co and Fe undergo reversible structural transformation. Moreover, minor Fe doping significantly suppresses the conversion of Co³⁺ to inactive sites due to the geometric site confinement effect of iron ions, thus forcing the restoration of Co²⁺(*Td*) and maintaining continuous activation of these sites. This result is further supported by comparing the O 1s XPS spectra before and after the OER (Figure 7-30). A noticeable shift of the main peak towards lower binding energy in the BSCF5528 catalyst after OER indicates the formation of more inactive lattice oxygen, exhibits poor structural reversibility.

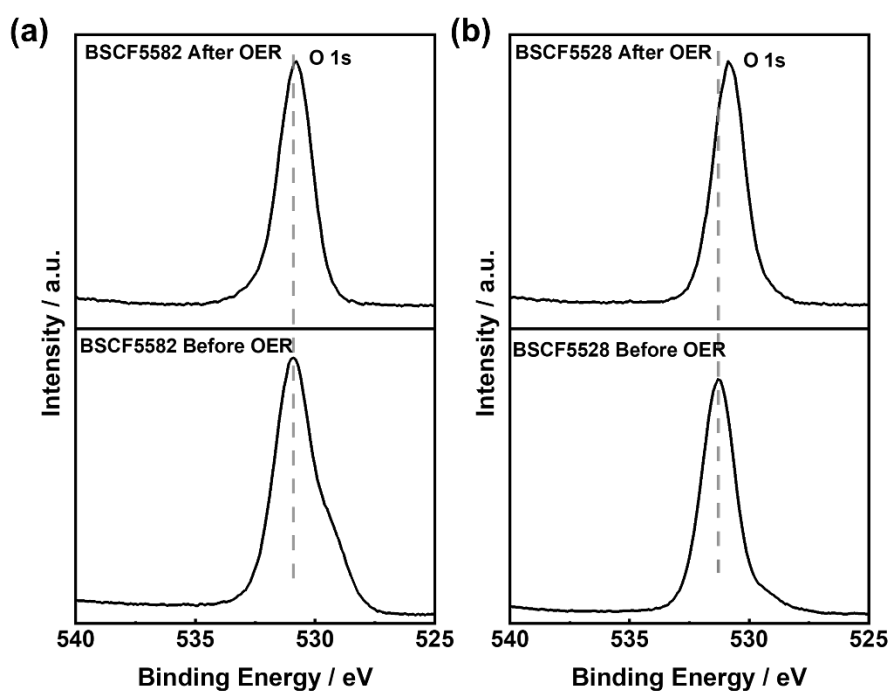


Figure 7-30. O 1s XPS spectra of (a) BSCF5582 and (b) BSCF5528 before and after OER.

EXAFS fitting detail

The following CIF-files were used to generated the models for the fit (ICSD collection code is given in brackets): CoOOH(22285), Co₃O₄ (27497), and FeOOH(239322). The corresponding R space curve fitting results of Co/Fe K-edge for the BSCF5582 and BSCF5528

catalysts (Figure 7-31 and 7-32). Fitting details: S_0^2 was fixed at 0.80, which was obtained by fitting the reference foils. Fits were undergone in R-space for $1.0 \leq R \leq 3.0$ Å, and the k^3 weighting for $\Delta k = 3 - 10$ Å⁻¹.

In Table S3 and S4, the coordination number of Co-O (CN_{Co-O}) for both BSC and BSCF increase with applied potential, indicating the development of additional Co–O coordination in Co-O(OH) species during the OER process. The changes in CN_{Co-Co} values reflect the formation and evolution of Co–Co coordination shells. The two Co–Co peaks observed at approximately 2.87-2.89 Å and 2.96-2.99 Å correspond to Co-Co(OH) and Co-Co(Td) coordination, denoted as CN_{Oh} and CN_{Td} , respectively. In BSCF5582, the growth of Co-O(OH) species during anodic polarization leads to an increase in CN_{Oh} and a decrease in CN_{Td} . The elongation of the Fe-O bond length from 1.92 to 2.01 Å is attributed to the formation of Fe-OH intermediates, while the increase in Fe-Fe(OH) distance from 3.01 to 3.07 Å indicates a transition from Fe₃O₄ to FeOOH configuration. In contrast, BSCF5528 shows only minor changes in the coordination numbers of both Co–Co shells during anodic polarization. Additionally, the shortening of the Fe-Fe(OH) bond length from 3.11 to 3.06 Å suggests a partial transition of Fe³⁺ from Td to Oh sites, associated with the formation of FeOOH as the primary active site.

