

Doctor of Philosophy

Structural Studies of
Pt-Based Electrocatalysts
for Polymer Electrolyte Fuel Cells
白金系燃料電池用カソード触媒の構造
と活性に関する研究

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Chapter 1. Introduction

1.1 Hydrogen energy

1.1.1 Hydrogen and the global environment

Today's society and economy are heavily reliant on energy, as its uninterrupted supply is crucial for life, work, and economic and social welfare. However, the present-day energy supply and application systems suffer from numerous drawbacks. The global energy trends are still not sustainable in many aspects, e.g., from the viewpoints of the environment, economics, and society, with fossil fuels such as coal, crude oil, and natural gas accounting for >80% of the global energy consumption.¹⁻³ The emissions of CO₂ due to energy consumption are expected to double in 2050⁴ and have already increased the average global temperature (compared to that of the pre-industrial era) by ~1.5 °C.⁵ Thus, new energy patterns and low-carbon-emission technologies are urgently needed to change the current pattern of energy consumption.

Newly developed energy technologies such as renewable energy, carbon capture and storage nuclear power, transport technologies, and hydrogen energy are expected to aid further development and reduce greenhouse gas emissions.⁶⁻¹⁴ In particular, hydrogen energy is an important solution to the environmental problems due to energy consumption-related CO₂ emissions. As hydrogen-based electricity generators feature water as the only by-product, a shift from fossil fuels (e.g., gasoline) to hydrogen is expected to eliminate greenhouse gas emission and air pollution.

However, depending on the employed resources, hydrogen production may not always be environmentally friendly. Today, hydrogen is mainly produced via the reforming of fossil fuels such as natural gas, which leads to the emission of greenhouse gases and is therefore not environmentally friendly. Conversely, the production of hydrogen via renewable energy-powered water electrolysis is a sustainable and environmentally friendly method.¹⁵⁻¹⁷ In this situation, hydrogen is an important energy carrier, especially for variable renewable energy (VRE) sources such as solar and wind energy,¹⁸ allowing one to achieve VRE storage and transport, expand the scope of renewable energy application, and promote the establishment of a low-CO₂-emission society.

Even fossil fuel-derived hydrogen has a positive influence on the environment, as

in this case, greenhouse (CO_2) and polluting (CO , SO_2) gases as well as dust emissions are concentrated in the primary utilization step, unlike in the case of fossil fuel usage in separate units.¹⁹

With the development of photocatalytic water splitting, hydrogen has emerged as a novel renewable energy carrier for the global energy system.^{20,21} Photocatalytic water splitting transforms the energy of sunlight into hydrogen and is thus another means of solar energy harvesting besides photovoltaics and solar-thermal electricity generation technologies. Although the energy conversion efficiency of photocatalytic water splitting remains low,^{20,21} this technique would offer low-cost carbon-free hydrogen production when properly developed and could therefore strongly contribute to the global energy system and the establishment of a carbon-free energy ecosystem.

1.1.2 Application of hydrogen energy

Hydrogen is considered to be applicable in the fields of transportation, construction, industry, power generation, etc. As an expected near-zero emission energy, hydrogen can connect different forms of energy and energy consumption units to build energy transmission and distribution (T&D) networks (Figure 1).¹⁹ Moreover, hydrogen can be transformed into any type of primary or secondary energy and can be used in many facilities as a fuel cell component.

As mentioned above, hydrogen can contribute to the storage, transport, and redistribution of VRE,^{18,19} the importance of which is expected to increase with the decreasing global supply of fossil fuel. Renewable energy sources such as solar, wind, and geothermal energy are unbalanced and cannot be stored and transported like fossil or nuclear fuel. Therefore, the transformation of renewable energy is important for achieving the redistribution of global VRE resources, with hydrogen viewed as a suitable energy carrier for this goal.

Hydrogen can also be used to store the excess electric energy generated by power plants²² and increase the thermal efficiency of thermal power plants, as their thermal and electrical energy is difficult to store by other means. The well-developed lithium batteries are currently more efficient at energy storage than hydrogen, although hydrogen and fuel cells are better suited for large-scale facilities such as gas turbine generators, power plants, and fuel-cell vehicles (FCVs).

Fuel cells are of key importance for hydrogen energy systems, directly

transforming the chemical energy of hydrogen into electric energy. Thus, the research and development of hydrogen fuel cells is vital for the global implementation of a hydrogen-based economy.

1.2 Fuel cells

1.2.1 Overview of fuel cells

As their name suggests, fuel cells generate electricity by liberating the chemical energy of fuels through their reactions with oxygen or other oxidizing agents. Hydrogen fuel cells were invented in 1839 by Lord Grove, generating electricity from hydrogen and oxygen gases,²³ and were first practically applied on satellites and space capsules in NASA space programs.²⁴ To date, fuel cells have found numerous industrial applications (power plants, VRE storage systems, and FCVs) due to their high energy efficiency and low emissions.^{18,19,25,26}

Fuel cells are mainly classified based on their electrolyte and working temperature, with the five main types of fuel cells used in research and application fields corresponding to (i) alkaline fuel cells (AFCs); (ii) phosphoric acid fuel cells (PAFCs); (iii) molten carbonate fuel cells (MCFCs); (iv) solid oxide fuel cells (SOFCs); and (v) polymer electrolyte fuel cells (PEFCs).²⁷ Common AFCs contain a concentrated solution of KOH as the electrolyte, are operated at ~ 100 °C, and are mainly used in space shuttles and space stations. PAFCs, which use high-concentration phosphoric acid as the electrolyte and are usually operated at 150–200 °C, were the first type of commercialized fuel cells applied in factories, hospitals, and hotels. MCFCs require a high operating temperature of ~ 650 °C, use molten lithium-potassium carbonate as an electrolyte, and are mainly intended for large-scale industrial use. SOFCs use a solid electrolyte, most commonly a ceramic denoted as yttria-stabilized zirconia (YSZ), are operated at 800–1000 °C, and are intended for medium- and large-scale power applications. PEFCs contain a solid polymer electrolyte and are operated at ~ 80 °C, thus offering the benefits of high energy density and suitability for small-scale devices such as FCVs.

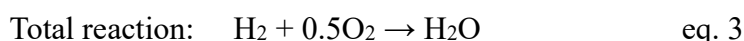
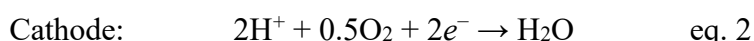
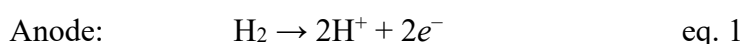
Compared with gasoline vehicles, FCVs offer the advantages of zero emissions, non-combustion systems, and higher energy efficiency.^{25,26} As fuel cells directly transform chemical energy into electric energy without being restricted by the Carnot cycle, their theoretical and practical energy conversion efficiencies are quite high.

Specifically, gasoline vehicles feature an energy efficiency of only ~15% because of the restrictions imposed by the Carnot cycle and insufficient combustion,²⁸ whereas the general energy efficiency of FCVs can reach 40%.²⁹

FCVs and PEFCs provide opportunities for the wide use of hydrogen energy in daily lives and reduce the pollution due to individual devices. Several civilian-use FCVs have already been developed, as exemplified by MIRAI (Toyota) and FCX CLARITY (Honda). In Japan, hydrogen charging and storage stations have been built to keep up with FCV development. However, the widespread use of FCVs is hindered by the high cost of noble metal catalysts, issues related to hydrogen storage security, and insufficient PEFC stability and performance. Therefore, the development of low-cost high-performance PEFCs is a task of high practical significance.

1.2.2 Working principle of PEFCs

A PEFC typically comprises an anode, cathode, and a polymer electrolyte that provides the pathway for protons to move between the two fuel cell sides (Figure 2). The anodic oxidation and cathodic reduction reactions are promoted by catalysts deposited on the electrodes. During these reactions, hydrogen ions are drawn through the electrolyte, while electrons flowing from the anode to the cathode through the external circuit produce an electric current. At the cathode, oxygen reacts with hydrogen ions and electrons to generate water.



The above reactions in PEFCs are quite simple and produce water as the only product. These fuel cells offer the advantages of low operating temperatures, decreased pollutant emission, short start-up time, smart size availability, and a wide application range. However, the commercialization of PEFCs remains hindered by numerous obstacles, especially those regarding the catalysts deposited on the cathode.

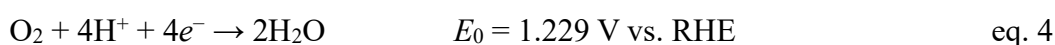
1.2.3 Oxygen reduction reaction

The oxygen reduction reaction (ORR) is one of the most important reactions for electrochemistry and electrocatalysis research. The ORR plays an important role in electrochemical energy conversion, although it still needs further development owing

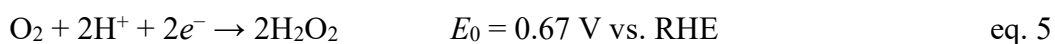
to the demand for better catalyst activity and the limited understanding of the ORR mechanism on the electrocatalyst surface.

Oxygen reduction is a multi-step multi-electron reaction. Many fundamental studies of the ORR focus on the four-electron reduction mechanism, which is sensitive to the catalyst surface and the electronic properties of atoms. Four-electron reduction includes several elementary reactions (e.g., electron transfer and chemical steps) and can proceed via various pathways.³⁰⁻³³ In acidic aqueous media, which resemble the environment of PEFC cathodes, the basic two pathways are the direct four-electron pathway and the peroxide pathway (Figure 3).³³

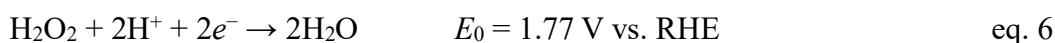
Direct four-electron pathway in acidic solution:



Peroxide pathway:



In acidic solutions, peroxide can be further reduced or decomposes:



As dissociation energy of the O=O bond is rather high (494 kJ/mol), four-electron reduction can only occur on specific metals. Conversely, the dissociation energy of the O–O bond in H₂O₂ is relatively low, and H₂O₂ dissociation therefore easily occurs on many surfaces.

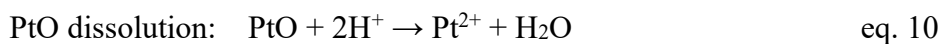
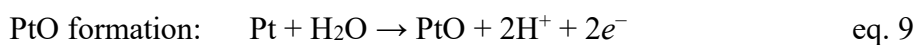
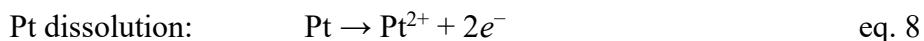
Three surface intermediates (*OOH, *O, and *OH) are involved in oxygen reduction; thus, the energy of O/OH adsorption on the catalyst surface is related to ORR activity.³⁴ The adsorption status of O/OH on the catalyst surface, which is the main parameter responsible for the variation of ORR activity among the different catalysts, is determined by factors such as metal-oxygen binding energy, coverage of available sites on the catalyst surface by intermediates, and other reasons affecting binding energy or coverage. These factors are introduced in the following sections of this chapter and need to be theoretically analyzed and further developed to improve the ORR activity of cathode catalysts.