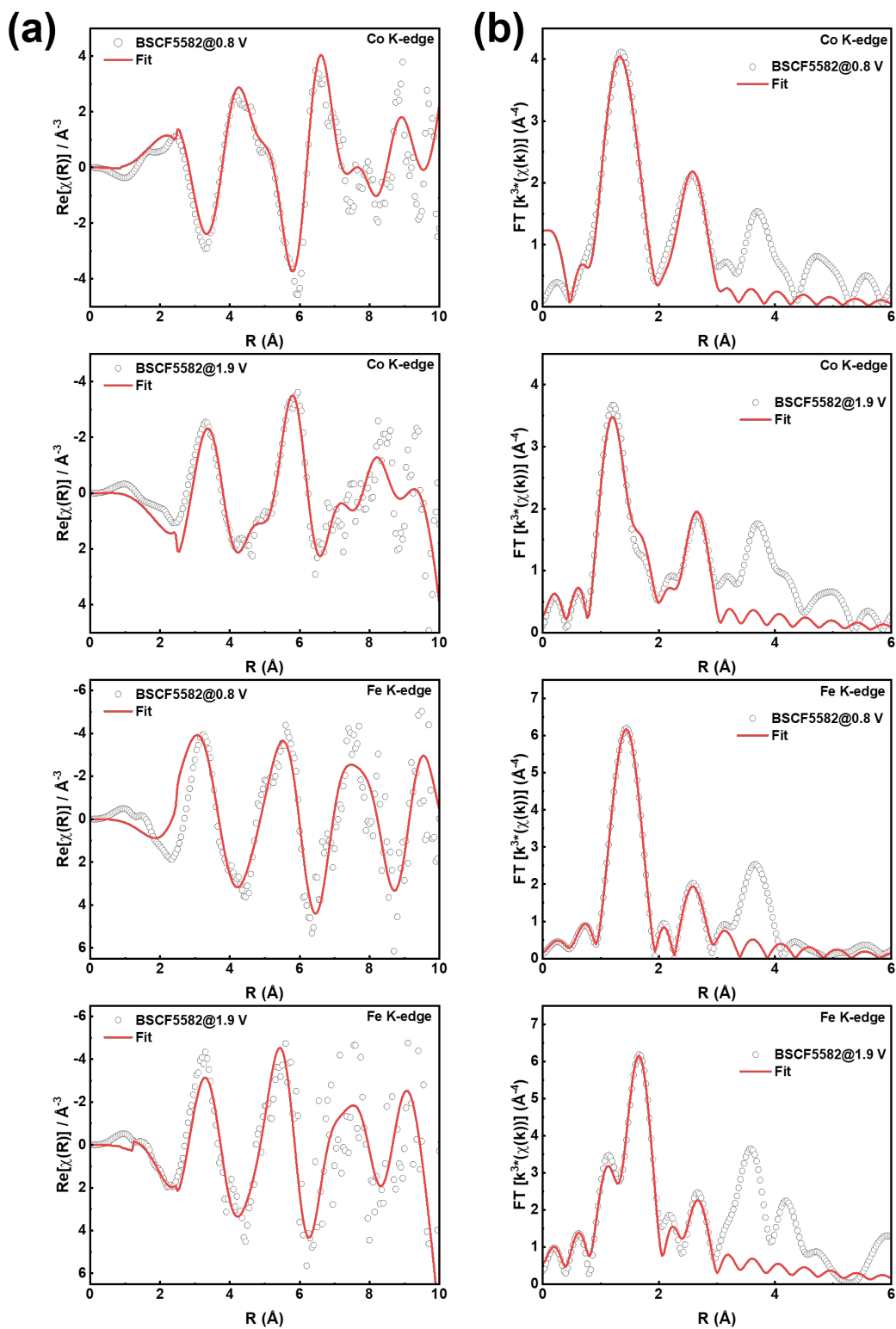


Figure 7-31. Co and Fe K-edge EXAFS fitting curves in R-space and k-space for BSCF5582.