1.2.4 Cathode catalysts and their issues

FCVs have drawn much attention because of their high energy density, environmental friendliness, and connection to the hydrogen energy system. However,

the wide commercialization of FCVs and PEFCs is hindered by the high cost of the latter, which is mainly due to the high cost and low durability of the electrode catalyst, with expensive noble metals (e.g., Pt) used as cathode and anode catalysts accounting for 50% of the PEFC manufacturing cost.³⁴ In addition to being expensive, Pt is easily poisoned under strongly acidic conditions. This poisoning results in inefficient reaction kinetics and degradation effects, contributing to >65% of cathode performance loss and deteriorating the performance of the entire PEFC.³⁵

Commercial PEFCs typically use carbon-supported Pt (Pt/C) catalysts. Most often, Pt nanoparticles are supported on activated carbon to maximize surface area and activity, with the aggregation and growth of these particles viewed as the main reason of catalyst degradation in PEFCs. It is believed that particles in nanostructures tend to gather and form larger particles,³⁶ which reduces the surface area of Pt nanoparticles and decreases their catalytic activity. The fact that the growth of Pt nanoparticles on the electrode has been observed for a fresh membrane electrode assembly (MEA), which is the core part of PEFCs and includes catalyst-loaded electrodes, indicates that agglomeration occurs already during MEA preparation.^{37,38} Ferreira et al. used transmission electron microscopy to characterize Pt nanoparticles in an MEA before and after its degradation, revealing that some Pt nanoparticles dissolved in the polymer electrolyte and were re-deposited onto other Pt nanoparticles to increase their size, a phenomenon known as Ostwald ripening.³⁹ Pt loss and migration are the main reasons for catalyst layer degradation. Luo et al. used atomic absorption spectroscopy to analyze a PEFC stack after 200-h standard operation, showing that the stack experienced a serious Pt loss upon aging, namely from 20 to 13.5%.⁴⁰ Pt migration in MEAs has also been reported, resulting in the dispersion of Pt particles in the electrolyte or their concentration on the surface between the catalyst layer and the electrolyte.^{39,41,42} These Pt particles, originating from Pt on the electrode, dissolve and diffuse into the electrolyte, subsequently precipitating in the ionomer phase or on the electrode due to the occurrence of the hydrogen reduction reaction involving Pt ions diffusing to the anode. Darling and Meyer suggested the following Pt dissolution mechanism³⁹:



The loss of Pt and its migration to the electrolyte reduce the availability of Pt/C on the

cathode and influence electrolyte properties and PEFC performance.

To reduce the cost of PEFCs, researchers are seeking ways to reduce Pt usage and improve the durability and activity of cathode catalysts. However, the realization of this goal requires a deep understanding of the mechanism of the ORR on the cathode catalyst and factors controlling ORR activity.

1.3 Factors influencing the ORR

1.3.1 *d*-Band theory

The past several decades have witnessed breakthrough theoretical studies on atomic-level factors determining catalyst activity. The *d*-band theory, developed by Hammer and Norskov, suggests that the energy of adsorption on metal surfaces is mainly determined by the electronic states in the metal valence band.⁴³ In general, the *sp*-states of metals are constant, and the above adsorption energy is therefore mainly determined by the coupling between the adsorbate and *d*-states. Calculations indicate the occurrence of weak and strong chemisorption during the interaction of the adsorbate with *d*-bands.⁴³ The width of the *d*-band decreases with increasing element energy, and the *d*-band center shifts upward and approaches the Fermi level, which results in the appearance of a distinctive antibonding state above the band. As these antibonding states are above the Fermi level, they are empty, and the bond becomes progressively stronger as the number of empty antibonding states increases. Thus, the position of the *d*-band center determines the adsorbate–metal surface binding energy, and ORR activity is therefore dependent on the metal surface type.

To probe the energy of oxygen adsorption on various metals, Hammer and Norskov performed calculations of the O–metal binding energy and local density after the *d*-state was hybridized with the O 2*p*-state (Figure 4)⁴³ for Ru, Ni, Cu, Pd, Ag, Pt, and Au. Notably, Cu, Ag, and Au had the weakest binding energies, as their antibonding states lied below the Fermi level and were therefore occupied by electrons, which led to weak chemisorption, decreased binding energy, and a less stable adsorption status. In the case of Au, the O–Au bond was even weaker than the O–O bond, i.e., O₂ was predicted not to dissociate on the Au surface. On the other hand, the energy level of Ru hybridized with the O₂ *sp*-state was even lower than that of oxygen, which led to very strong binding and highly stable adsorption on the surface. Pt, Ni, and Pd were shown to possess a relatively suitable oxygen hybridization state (with an energy lower than

that of the oxygen bonding state) and an anti-bonding state (with an energy higher than that of the Fermi level), thus being a better choice as ORR electrocatalysts. The *d*-band theory provides a theoretical method of illustrating and predicting the energy of adsorbate binding to metal surfaces, facilitating the design of highly active catalysts and helping to understand ORR activity–influencing factors such as the strain and ligand effects, as is described below.

1.3.2 Ligand and strain effects

The ORR activity of catalysts can be increased in many ways such as the design of bi- or multimetallic alloys^{44,45} or the formation of core-shell catalysts.^{46,47} Metal atoms surrounding each other significantly influence both electronic structure and bond distance to change the position of the *d*-band center and the adsorbate–metal binding energy, thus affecting ORR activity.

The ligand effect is essentially responsible for the electrons between the surface and the substrate atoms to the surface, leading to a change in surface properties. The strain effect is due to the fact that the average bond distance between metal atoms is typically different from that in the bulk (pure metal) phase, resulting in different properties on the surface. These two effects often occur together to influence electrocatalytic activity.

Norskov et al. reported that the width of the *d*-band can be determined by the metal coordination number, which can, in turn, affect the position of the *d*-band center.⁴⁸ On the Pt (111) surface, which has the most close-packed arrangement, Pt has a coordination number of nine, while a value of eight is observed for the Pt (100) surface, which has a relatively open arrangement. The (110) surface and step atoms have a coordination number of seven, while the kink atoms on the (1185) surface have a coordination number of six. Calculations of the *d*-band densities of Pt atoms on different surfaces (Figure 5)⁴⁸ reveal that kink atoms on the (1185) surface feature a *d*-band centered 1 eV closer to the Fermi level than the band of atoms on the (111) surface, which could lead to a change in adsorbate binding energy and ORR activity due to the ligand effect.

Schmid et al. used scanning tunneling microscopy to observe the CO coverage sites on a PtCo (111) surface,⁴⁹ showing that Pt atoms with 1–2 neighboring Co atoms weakly bind CO molecules, i.e., the corresponding CO binding sites are rarely occupied.

On the other hand, Pt atoms with 4–5 Co neighbors are better at CO adsorption. First-principles density functional theory calculations accounting for the PtCo alloying surface and the substrate influence suggest a nearly 0.2-eV shift of the *d*-band center upon going from Pt atoms with less Co neighbors to Pt atoms with more Co neighbors. In addition, the binding energy of CO to the Co atoms in the alloy was calculated to be 0.18 eV less than that to Co atoms in pure Co. In the alloyed catalyst, the ligand effect from atoms surrounding the surface and the substrate had an obvious influence on the adsorbate–metal binding energy.

To further understand the effect of the substrate on the surface atoms, a Pt (111) overlayer on a series of different 3*d* metals was used to study the effect of second-layer metals on the Pt surface. Near-surface alloys of this type (also described as a Pt shell on metals) have been developed as PEFC cathode catalysts to improve ORR activity.^{46,47,50,51} Norskov et al. calculated the position of the *d*-band center of Pt (111) on various subsurface metals, showing that it shifted to lower energies as the second-layer metal moved to the left side of the periodic table.⁴⁹ The O–Pt adsorption energy increased as the *d*-band center shifted up and close to the Fermi level, in line with the previous discussion. The hybridization of the *d*-state of surface Pt atoms with that of second-layer metals led to a ligand effect toward the Pt atoms. At the same time, other researchers indicated that the lattice constant of overlayer atoms can also be influenced by the substrate, which leads to a change in bond distance between the overlayer atoms relative to that of the pure metal and also affects adsorption energy.^{52,53} Adzic et al. performed electrochemical measurements for Pt monolayers deposited on different single-crystal electrodes such as Ru (0001), Ir (111), Rh (111), Au (111), and Pd (111),⁵³ revealing the strong dependence of ORR activity on the supporting metal. The Pt monolayer deposited on the Pd (111) surface was most active, while that deposited on the Ru (0001) surface was least active. Combined with those of previous density functional theory calculations,⁵⁴ the obtained results revealed that compared with Pt (111), the Pt monolayer on Ru (0001) and Rh (111) shows compressive strain, while the Pt monolayer on Au (111) exhibits strain stretching. The binding energy was linearly correlated to *d*-band center position (Figure 6),⁵³ which indicated that compressive strain leads to a downshift in *d*-state energy and that extended strain affects this shift. A volcano-type dependence of catalytic activity on *d*-band center position was obtained (Figure 6).⁵³ According to Adzic, with increasing overcompression strain and oxygen–

metal binding energy (Ir (111)), the hydrogenation of oxygen species becomes difficult and becomes the rate-limiting factor of the ORR. On the contrary, for stretching strain and weak oxygen–metal binding energy (Au (111)), the dissociation of oxygen on the metal surface becomes the rate-limiting factor. The Pd (111) surface with a Pt monolayer behaved similarly to Pt (111) and exhibited an even higher ORR activity because of the appropriate position of the *d*-band center. This result indicates that the strain effect significantly influences the *d*-band center position and catalyst activity.

As mentioned above, the ligand and strain effects have been investigated in detail to gain an in-depth understanding of catalytic activity improvement principles. In practice, ORR activity is also affected by numerous other factors that need to be investigated and may be explained by the ligand and strain effect.

1.3.3 Coverage of adsorbed species

Based on the above, the energy of intermediate binding to the metal determines the status of species adsorbed on the catalyst surface and ORR kinetics. Thus, the coverage of the catalyst surface with oxygen species needs further investigation to shed light on the ORR mechanism and estimate the ORR activity of different catalysts.

Sepa et al. indicated that the mechanism of oxygen species adsorption depends on the pH and the potential of the rotating Pt disk electrode during the ORR.⁵⁵ Tafel plots obtained in acidic solutions feature two regions with slopes of approximately -60 mV dec^{-1} (low current density) and -120 mV dec^{-1} (high current density), as shown in Figure 7.⁵⁵ This behavior was ascribed to the change in the mechanism of reaction intermediate adsorption on the Pt surface from Temkin to Langmuirian as well as to the effect of coverage on oxygen dissociation on the Pt surface.⁵⁶⁻⁵⁸

Imai et al. evaluated the coverage of oxide species on carbon-supported Pt nanoparticles and found that these species changed with increasing potential,⁵⁹ as is summarized below.



Oxide species coverage can be estimated from the observed oxidation current as the ratio of oxidation and hydrogen adsorption charges (Figure 8).⁵⁹ With increasing potential, OH_{ads} started to adsorb on the Pt surface at low potential, and at 1.08 V vs.

RHE, the surface was almost fully covered with adsorbed OH (oxygen coverage = 1.0). The increase in oxygen coverage observed between 1.08 and 1.35 V vs. RHE indicated that Pt–OH transformed to Pt–O, with PtO₂ formation occurring at 1.35 V vs. RHE, while oxygen coverage exceeded 2.0. The oxide species coverage and change of oxide species adsorption on the Pt surface were quantified in terms of the Tafel slope and suggested that different adsorption mechanisms might operate upon potential change.

Markovic et al. concluded that both intermediate adsorption and bisulfate anions can inhibit the ORR activity of Pt (111).⁵⁶⁻⁵⁸ The hydroxyl species (OH_{ads}) adsorbed on the Pt surface, which do not participate in hydrogenation, may prevent the dissociation of new O₂ molecules and thus inhibit oxygen reduction, while the strong adsorption of the bisulfate anion on the Pt surface may prevent the adsorption of relatively weakly held intermediates. Thus, the adsorption of OH_{ads} and bisulfate anions on the active Pt sites blocks that of O₂ molecules and prevents oxygen dissociation and, hence, the ORR on the Pt surface. The relationship between catalyst activity and surface coverage by adsorbed species, including OH_{ads}, bisulfate anions, and other species was summarized by Markovic et al.⁵⁶

$$i_s = i_0(1 - \theta) x \exp \left[-\frac{\alpha F(E - E^{eq})}{RT} \right] \exp \left(-\frac{\Delta G_\theta}{RT} \right) \quad \text{eq. 14}$$

where i_s the specific activity, i_0 is the exchange current density, θ is the total surface coverage by adsorbed species including anionic and oxide species, x is the number of Pt sites occupied by the adsorbed ion, α is the symmetry factor, E is the applied potential, E^{eq} is the equilibrium potential of the ORR, ΔG_θ is a parameter characterizing the change rate of the apparent standard Gibbs energy of adsorption with the surface coverage by the adsorbing species, F is the Faraday constant, R is the universal gas constant, and T is the temperature.

Among the many species whose adsorption effects have been studied for the Pt surface, the specific adsorption effect of sulfo groups in perfluorosulfonic acid ionomers is one of the most important topics for PEFC commercialization. Perfluorosulfonic acid ionomers such as Nafion[®] are commonly included in the anode and cathode catalyst layers of PEFCs and proton conductors to enhance proton-electron contact, enlarge the reaction zone, and promote the ORR.⁶⁰⁻⁶² Figure 9⁶³ shows that the commonly used Nafion[®] ionomer features a polytetrafluoroethylene (PTFE) main chain

that provides chemical and physical stability. The high electronegativity of fluorine atoms in the side chain makes the sulfonic acid groups superacidic and thus results in high proton conductivity. As sulfonic acid groups are strongly adsorbed and can therefore block the active sites on the Pt surface, the influence of the specific adsorption of Nafion[®] on the Pt surface has attracted much attention.

Markovic et al. evaluated the specific adsorption of Nafion[®] on the Pt (111) surface and compared it with the adsorption of bisulfate anions in H₂SO₄.⁶⁴ Cyclic voltammograms recorded for the Pt (111) disk electrode revealed obvious adsorption and desorption peaks between 0.45 and 0.54 V for Pt (111) capped with Nafion[®] or exposed to H₂SO₄, whereas no such peaks were observed in HClO₄. The similar features observed for Nafion[®] and H₂SO₄ indicated that their specific adsorption behaviors were closely related, confirming that the sulfonic acid groups of Nafion[®] led to its specific adsorption on the Pt surface to block the active sites and inhibit ORR activity.

Knowledge of the specific adsorption of Nafion[®] was used to characterize the inhibitory effect for the ORR on polycrystalline Pt, Pt nanoparticles supported on active carbon (Pt/C), Pt alloys, and other practical catalysts.⁶⁵⁻⁷⁰ Meanwhile, research has been conducted to reduce the ORR inhibitory effect of this ionomer. Shinozaki et al. evaluated the ORR activity of Pt nanoparticles supported on various carbons and found that catalysts with high surface area could mitigate the loss in activity, as Pt nanoparticles located inside the pores of high-surface-area carbon were not covered by the ionomer, as its molecules could not enter the micropores. The same trend was observed for Pt-based alloy catalysts, indicating that in the case of porous carbons with 4–7-nm pore openings,⁶⁹ nanoparticle catalysts located in the pores could avoid the specific adsorption of the ionomer, which allowed the ORR to occur on the catalyst surface. Modification of the Pt surface with hydrophobic ionic liquids has also been considered as another way of protecting the surface of Pt-based catalysts from specifically adsorbed species and improving the ORR activity.⁷¹⁻⁷⁶ As ionic liquids possess considerable ionic conductivity^{77,78} and high oxygen permeability,^{71,79} Pt surfaces covered with ionic liquids possess properties that prevent the oxidation of surface Pt atoms and hinder the specific adsorption of nonreactive species. Snyder et al. compared the cyclic voltammetry behavior and ORR activity of a naked Pt (111) surface with those of Nafion[®]-capped and Nafion[®]-capped + ionic liquid–modified ones.⁸⁰ For the Nafion[®]-capped Pt (111) surface, the abovementioned specific adsorption peak of

sulfonic acid was observed, indicating that the ionic liquid could prevent the specific adsorption of the sulfonic acid groups of Nafion® on this surface. In addition, the Nafion®-capped + ionic liquid–modified Pt was more active than simply Nafion®-capped Pt.

Thus, the status of adsorbed species (including oxide species and sulfonic acids) on the catalyst surface has an obvious influence on ORR activity. However, further research and the elucidation of other influencing factors are required to reduce the specific adsorption and improve catalyst activity.

1.3.4 Temperature effect

As the PEFC working temperature is close to 80 °C, whereas most ORR activity and other electrochemical evaluations of catalysts in the half-cell with rotating disk electrodes (RDEs) are performed at room temperature, one should consider the influence of temperature, including its possible effects on catalyst properties such as ORR activity (eq. 15). The influence of temperature on the behavior of Pt and Pt-alloy catalysts has been evaluated using electrochemical measurements.⁸¹⁻⁸⁴ Paulus et al. evaluated the ORR activity of a Pt/C-coated RDE in aqueous H₂SO₄ at 20–80 °C. Figure 10⁸¹ shows the diffusion-limited current density ($j_{d,RDE}$) of the Pt/C catalyst at various temperatures, revealing that this current density is stable in the range of 20–60 °C but shows a remarkable decrease at 80 °C.

$$j_{d,RDE} = 0.620nFD^{2/3} \nu^{-1/6} c_0 \omega^{1/2} \quad \text{eq. 15}$$

where D is the O₂ diffusion coefficient in the electrolyte, ν is the kinematic viscosity, c_0 is the oxygen concentration of the electrolyte, and ω is the rotation rate. The temperature dependence of the diffusion coefficient of a dissolved gas is proportional to the ratio of temperature, T (in K), and dynamic viscosity, η . Moreover, ν can be expressed as the ratio of dynamic viscosity to electrolyte density, ρ .

$$D \propto \frac{T}{\eta} \quad \text{eq. 16}$$

$$\nu = \frac{\eta}{\rho} \quad \text{eq. 17}$$

The above equations can be combined with the normalized temperature dependence of the diffusion-limited current density (Figure 10) to express the temperature dependence of the diffusion-limited current density as

$$\frac{j_{d,T}}{j_{d,20^{\circ}\text{C}}} = \frac{P_T C_T (1 - p_{H_2O,T})}{P_{20^{\circ}\text{C}} C_{20^{\circ}\text{C}} (1 - p_{H_2O,20^{\circ}\text{C}})} \quad \text{eq. 18}$$

According to eq. 18, the diffusion-limited current density was not notable between 20 and 60 °C, whereas a severe increase in vapor pressure led to a decrease in O₂ solubility at 80 °C, which indicated that a decrease in O₂ concentration contributes to the low current density at high temperatures.

Based on the results of Paulus et al., Watanabe et al. developed an evaluation of the ORR activity–temperature relationship using the channel-flow electrode method.⁸² The O₂ concentration correction at different temperatures was performed through calculations and increases of O₂ partial pressure in the flow channel, which accounted for the decreased O₂ solubility at high temperatures. With the calculated O₂ concentration [O₂] in hand, the ORR rate constant k_{orr} was discussed to evaluate ORR activity as a function of [O₂] and kinetically controlled current I_K :

$$I_K/4FA = -(1 - \theta)^m k_{orr} [O_2] [H^+] \quad \text{eq. 19}$$

where F is the Faraday constant, A is the electrode area (real surface area), θ is the coverage of the adsorbed species such as oxides or adsorbed anions, m is the number of active sites required for the absorption of one O₂ molecule, $(1 - \theta)$ is the fraction of active sites on the Pt surface, and $[H^+]$ is the bulk concentration of H⁺ in the electrolyte.

As Figure 11 shows, the apparent rate constant increases with increasing temperature, and behaves according to the general Arrhenius equation, which indicates that the ORR activity of the Pt/C catalyst is directly proportional to temperature, and the ORR mechanism is simple.⁸²

However, some alloy or core-shell catalysts have structures completely different from those of ordinary Pt catalysts and are therefore expected to exhibit a different ORR activity behavior at high temperatures according to the influence of the ligand or strain effect.

Based on the abovementioned theory and factors influencing ORR activity, various kinds of catalysts have been developed. It is important to consider both performance durability and many other factors, including the costs and resources of the new catalysts. In the next chapter, new Pt-based catalysts, including shape/morphology-controlled Pt catalysts, Pt alloy catalysts, and core-shell catalysts with Pt shells, are introduced, and their (dis)advantages and future development are discussed.

1.4 ORR catalysts

1.4.1 Pt catalysts

Despite the search for alternatives, Pt remains the most commonly used ORR catalyst because of its relatively high chemical stability, exchange current density, and work function.⁸⁵ According to Figure 12,⁸⁶ compared with catalysts based on other noble metals, Pt-based catalysts possess relatively high activity with an appropriate binding energy for the adsorption of species in acidic solution.

However, Pt is rare and expensive. To reduce the cost of the cathode catalyst, some researchers have attempted to control the structure of Pt nanoparticles, as exemplified by the use of spherical, cubic, and tetrahedral particles,⁸⁷⁻⁸⁹ and thus enhance ORR activity by exposing more active facets and more reactive sites on the surface. Morphology-controlled Pt nanoparticle catalysts such as 1D nanowires, 2D nanoplates, and 3D nanoframes⁹⁰⁻⁹² have also been considered, helping to achieve a relatively high Pt surface area, provide more active sites for the adsorption of reaction intermediates, and increase catalytic activity. In addition, morphology-controlled Pt catalysts may provide more active facets for enhanced activity.

The use of shape-/morphology-controlled Pt nanoparticles helps not only to increase the specific surface area of catalysts but also to reduce their cost. However, considering the effect of nanoparticle aggregation, the maintenance of structure and durability needs further investigation.