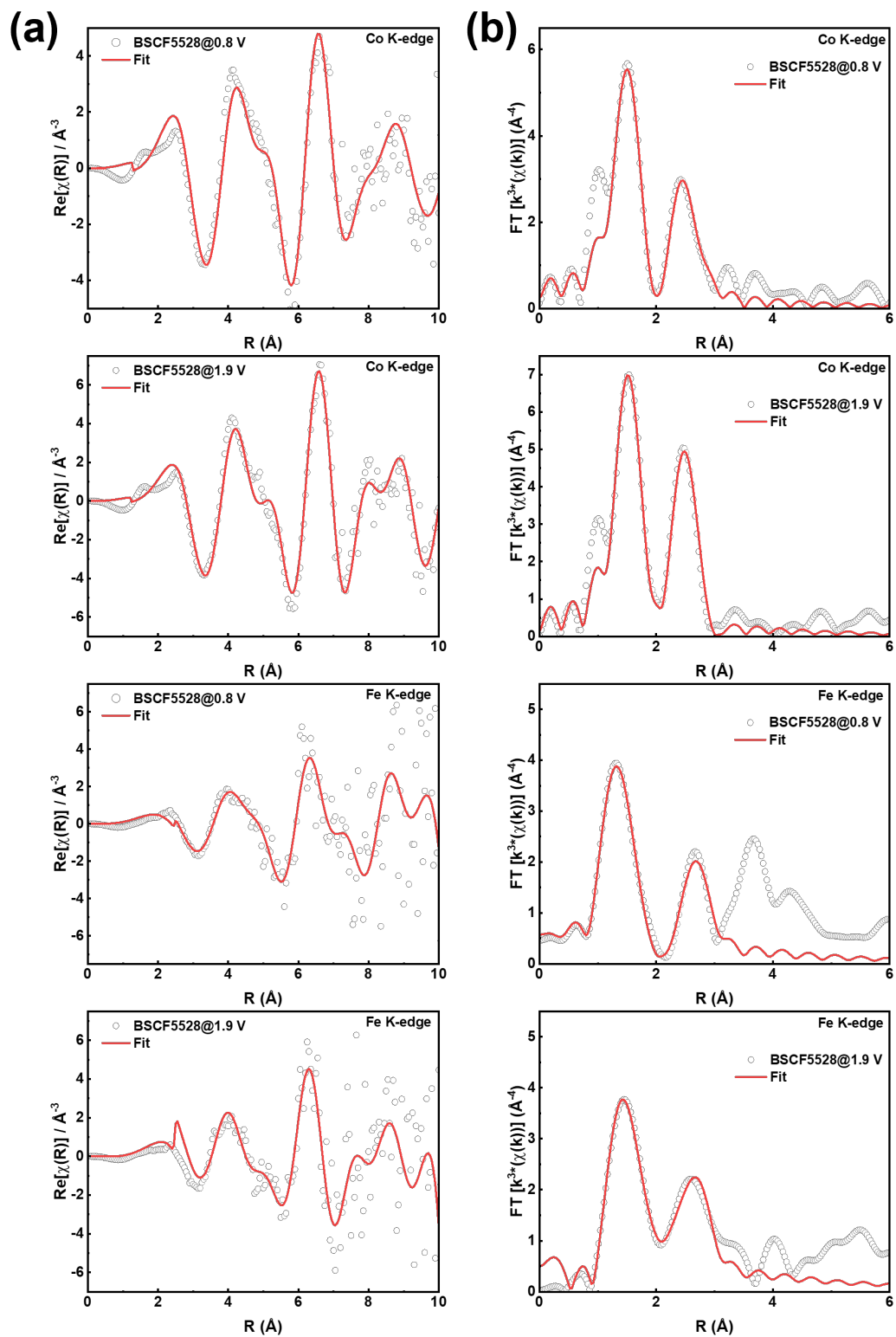


Figure 7-32. Co and Fe K-edge EXAFS fitting curves in R-space and k-space for BSCF5528.