1.4.2 Pt alloy catalysts

The alloying of Pt with various transition metals was employed to improve catalyst activity and reduce cost. Many researchers have reported that alloy catalysts exhibit enhanced ORR activity. Mukerjee and Srinivasan evaluated the performance of Pt-Co, Pt-Cr, and Pt-Ni alloy catalysts,⁹³ showing that these Pt-based alloy catalysts achieve 20–30 mV higher current densities than pure Pt in the low-current-density Tafel region. Pt-based alloys including Pt-Fe, Pt-Mn, Pt-Ti, and Pt-Cu have also been evaluated by Gasteiger et al.,⁹⁴ featuring Tafel slopes of $\sim 60 \text{ mV dec}^{-1}$ in the low-current-density region, which were similar to the values observed for pure Pt catalysts. This finding suggests that Pt-based alloy and pure Pt catalysts exhibit identical mechanisms of intermediate species adsorption and the ORR.

Since Pt-based alloy catalysts were investigated to reduce cost and improve ORR activity, many alloy catalysts have been designed based on *d*-band theory as well as ligand and strain effect among the atoms of different elements, as mentioned above. Atoms smaller than Pt would enter the crystal structure and induce lattice contraction to influence the dissociative adsorption of oxygen and enhance catalytic activity. The electronic effects of the atoms of different elements are also considerable, leading to a shift of the *d*-band center and enhanced activity.⁹⁴⁻⁹⁶ Considering the strain effect in alloy catalysts, strain-controlled catalysts including mass-selected Pt_xY and Pt_xGd nanoparticles possess remarkably high mass activity^{97, 98} that is ascribed to the formation of a compressed Pt shell on the surface. The shape control method also works for Pt-based alloy catalysts. Octahedral Mo-doped Pt-Ni nanoparticles can achieve a mass activity of 7.0 A/mg_{Pt},⁹⁹ as they provide more active Pt₃Ni (111) facets and exhibit enhanced ORR activity.¹⁰⁰ A morphology control method was also applied to Pt-based alloy catalysts. Strained Pt-Pb nanoplates¹⁰¹ achieved a mass activity of 4.3 A/mg_{Pt} due to the combination of strain effects and an increased surface-to-volume ratio. Pt₃Ni nanoframes presented an outstanding mass activity of 5.7 A/mg_{Pt} and high stability.¹⁰² However, the distribution of atoms in alloys complicates the precise analysis of practical catalysts, and the stability of shape-controlled nanoparticles presents a further challenge for retaining their activity during long-time practical use.

1.4.3 Core-shell catalysts

In contrast to Pt alloy catalysts, Pt-shell core-shell catalysts represent another bimetallic structure that changes the properties of Pt atoms on the surface to increase ORR activity and reduce the usage of Pt in the cathode catalysts of PEFCs.

Pt-shell core-shell catalysts comprise pure metal or alloy nanoparticles coated by a thin Pt shell, which decreases Pt usage and dramatically improves the efficiency of Pt utilization, as the ORR occurs only on the catalyst surface. As discussed earlier, Pt monolayers have been deposited on different single-crystal electrodes including Ru (0001), Ir (111), Rh (111), Au (111), and Pd (111)⁵³ to confirm the strain effect and the ligand effect due to the substrate of the alloy catalyst as well as to provide guidelines for the design of Pt monolayer core-shell catalysts. Pt monolayers deposited on various metal surfaces are influenced by the compressive or tensile properties of Pt–Pt bonds, which, combined with the ligand effect of the substrate on core metals, induce a change

of *d*-band center position and the energy of adsorbate binding while increasing ORR activity.

Adzic et al. demonstrated these features by synthesizing Ru nanoparticles coated with a one-Pt-atom-thick layer as a CO-tolerant electrocatalyst for hydrogen oxidation¹⁰³ and used Cu underpotential deposition (UPD) to prepare a Pt monolayer supported on Pd nanoparticles for the ORR¹⁰⁴ (Figure 13).¹⁰⁵ During UPD, submonolayers or monolayers are formed on core metals under potential control. The coated core metals are transferred to a Pt solution, where Cu is replaced by Pt via simple redox exchange. The thus synthesized Pt monolayer nanoparticles have several advantages. Pt atoms are almost exclusively deposited on the catalyst surface (i.e., the Pt utilization efficiency is close to 100%) and take part in the ORR. The remarkable electrocatalytic properties arise from the combination of substrate-induced strain effect and the ligand effect due to the electronic interaction between the Pt monolayer and the substrate. Moreover, the decreased oxidation of the Pt monolayer resulting from the interaction with a suitable substrate results in increased stability.^{103,106} Pt monolayer catalysts are suitable model catalysts, as all Pt atoms in the Pt monolayer are involved in the reaction because they are in contact with the reactants, which results in a direct correlation between catalytic and physical properties. In a typical conventional catalyst with 5-nm Pt/C nanoparticles, 70% of bulk Pt atoms do not interact with the reactant,¹⁰⁶ and the measured properties are mostly determined by the bulk Pt atoms.

The ORR activity of core-shell catalysts can be controlled by adjusting particle size, shell thickness, facets, and core materials.¹⁰⁶⁻¹⁰⁹ Pd₉Au cores showed attractive ORR activity and a decreased activity loss of only 6% after 100 000 cyclic durability tests (0.6–1.0 V vs. RHE at 80 °C).¹⁰⁶ Pt monolayers on 4-nm Pd nanoparticles and 4.6-nm Pd₃Co nanoparticles exhibited activities of 1.0 and 1.6 mA μg⁻¹Pt, respectively, which were 5–9 times higher than those of pure Pt nanoparticle catalysts. Density functional theory calculations predicted that nano-size and shape-controlled core-shell catalysts can exhibit three-fold higher ORR activity than pure Pt nanoparticle catalysts¹⁰⁷. Adzic et al. suggested that by changing the particle size, shape, and Pt shell thickness, one can modify the proportion of highly active facets to increase ORR activity. Wang et al. synthesized a Pt monolayer on Pd/C using different surface roughnesses and particle systems by Cu UPD and evaluated the Pt–Pt bond distance on the surface based on extended X-ray absorption fine structure (EXAFS) and X-ray

adsorption fine structure (XAFS) measurements.¹⁰⁹ The Pt–Pt bond distance on the Pt surface was negatively correlated with specific the ORR activity of the Pt-monolayer Pd-core catalyst, which indicated that the core size and surface roughness of the core-shell catalyst influence the interatomic distance of the Pt surface, causing an obvious strain effect and influencing ORR activity. However, based on the possibly different thermal behaviors of different atoms, ORR activity at high temperatures may be influenced by the hetero contact between the Pt shell and core atoms. There is a possibility that the local structures of the Pt monolayer depend on temperature and influence the status of the *d*-band center and ORR activity. However, the related reports are scarce, and further investigations of the strain and ligand effects of core-shell catalysts at high temperatures are necessary.

Pt monolayers were also deposited on the surfaces of non-noble-metal and morphology-controlled cores. Adzic et al. developed TiNiN cores covered with a Pt monolayer, achieving an activity of 0.83 mA μg^{-1} without a noble core.¹¹⁰ Nitride metal cores (e.g., NiN, FeN, and CoN) with a Pt monolayer have specific and mass activities several times higher than those of commercial Pt/C catalysts.¹¹¹ A Pt monolayer has also been deposited on Pd nanowires to achieve a high activity of 1.83 mA μg^{-1} ,¹¹² which was ascribed to the formation of a highly uncoordinated surface configuration and increased Pt surface area.⁹⁰

The above core-shell electrocatalysts may allow one to alleviate some of the major problems of existing fuel cell technologies by simultaneously decreasing the amount of required Pt (and hence, the cost) and enhancing performance.

1.5 Objective

As mentioned above, the plentiful development of various catalysts and treatments is based on an understanding of the theoretical influencing factors such as the strain effect, ligand effect, and adsorption species. To further improve the ORR activity of PEFC cathodes, one should understand the operation mechanism of newly developed catalysts and treatments. Operando X-ray absorption spectroscopy (XAS) is a valuable tool for analyzing the strain and ligand effects through changes in the interatomic distance, coordination number, and other local structures for different catalyst reaction statuses. This method can also be used to probe the electronic structure, which is

correlated with the ligand effect and species adsorbed on the Pt surface.

In this study, we report the ORR activities of Pt-based electrocatalysts such as Pt nanoparticles and Pd-Pt core-shell catalysts, revealing the effects of temperature, particle size, specific adsorption, and other factors and analyzing the effects of these factors on catalyst electronic structure and local structure changes by operando XAS. The correlation established between the catalyst structure and activity change is used to gain valuable mechanistic insights and shed light on the major influencing factors, thus facilitating the further design of cathode catalysts employed in PEFCs.

1.6 Outline of thesis

This seven-chapter thesis describes the development of electrochemical and operando XAS methods at the local structure level to analyze the detailed mechanism of how certain factors such as core-shell structure, temperature, and ionomer adsorption affect the ORR activity of Pt-based cathode catalysts.

Chapter 1 presents a general overview of the research background, fuel cell operation mechanism, and factors influencing the ORR activity of cathode catalysts.

Chapter 2 discusses the effect of temperature on the ORR activity of Pd-core Pt-shell catalysts with various particle sizes, revealing that this activity decreases at high temperatures (e.g., at temperatures close to the PEFC working temperature (60 °C)). As the thermal expansion coefficient of Pd exceeds that of Pt, the thermal expansion of the Pd core at high temperatures leads to extreme Pt-Pt bond extension and decreases the compressive strain effect and ORR activity. Catalysts with smaller Pd cores experience less dramatic thermal expansion and retain higher ORR activity.

In Chapter 3, the effect of the specific absorption of ionomers on Pt/C catalysts is quantitatively evaluated by electrochemical measurements and operando XAS, and the ORR activity of these catalysts is shown to decrease with increasing ionomer/carbon ratio. Operando XAS analysis is used to quantitatively evaluate the specific absorption of ionomers at the active potential for various ionomer/carbon ratios, illustrating the relationship between the ORR activity and the 5*d* orbital vacancy.

In Chapter 4, the effect of the specific adsorption of ionomers on Pd-core Pt-shell catalysts is quantitatively evaluated through electrochemical measurements and operando XAS analysis, and ORR activity is shown to decrease with increasing

ionomer/carbon ratio. Operando XAS analysis of Pd-core Pt-shell catalysts is shown to avoid the receiving of signals from the Pt bulk and allows one to focus on information pertaining to the effect of ionomer-specific absorption on the catalyst surface and thus quantitatively evaluate the specific adsorption of the ionomer from the *5d* orbital vacancy.

In Chapter 5, the inhibitory effect of the ionomer-specific absorption of microporous carbon-supported Pt catalysts is evaluated through electrochemical measurements and operando XAS analysis. A microporous carbon support with a proper pore diameter is shown to protect the Pt nanoparticles buried in the micropores from ionomer-specific absorption, but can also occur oxygen reduction reaction at the same time.