Table 7-3. The corresponding R space curve fitting results of Co and Fe K-edge for the BSCF5582 catalysts varying different potential

BSCF5582	Shell	CN	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R factor
0.8 V	Co-O	3.4(3)	1.89(5)	0.008	0.11	0.006
	Co-Co _(Oh)	5.0(2)	2.87(4)	0.029	0.07	
	Co-Co _(Td)	3.3(5)	2.97(5)	0.015	-2.51	
1.9 V	Co-O	4.4(6)	1.86(3)	0.016	-0.45	0.016
	Co-Co _(Oh)	6.1(2)	2.88(7)	0.036	0.07	
	Co-Co _(Td)	2.2(5)	2.96(7)	0.018	0.02	
0.8 V	Fe-O	4.0(5)	1.92(6)	0.004	-6.23	0.002
	Fe-Fe _(Oh)	0.9(8)	3.01(5)	0.006	-1.65	
1.9 V	Fe-O	3.2(4)	2.01(8)	0.005	5.91	0.028
	Fe-Fe _(Oh)	2.5(9)	3.07(7)	0.007	-1.20	

Table 7-4. The corresponding R space curve fitting results of Co and Fe K-edge for the BSCF5528 catalysts varying different potential

BSCF5528	Shell	CN	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R factor
0.8 V	Co-O	3.1(6)	1.93(8)	0.006	6.28	0.027
	Co-Co _(Oh)	6.4(6)	2.89(7)	0.009	0.07	
	Co-Co _(Td)	1.2(4)	2.98(7)	0.002	4.59	
1.9 V	Co-O	3.3(3)	1.94(5)	0.003	5.87	0.009
	Co-Co _(Oh)	6.6(2)	2.88(3)	0.015	0.01	
	Co-Co _(Td)	1.1(5)	2.99(3)	0.039	4.59	
0.8 V	Fe-O	2.1(7)	1.93(4)	0.003	-6.00	0.014
	Fe-Fe _(Oh)	1.5(7)	3.11(7)	0.006	-1.65	
1.9 V	Fe-O	2.2(8)	2.03(3)	0.001	0.62	0.001
	Fe-Fe _(Oh)	2.7(6)	3.06(8)	0.010	-1.58	

7.4 Conclusion

The study synthesized and characterized four different $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0, 0.2, 0.8, 1$) catalysts with varying Fe doping levels to evaluate their OER performance using RDE and forced-flow cell techniques. Employing advanced *operando* XAS, including Co/Fe K-edge, Co/Fe L-edge, and O K-edge measurements, the dynamic structural and electronic changes of the catalysts during OER were thoroughly investigated. The results demonstrate that the outstanding OER performance of BSCF catalysts, particularly BSCF5582, is primarily due to the unique interplay of their crystal structure and spin states. Minor Fe doping preferentially occupies octahedral sites, influencing the electronic state of Co^{3+} . As the applied potential increases, $\text{Co}^{2+}(T_d)$ transitions to $\text{Co}^{3+}(O_h)$, forming CoOOH and creating active sites for the OER process. Additionally, Fe promotes the formation of high-spin Co^{3+} , enhancing electron transfer and the adsorption of intermediates like OH and OOH. In contrast, BSCF5528, with significant Fe doping, stabilizes Co^{3+} in octahedral sites without notable changes in oxidation state, leading to lower overall activity due to a less favorable electronic structure and reduced Co content. Fe^{3+} transitions from T_d to O_h sites at high potentials, forming FeOOH and further oxidizing to $\text{Fe}^{3+\delta}$, acting as a primary reaction site for OER. *operando* O K-edge XAS analysis reveals that the formation of reducible $\text{Fe}^{3+}/\text{Co}^{3+}\text{-O}$ sites, particularly $\mu_2\text{-O(H)}$ bridges between high-spin Co/Fe ions, significantly enhances OER electrocatalysis, with Fe doping effectively regulating the coordination environment and bonding states, thereby affecting overall activity. This comprehensive analysis underscores the pivotal role of Fe doping in enhancing the OER catalytic performance of BSCF catalysts, offering valuable insights for the design and development of efficient OER electrocatalysts.

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Chapter 8. General Conclusion

Advancing energy conversion technologies such as fuel cells and water electrolysis hinges on the development of efficient and stable electrocatalysts. This thesis focuses on the design, synthesis, and characterization of novel catalytic materials to enhance the ORR in fuel cells and the OER in water electrolysis. We investigated a series of catalysts, including Pd@Pt core–shell nanowires, PtNi nanowires, PtCoNi ternary intermetallic nanowires, IrO_x catalysts, iridium-based perovskite oxides, and BSCF materials. By employing advanced synthesis methods and characterization techniques such as *operando* XAS, PDF analysis, and theoretical calculations, we explored how the structural and electronic properties of these catalysts enhance their catalytic activity and stability. By elucidating the structure–activity–stability relationships of these catalysts under different electrochemical conditions, we aim to design catalysts with excellent performance and durability, thereby improving the efficiency of fuel cells and promoting the sustainable development of hydrogen production through water electrolysis.

Chapter 2 explores the synthesis and enhanced ORR performance of Pd@Pt core–shell nanowire catalysts. By utilizing a modified galvanic cell method, the study achieves uniform Pt shell coverage on Pd nanowires, circumventing the need for complex control systems required by the Cu-UPD method. The Pd@Pt nanowires, characterized by advanced techniques such as *operando* XAS, demonstrate superior ORR mass and specific activities, along with shortened Pt–Pt bonds and reduced oxygen binding energy. These structural and electronic features contribute to the catalyst's increased stability and activity, presenting a promising strategy for ORR applications in fuel cells.

Chapter 3 focuses on the development and analysis of ORR catalysts based on PtNi nanowires. By post-annealing PtNi nanowires with high nickel content, a platinum-rich surface layer is formed, enhancing the catalyst's stability and activity. Techniques such as PDF analysis and *operando* XAS were employed to deeply investigate the catalyst's structural and electronic states. The study found that the Pt-rich surface effectively suppresses Pt oxidation and Ni

dissolution at high potentials, significantly improving the ORR specific activity. This research provides valuable structural insights and optimization strategies for the design of future low-platinum catalysts.

Chapter 4 investigates the application of PtCoNi ternary intermetallic nanowires as ORR catalysts in PEMFCs. Through wet chemical synthesis, PtCoNi nanowires with an $L1_0$ ordered structure were obtained, exhibiting excellent ORR activity and stability. Advanced characterization techniques, including HERFD-XAS, revealed the dynamic changes in the electronic structure and coordination environment of the catalyst during the reaction. The structural characteristics of the $L1_0$ phase effectively suppress Pt oxidation and maintain the stability of Co and Ni. Electrochemical tests demonstrating good electrocatalytic performance and durability, highlighting its potential for practical fuel cell applications.

Chapter 5 examines the effects of structure and anion environment on the performance of IrO_x catalysts in the OER. Using *operando* XAS and PDF analysis, the behaviors of amorphous SA3.5 and crystalline SA58 IrO_x were tested under different acidic conditions. The study showed that the amorphous SA3.5, rich in low-coordination unsaturated sites, exhibits high OER activity but suffers from decreased stability due to anion poisoning. In contrast, the crystalline SA58 displays higher stability but lower catalytic activity. DFT calculations further revealed the impact of anion adsorption, particularly how phosphate anions increase the oxidation state of iridium, thereby reducing OER efficiency. The results elucidate the relationship between structure, activity, and stability in IrO_x catalysts, providing new guidance for the design of next-generation electrocatalysts for sustainable hydrogen production.