In Chapter 6, the enhancement of the ORR activity of Pt/C and Pd-core Pt-shell catalysts upon modification with ionic liquids (ILs) is evaluated. Electrochemical analysis reveals that modification with [MTBD][NTf₂] decreases the coverage of the Pt surface with oxide species, which is ascribed to the concomitant suppression of Pt surface oxidation. According to operando XAS of Pt/Pd/C, charge transfer from Pt to adsorbed oxygen species at higher potentials increases the energy of unoccupied Pt *5d* states and confirms that the IL modification of Pt/Pd/C suppresses surface oxidation.

Chapter 7 summarizes the conclusions of this study and presents the future prospects of polymer membrane electrode fuel cells.

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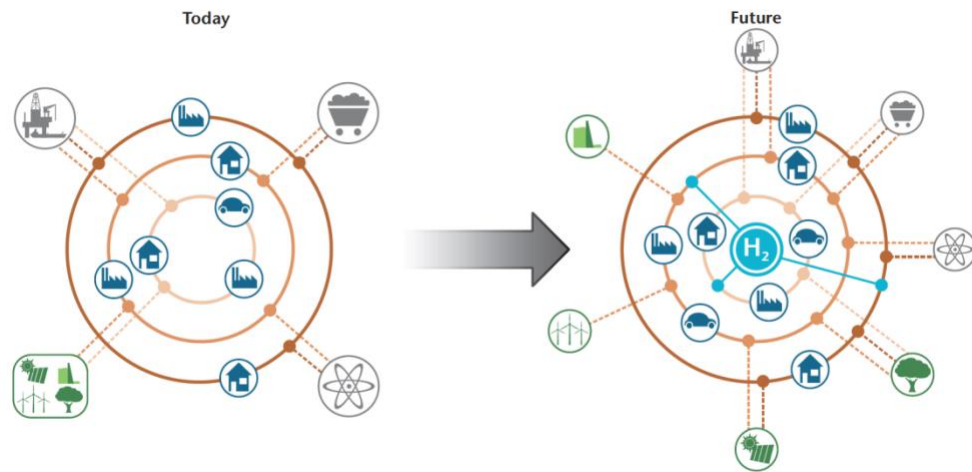


Figure 1. The T&D linkage formed by hydrogen in the future.¹⁹

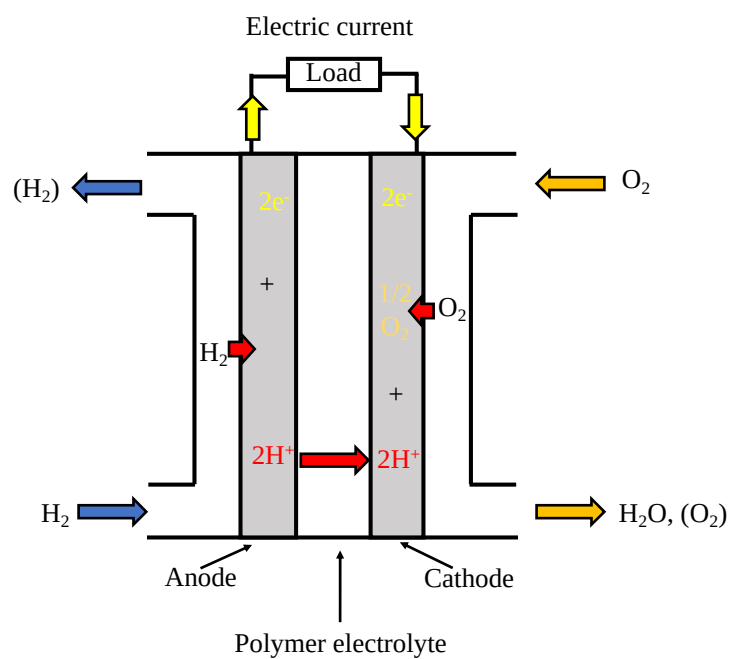


Figure 2. Schematics of a PEFC.

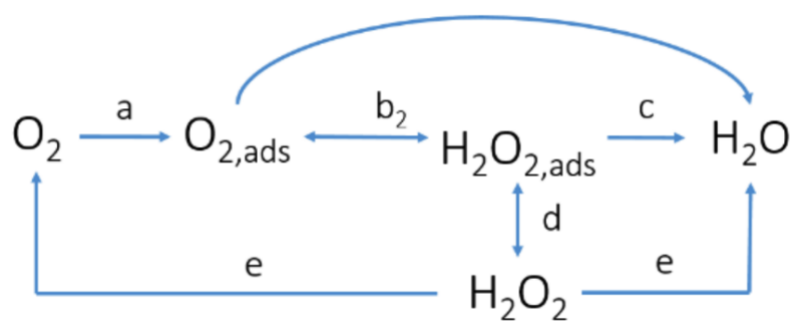


Figure 3. Possible ORR pathways.³³

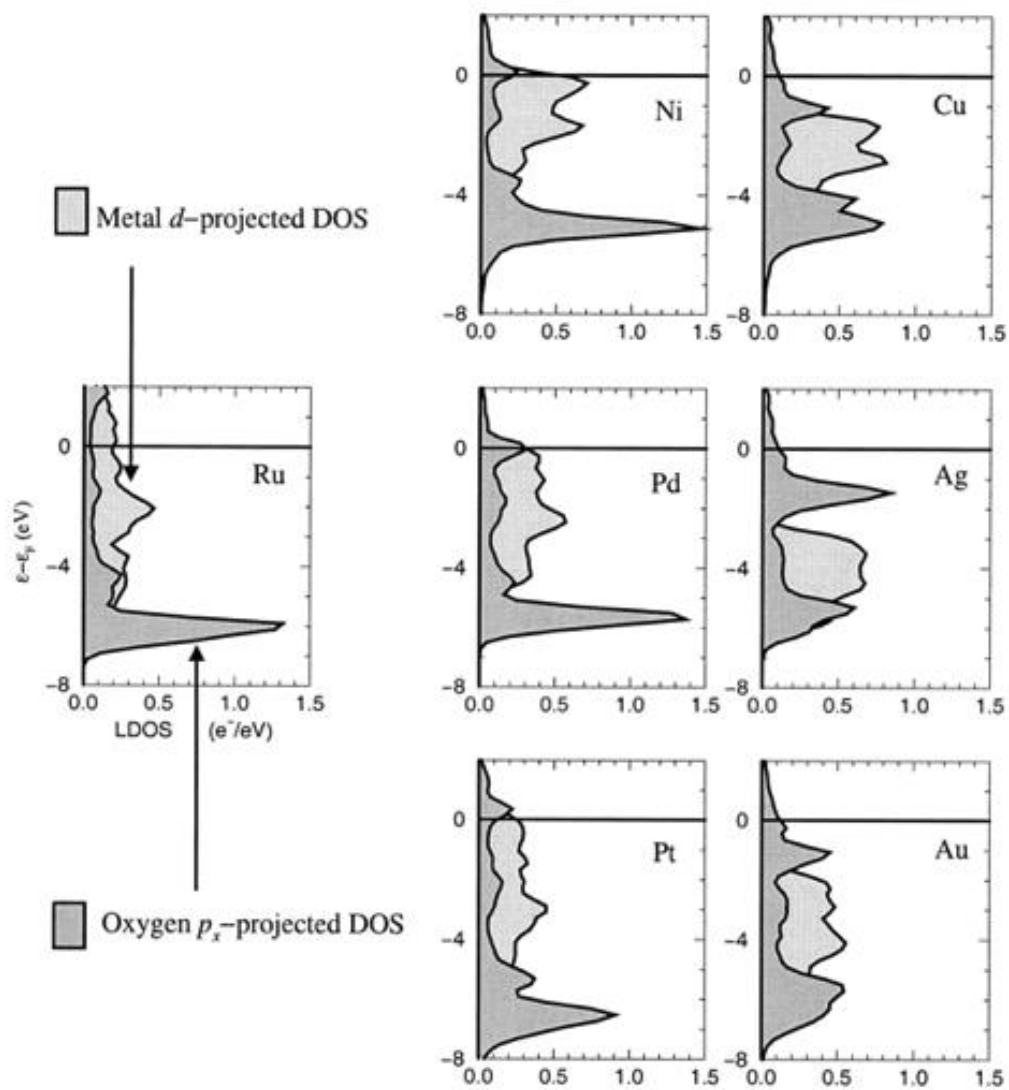


Figure 4. Local density of states (DOS) projected onto the oxygen $2p_x$ state (dark-shaded area) for atomic oxygen 1.3 Å above the close-packed surfaces of late transition metals. The light-shaded areas give the metal d -projected DOS for the respective metal surfaces before oxygen chemisorption.⁴³

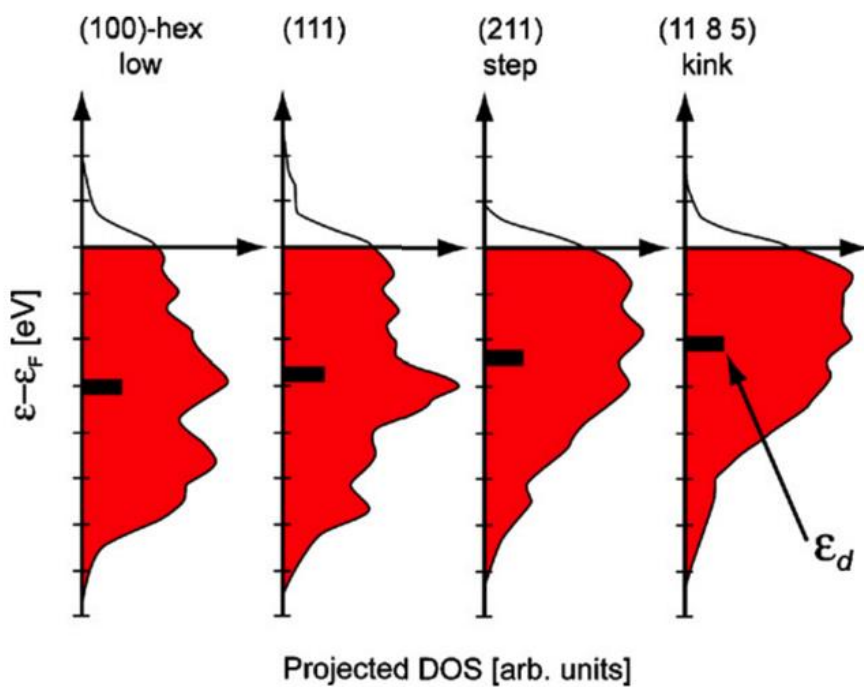


Figure 5. Calculated d -projected densities of states for Pt surfaces (hexagonally reconstructed (100) surface, close-packed (111) surface, step atoms on (211) surface, and kink atoms on (1185) surface) with decreasing atom density.⁴⁸

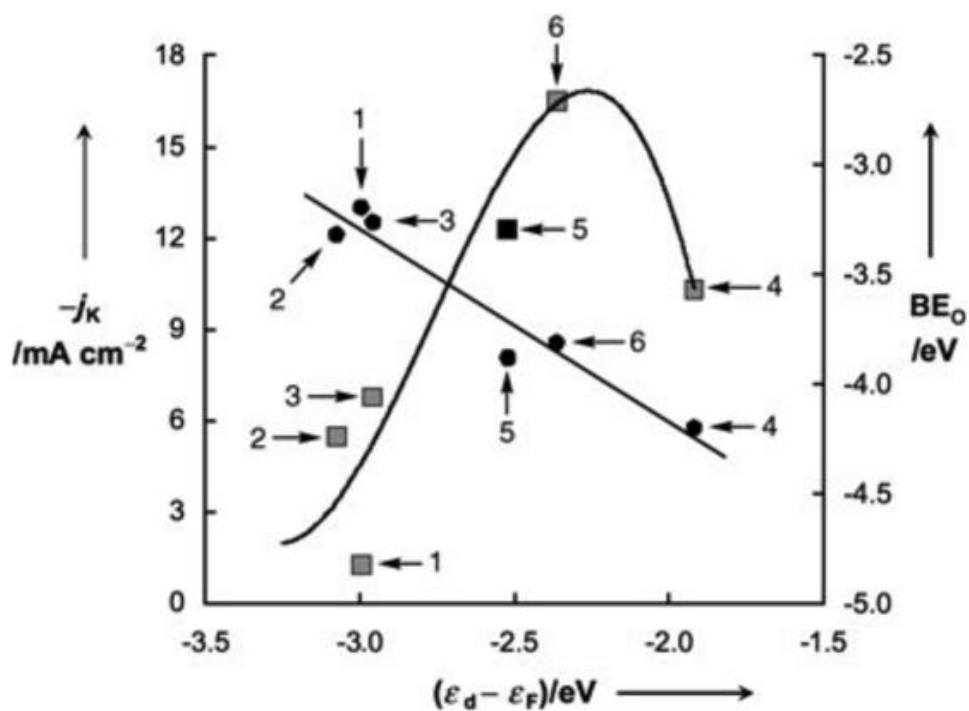


Figure 6. Kinetic currents (j_K ; squares) at 0.8 V for O_2 reduction on Pt monolayers supported on different single-crystal surfaces in 0.1 M $HClO_4$ solution and calculated binding energies of atomic oxygen (BE_O ; filled circles) as functions of calculated d -band center ($\epsilon_d - \epsilon_F$: relative to the Fermi level) position of the respective clean Pt monolayers. Labels: 1. PtML/Ru(0001), 2. PtML/Ir(111), 3. PtML/Rh(111), 4. PtML/Au(111), 5. Pt(111), 6. PtML/Pd(111).⁵³

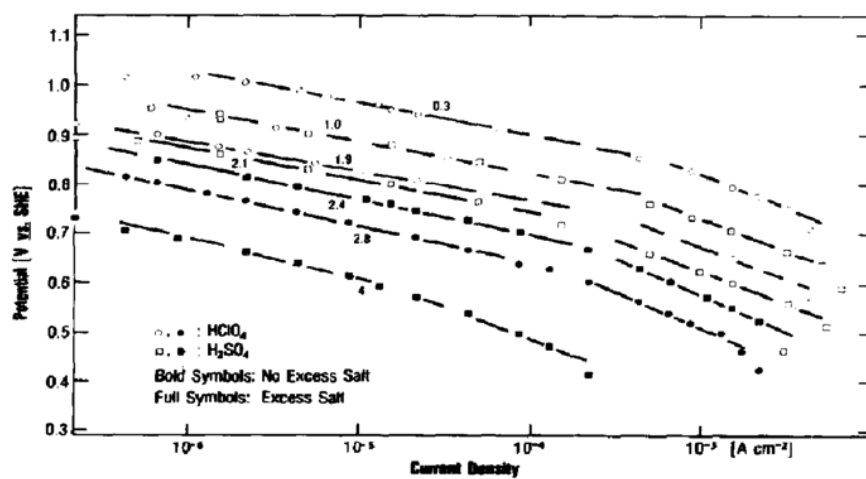


Figure 7. V - $\log i$ relationships in H₂SO₄ and HClO₄ solutions of different pH.⁵⁵

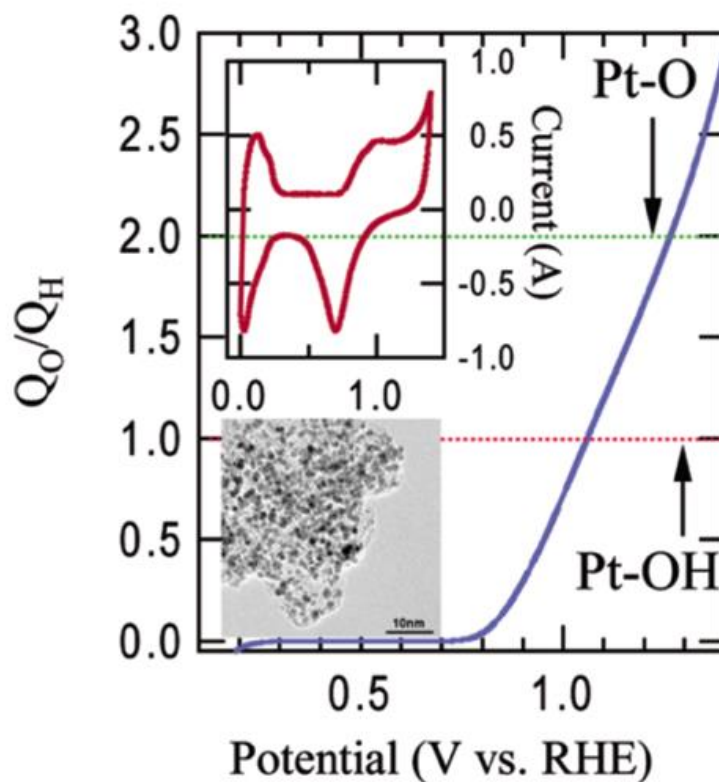


Figure 8. Potential-dependent degree of oxidation estimated as the ratio of the oxidation charge to the hydrogen adsorption charge assuming successive oxidation reactions. Assuming that the active sites are the same for hydrogen adsorption and surface oxidation, oxidation/hydrogen adsorption charge ratios of 1, 2, and 4 correspond to Pt-OH adsorption, Pt-O adsorption, and nominal PtO₂ formation, respectively. Inset shows the cyclic voltammogram of the catalyst-coated electrode⁵⁹.

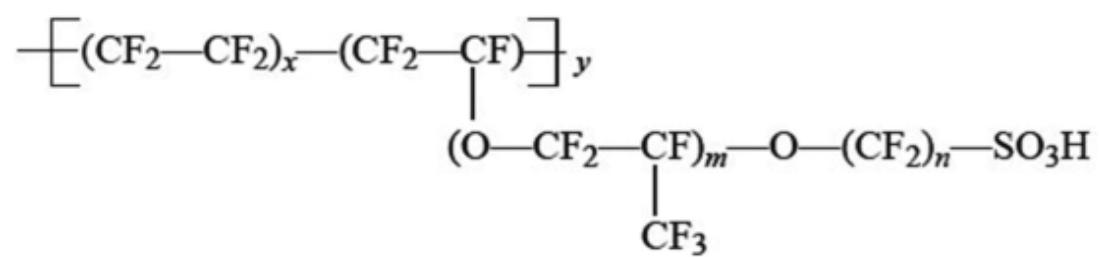


Figure 9. Chemical structure of Nafion[®] ($x = 5\text{--}13.5$, $y = 1$, $m \geq 1$, $n = 2.3$).⁶³

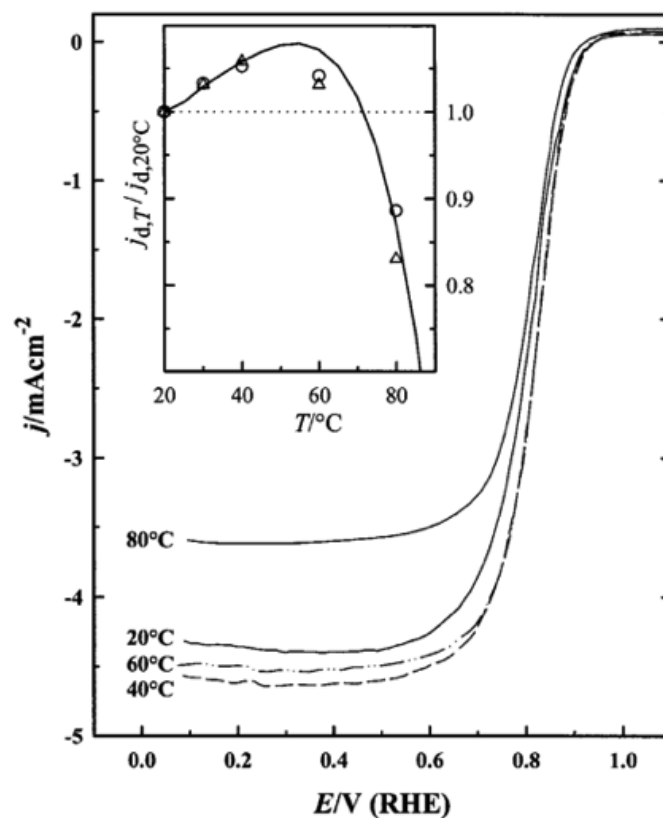


Figure 10. Potentiodynamic (5mV s^{-1}) ORR current densities recorded on a thin-film Pt/Vulcan R(R)DE at 1600 rpm as a function of temperature. Inset: Theoretical temperature dependence of diffusion-limited current density calculated assuming the physicochemical properties of pure water.⁸¹

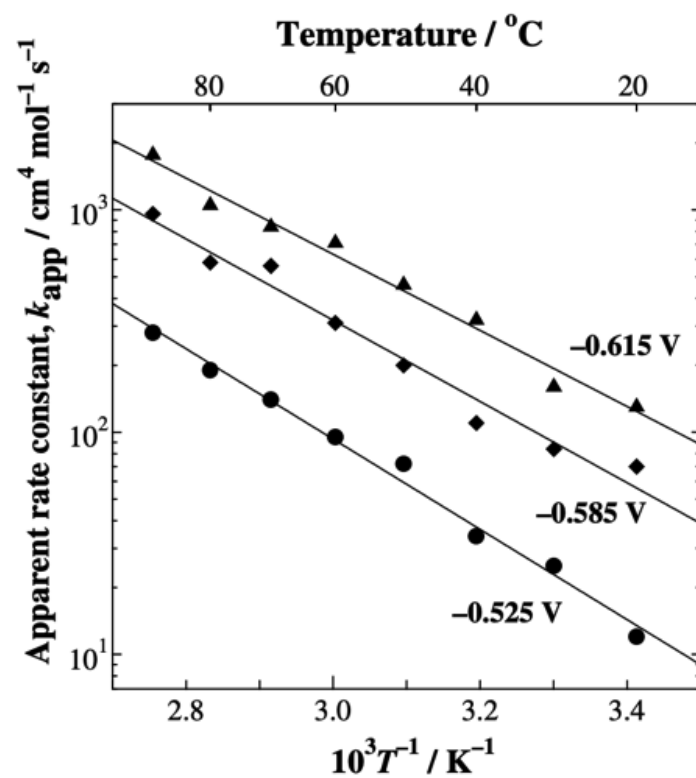


Figure 11. Arrhenius plots for the apparent rate constant k_{app} at 0.525, 0.585, and 0.615 V vs. E_0 .⁸²