Chapter 6 focuses on the study of iridium-based perovskite oxides as OER catalysts, primarily using *operando* XAS to reveal their structure–activity relationships. Four iridium-based perovskite oxides with different structures (9R- BaIrO_3 , 6H- SrIrO_3 , 3C- SrIrO_3 , and BCC- SrIrO_3) were synthesized, and their OER performances were tested under HClO_4 solution. The results showed that 9R- BaIrO_3 exhibits the best performance in terms of low overpotential and good durability. Its excellent performance is attributed to the unique face-sharing $[\text{IrO}_6]$ octahedral trimer structure and significant surface hydroxylation. *Operando* XAS analyses at

the Ir L₃-edge and O K-edge revealed that changes in the oxidation state of iridium species and the shortening of Ir–O bonds are crucial to catalytic activity.

Chapter 7 investigates the activity mechanism of Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-δ} (BSCF) as an OER catalyst in alkaline media, particularly exploring the effects of Co and Fe elements at different doping concentrations on catalytic performance. Electrochemical tests of the BSCF series catalysts were conducted using RDE and a newly proposed forced-flow cell method. It was observed that appropriate Fe doping significantly enhances the OER activity of BSCF. Additionally, *operando* XAS techniques—including Co/Fe K-edge and L-edge as well as surface-sensitive O K-edge measurements—were used to deeply analyze the dynamic changes in the structure and electronic states of BSCF catalysts during the reaction. The study indicates that a small amount of Fe doping promotes the formation of high-spin Co ions and the transformation from Co²⁺(*Td*) to Co³⁺(*Oh*), leading to the generation of the active CoOOH phase, which contributes to improved catalytic activity.

By distinctly addressing the challenges in ORR and OER within their specific applications, this thesis provides valuable insights into the mechanisms governing these critical reactions. The findings offer practical strategies for developing next-generation electrocatalysts, contributing to the advancement of fuel cell technology and the sustainable production of hydrogen through water electrolysis. Ultimately, this work aims to pave the way for more efficient and sustainable energy conversion systems.

List of Publications

1. **Cao, W.;** Kumar, M.*; Thakur, N.; Uchiyama, T.; Gao, Y.; Tominaka, S.; Machida, A.; Watanabe, T.; Sato, R.; Teranishi, T.; Matsumoto, M.; Imai, H.; Sakurai, Y.; Uchimoto, Y. A Modified Galvanic Cell Synthesis of Pd@Pt Core–Shell Nanowire Catalysts: Structural Insights and Enhanced ORR Performance. *ACS Appl. Energy Mater.* **2024**, 7 (19), 8515-8525. (Chapter 2)

2. **Cao, W.;** Thakur, N.*; Kumar, M.; Uchiyama, T.; Gao, Y.; Tominaka, S.; Machida, A.; Watanabe, T.; Sato, R.; Teranishi, T.; Matsumoto, M.; Imai, H.; Sakurai, Y.; Uchimoto, Y. Structural Insights and Electronic State Analysis of PtNi Nanowire Catalysts by *operando* High-Energy Resolution Fluorescence Detection X-ray Absorption Spectroscopy. *J. Mater. Chem. A* **2024**, 12, 293843-293853. (Chapter 3)

3. **Cao, W.;** Thakur, N.*; Kumar, M.; Matsumoto M. *; Sato, R.; Teranishi, T.; Imai, H.; Uchimoto, Y. Structural Control of PtNi Catalysts through Precise Synthesis Conditions and Elucidation of Property Determinants by *operando* XAS Analysis. *Electrochemistry*, accepted. (Chapter 4)

4. Gao, Y.; Thakur, N.; Uchiyama, T.; **Cao, W.;** Yamamoto, K.; Watanabe, T.; Kumar, M.; Sato, R.; Teranishi, T.; Imai, H.; Sakurai, Y.; Uchimoto, Y. Investigating Degradation Mechanisms in PtCo Alloy Catalysts: The Role of Co Content and a Pt-Rich Shell Using *Operando* High-Energy Resolution Fluorescence Detection X-ray Absorption Spectroscopy. *ACS Appl. Mater. Interfaces* **2023**, 15 (45), 52473-52484.

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Many countries around the world continue to endure the devastations of war and conflict. I wish to convey my heartfelt hope that peace will soon prevail. May children everywhere be free from the threat of violence and grow up in a world where they can thrive in safety and harmony.

Weijie Cao (曹伟杰)

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