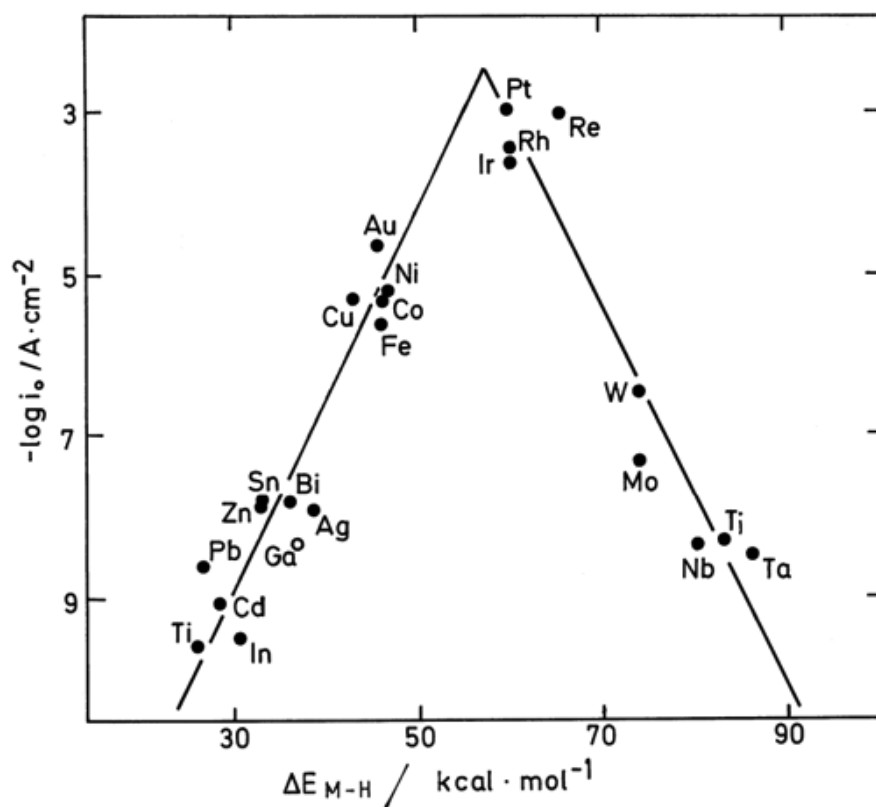


Figure 12. Logarithmic plot of exchange current densities for cathodic hydrogen evolution vs. the bonding adsorption strength of intermediate metal–hydrogen bonds formed during the electrode reaction itself.⁸⁶

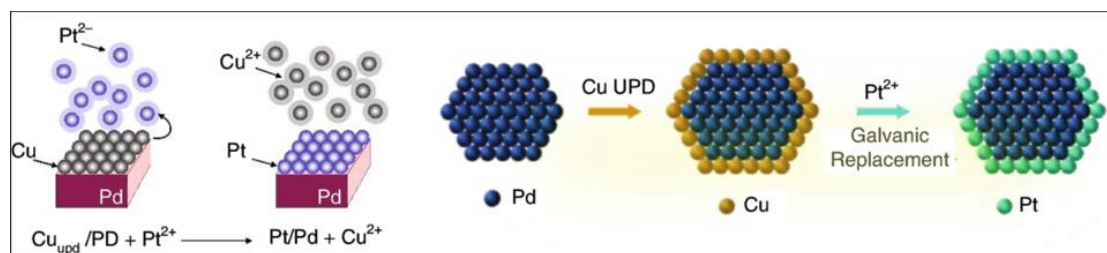


Figure 13. Schematics of the galvanic displacement of a Cu UPD monolayer by Pt. Blue and gray spheres represent Pt and Cu atoms, respectively. The clouds around the spheres indicate ions.¹⁰⁵

Chapter 2. Effect of Temperature on Oxygen Reduction Reaction Kinetics for Pd Core - Pt Shell Catalyst with different core size

2.1 Introduction

Polymer electrolyte fuel cells (PEFCs) are expected to be one of the main components of the global renewable energy system and pure hydrogen energy society of the future as they do not produce greenhouse gases during operation. Currently, PEFCs are already commercialized for low-temperature working conditions, especially in small-scale transportation systems such as fuel cell vehicles (FCVs) and residential cogeneration systems¹⁻⁵. However, several problems remain unsolved, preventing the large-scale use of PEFCs. One major obstacle to the commercialization FCVs is the high cost of the Pt cathode catalysts used for the oxygen reduction reaction (ORR), resulting in inefficient reaction kinetics and degradation effects under the strong acidic conditions⁶⁻⁹. Therefore, high performance, high durability, and less expensive catalyst are expected to widen the use of PEFC devices.

Many studies have reported that the mass activity of Pt-based catalysts can be enhanced by increasing the active Pt surface area and changing the electronic state of Pt. Adzic's group studied Pt-based electrocatalysts synthesized by galvanic displacement of a Cu monolayer on Pd which exhibited high Pt mass activities¹⁰⁻¹⁷. Pt-based core-shell catalysts possess less Pt loading, which proved successful in the preparation of low Pt load electrocatalysts¹⁸⁻²¹. Core-shell catalysts also have other features that make this structure attractive, mainly because of their potential to control the ORR activity by controlling the core materials, particle size, shell thickness, and facets^{13,18, 22-28}. The activity of the Pt catalyst is related to the substrate-induced strain, whether tensile or compressive, in combination with the ligand effect^{29, 30}. The status of the *d*-band on the Pt surface layer, which is modified by ligand and strain effects, can influence the binding strength and absorption properties of the oxide species. Therefore, the moderate compressive strain of the Pt surface layer enhances its activity for the ORR. Among the parameters that influence the ORR activity of core-shell catalysts, core size has been demonstrated to affect activity through many ways^{13,41}. The core size

could affect the ORR activity by changing the active facet proportion on the Pt surface, the electronic status of shell atoms, and the lattice strain^{13,41}.

Some studies have shown that the activity values evaluated for the same catalysts through MEA (membrane electrode assembly) were lower than RDE (rotating disk electrode) measurement, whose reasons are still under discussion³¹⁻³⁷. For example, the fuel cell performances of Pd-core Pt-shell catalysts (Pt/Pd/C) and the conventional Pt/C were compared through MEA measurements, and their assessment indicated that the I-V performance of Pt/Pd/C was comparable to that of 50 wt.%Pt/C, although the specific activity of Pt/Pd/C was higher than that of Pt/C by approximately a factor of two using RDE measurement in half cells with liquid electrolyte³¹. One of the differences between the RDE and the MEA measurement results may be the difference of the measurement temperature. Quantitative evaluation of ORR activities at high temperatures has been reported for pure Pt and Pt-M alloy (M=3d transition metals) catalysts^{38,39}, confirming behaviors in accordance with the general Arrhenius equation. These results indicate that temperature was not the main reason for Pt-based catalysts. In contrast, few studies have investigated the effect of temperature on Pt/Pd/C³¹. Pt/Pd/C are completely different in structure from ordinary Pt catalyst; therefore, the different thermal behavior of the ORR activity at high temperatures may be expected due to the hetero contact between the Pt shell and core atoms. There is a possibility that the local structures of the Pt monolayer differ depending on the temperature and influence the status of the *d*-band center and the ORR activity.

operando X-ray absorption spectroscopy (XAS) represents valuable tools to analyze the strain effects through the changes in the Pt-Pt bond length of in Pt alloy and core-shell catalysts as reported including our previous studies⁴⁰⁻⁴⁵. In general, the electrochemical properties of the catalyst have always been investigated using a thin catalyst layer on RDE. However, in most reports, *operando* XAS is conducted in the transmission mode, which requires a large amount of Pt catalyst to obtain enough signal ($\Delta\mu t \sim 1$)^{41,44,46}. This could cause the reaction distribution in the catalyst layer along the cross-sectional direction under the O₂ saturated electrolyte. To solve this problem, the direct measurement of XAS on the catalyst casted on RDE was performed by few researchers^{47, 48}.

In this study, we measured the ORR activities and the coverage of oxide species of Pt/Pd/C with different core size (2.3, 4.3 and 8.0 nm) in the temperature range of 25–

60 °C. The Pt/Pd/C was synthesized by the deposition of Pt on Pd/C with galvanic displacement through underpotential deposition of Cu. *operando* X-ray absorption spectroscopy (XAS) was also used to observe the Pt-Pt bond distance in the catalyst and to illustrate the ORR activity temperature dependence of Pt/Pd/C. In addition, the exact same amount of catalyst loading ($\Delta\mu\text{t} \sim 0.02$) on RDE was utilized to avoid the influence of reaction distribution and ensure the correct results of *operando* XAS spectra under ORR conditions.

2.2 Experiment

2.2.1 Preparation of the Pt/Pd/C catalyst through Cu-underpotential deposition (Cu-UPD).

9.4 wt.% Pd/C, 30 wt.% Pd/C, and 32.2 wt.% Pd/C was produced by ISHIFUKU Metal Industry Co., Ltd. Japan. The average particle size of each catalyst was 2.3 nm, 4.3 nm and 8.0 nm respectively for 9.4 wt.% Pd/C, 30 wt.% Pd/C, and 32.2 wt.% Pd/C, confirmed by transmission electron microscope in Figure 1. The Pd/C catalyst ink consisted of a 2:3 ratio of water:2-propanal (99.99%, Wako) and the amount of Pd/C was adjusted to form a $5 \mu\text{g}_{\text{Pd}} \text{ cm}^{-2}$ catalyst layer after dropping 5 μL on a glassy carbon rotating disk electrode (GC RDE) (HOKUTO DENKO, area = 0.196 cm^2). The ink on the RDE was dried at 700 rpm at 25 °C. Subsequently, Nafion[®] solution was dropped on the RDE surface up to a thickness of 200 nm at 25 °C. The Pt/Pd/C was prepared by depositing Pt through galvanic displacement by Pt of an underpotentially deposited (UPD) Cu monolayer. The UPD measurements were carried out in a three-electrode cell at 25 °C. The counter electrode was a Pt mesh and the reference electrode was a reversible hydrogen electrode (RHE). After the deposition of Cu from 10 mM CuSO₄ in a 0.1 M HClO₄ solution, the RDE was rinsed with N₂-saturated water to remove Cu²⁺ from the solution and placed in a N₂ saturated 5.0 mM K₂PtCl₄ aqueous solution. After immersion for 8 min to completely replace Cu by Pt, the RDE was rinsed again with N₂-saturated water. A commercially available 30wt% Pt/C catalyst (TEC10V30E, Tanaka Kikinzoku Kogyo) was used as the reference sample. Figure 2 illustrates the cyclic voltammograms for the underpotential deposition of Cu on various Pd/C in 0.1 M HClO₄ with 10 mM CuSO₄. It shows the typical CV for underpotential deposition of Cu on Pd [49]. From this result, the potential was held at 0.31V (vs. RHE) during underpotential deposition of Cu. Each Pt/Pd/C was denoted as Pt/Pd(*d*)/C, *d* = 2.3, 4.3,

and 8.0 nm, where d indicates the average particle size of Pd in this study.

2.2.2 Electrochemical measurements.

As shown in Figure 3, The ORR activity measurements were carried out in a three-electrode water jacket cell connected with hot water circulator, controlling the temperatures between 25 and 60 °C. The temperature was monitored by platinum resistance thermometer. It was hard to warm up the solution over 70 °C without the evaporation of electrolyte, which make it almost impossible to evaluate the accurate ORR activity of the catalysts.

The counter electrode was a Pt mesh, and the reference electrode was an RHE. The RHE is prepared by immersing a Pt wire in the electrolyte in a glass tube equipped with inlet and outlet ports for H₂ gas. The RHE is inserted in the main electrochemical cell. Prior to the catalyst activity measurements, the potential was cycled 20 times between 0.02 and 1.1 V (vs. RHE) at 100 mV·s⁻¹ to obtain stable cyclic voltammogram in N₂-saturated 0.1 M HClO₄. The final cyclic voltammogram was obtained at 50 mV·s⁻¹. After the measurements, the electrolyte was saturated in O₂. As Pd metal may has the hydrogen storage properties even in the nanoparticles, we set the cyclic voltammogram range starting from 0.1V vs RHE. The different CV range among Pd/C, Pt/C and Pt/Pd/C also been adopted in the article from Adzic's group¹⁷. Data regarding oxygen reduction for all materials studied were analyzed using the Koutechy-Levich (K-L) equation at 0.9 V vs. RHE. The ORR activity was evaluated by preparing a sample for each temperature by the same method as described above and evaluated at least 5 times at every temperature. Cyclic voltammograms during Cu underpotential deposition process was shown in Figure 4. In addition, chronoamperogram of the corresponding Cu underpotential deposition process was shown in Figure 5. This results also have no significant difference among 5 times and the average Pt loading was 0.85 μg on the 0.196 cm² electrode area (4.3 μg_{Pt} cm⁻²). We also measured the activity of each catalyst at each temperature for 4-5 times, the linear sweep voltammetry curves showed in Figure 6 and 7. There was also almost no difference, indicating that the high reproducibility of our experiment. Pt loading of Pt/C catalyst on RDE was 5 μg_{Pt} cm⁻².

The coverage of oxide species was measured by linear sweep voltammetry in N₂-saturated 0.1 M HClO₄. First, the potential was swept from 0.4 V (vs. RHE) to the target potential (0.5 - 1.1 V vs. RHE) at 50 mV·s⁻¹, and then the potential was maintained for

approximately 5 min to obtain a stable current. Finally, the potential was again set to 0.4 V (vs. RHE). The integrated cathodic current was used to estimate the charge of oxide species based on the following reaction ($\text{Pt-OH} + \text{H}^+ + \text{e}^- \rightarrow \text{Pt} + \text{H}_2\text{O}$) also reports from other researchers^{50,51}. The coverage of oxide species was estimated through dividing the charge of oxide species by the underpotential deposition charge of hydrogen^{50,51}. The profiles for Pt/C are shown in Figure 8 as an example.

2.2.3 *operando* XAS measurements.

operando XAS measurements of the Pt L_{III}-edge of the Pt/C and Pt/Pd/C catalysts were carried out by using synchrotron radiation at the beamlines BL37XU and BL01B1 at SPring-8, Hyogo, Japan. The ring current was operated at 8 GeV with a ring current of 100 mA in the top-up mode. The measurement scheme was shown in Figure 9. Figure 10 and 11 showed the detail of *operando* cell. The material for the main body of the *operando* cell is made of poly ether ether ketone (PEEK). The catalyst coated RDE can be set on the center of the cell as working electrode. Ag/AgCl electrode (RE-8, EC Frontier CO., LTD., Japan) and carbon rod (3 mm ϕ , Tokai Carbon CO., LTD., Japan) were used as reference and counter electrode, respectively. The polytetrafluoroethylene (PTFE) tube on the bottom right part is for the O₂ gas inlet to the 0.1 M HClO₄ electrolyte to control the gas atmosphere. The check valve (MFTD-6V, AS ONE Corporation, Japan) is the gas outlet and also can prevent the internal pressure rise during bubbling the gas. Kapton® film of 25 μm was used as the X-ray window. The temperature was controlled by blowing heated air into a cell surrounded by a heat insulating shield. The temperature was monitored by platinum resistance thermometer through the check valve.

Data processing was performed using ATHENA and ARTEMIS, a suite of IFEFFIT software programs. We used the same catalyst loaded RDE described above as a measurement sample.

2.2.4 Transmission electron microscopy

Transmission electron microscope (TEM) and elemental mapping images was obtained by using JEM-F200 and SDD (Silicon drift detector, JEOL Ltd.) at 200 kV.

2.2.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) on a PHI Quantum 2000 system (ULVAC-PHI, Inc., Japan), using monochromated-Al-K α X-ray source operating at 40W and 1486.6eV.

2.2.6 High temperature X-ray diffraction

A high temperature X-ray diffraction (HT-XRD) was measured at BL02B2 and BL19B2 at SPring-8, Hyogo, Japan. The energy of the incident X-ray was 20 keV and the samples were fixed in quarts tube.

2.3 Results and discussion

2.3.1 TEM observation and XPS measurements

The TEM images and EDX (Energy dispersive X-ray spectroscopy) maps of Pd and Pt in Figure 12 showed the observation results of as-synthesized Pt/Pd/C. The EDX maps and their line profiles confirmed the formation of Pt shell on the Pd core, indicating the success of the Pd core Pt shell structure, similar with other report²². The as prepared Pt/Pd/C core-shell catalyst possess the atom ratio of Pt/Pd = 41/59, 32/68, and 29/71, respectively for Pt/Pd(2.3)/C, Pt/Pd(4.3)/C and Pt/Pd(8.0)/C the evaluation of EDX analysis.

According to XPS results in Figure 13a, the 4f peak single of Pt/Pd/C shifted to a higher binding energy (71.6eV) compared with the Pt/C (71.3eV). The peak position results close to other report⁵². The change of binding energy may contributed by the coupling of electronic between Pt shell and Pd substrate. The compressive strain effect of Pt shell on Pd core would be another factor lead the positive binding energy peak shift of Pt 4f in the Pt/Pd/C catalyst.

2.3.2 Electrochemical measurements

Figure 14 shows the cyclic voltammograms for Pt/C and Pt/Pd/C at various temperatures (25 - 60 °C). All catalysts exhibited slight changes in hydrogen adsorption/desorption behavior depending on the temperature. This may be related to the temperature dependence of the Pt-H bond energies on different Pt crystal planes although the details are still under investigation⁵³. In addition, the oxidation of Pt was enhanced in both catalysts as the temperature increased.

The ORR activity was investigated at different reaction temperatures (25 - 60 °C) for

the Pt/C and the Pt/Pd/C. The linear sweep voltammograms and the specific/mass activities were summarized in Table 1, respectively. Pt/Pd/C catalysts with various Pd core sizes exhibited the higher activity than Pt/C at 25 °C due to the compression effect from Pd core⁴¹. The specific and mass activity increased as the temperature increased for both catalysts. The Tafel plots of Pt/Pd/C were shown in Figure 15. The Tafel slopes of Pt/Pd/C were about 75 mV/decade higher than 0.85 V (vs. RHE) and 143 mV/decade lower than 0.85 V, which had an agreement with other reports^{54,55}. In addition, the Tafel slopes did not changed among Pt/Pd/C regardless of core size and temperature, indicating that there is no significant change of ORR mechanism. However, with increasing temperature, O₂ concentration in the solution decreases³⁸. Hence, any comparison of ORR activities requires prior corrections. We introduced the correction methods and equations proposed by Wakabayashi et al.³⁸, which allows the calculation of the apparent rate constant (k_{app}) as an indication of the reaction kinetics and activity. The summarization about the physical meaning of the parameters and the solid theoretical basis about apparent rate constant and the O₂ concentration correction at different temperature were shown below.

In this study, we introduced the correction methods and equations proposed by Wakabayashi et al.³⁸. We added the summarization about the physical meaning of the parameters and the solid theoretical basis about apparent rate constant (k_{app}) and the O₂ concentration correction at different temperature as follows:

The oxygen concentration in the electrolyte could calculate through the Henry's law:

$$[O_2] = k_H P_{(O_2)} \quad \text{eq. 1}$$

k_H is the Henry's law volatility constants, $P(O_2)$ is oxygen partial pressure and $[O_2]$ is O₂ concentration of in the bulk of electrolyte. The temperature dependence of k_H and $P(O_2)$ could be calculated:

$$k_H(T) = k_H(298 \text{ K}) \exp \left[-(\Delta H_{\text{soln}}/R) \left(\frac{1}{T} - \frac{1}{298} \right) \right] \quad \text{eq. 2}$$

$$P(O_2) = P_{\text{total}} - P(H_2O) \quad \text{eq. 3}$$

$k_H(298\text{K}) = 1.3\text{mM atm}^{-1}$, ΔH_{soln} is enthalpy of oxygen dissolution ($-\Delta H_{\text{soln}}/R = 1500 \text{ K}$). P_{total} is 1atm in this system and $P(H_2O)$ is the water vapor pressure. Through

(1), (2), (3) we can get the O₂ concentration [O₂] in this system in Table 2.

With the calculated O₂ concentration [O₂], Wakabayashi et al attempt to use rate constant k_{orr} to discuss the ORR, related to O₂ concentration [O₂] and kinetically controlled current I_K :

$$I_K/4FA = -(1 - \theta)^m k_{orr}[O_2][H^+] \quad \text{eq. 4}$$

F is Faraday constant, A is the electrode area (real surface area), θ is the coverage of the adsorbed species like oxides or adsorbed anions, m is the number of active sites needed for the absorption of 1 O₂ molecule, $(1-\theta)$ is the fraction of active sites on the Pt surface, $[H^+]$ is the bulk concentration of H⁺ in the electrolyte. Set the fraction of active sites at specific temperature and potential is fixed ($(1-\theta)^m = \text{constant}$) and (4) can be like (5):

$$I_K/4FA = -k_{app}[O_2][H^+] = -\text{constant} \times k_{orr}[O_2][H^+] \quad \text{eq. 5}$$

Therefore, in this experiment, we evaluate the apparent rate constant k_{app} which dependent with O₂ concentration [O₂] and experiment value of I_K to evaluate the activity of catalysts under various O₂ concentration.

A comparison of the apparent rate constants k_{app} for the Pt/Pd/C and Pt/C at various temperatures with the Arrhenius plots were shown in Figure 16. Pt/C showed linear relationships based on the Arrhenius equation, and the apparent activation energy was 34 kJ·mol⁻¹, which is in good agreement with a previous report^{38,39}. At 25 °C, the k_{app} of the Pt/Pd/C was increased with increasing in Pd core size. This might be due to the moderate compression effect from Pd core was realized in Pt/Pd(8.0)/C. This kind of core size dependence on ORR activity was also reported¹⁸. Upon increasing the temperature from 25 to 60 °C, the k_{app} of each Pt/Pd/C showed different trends depending on the core size, whereas the behavior of Pt/C could be described by a simple Arrhenius equation. A clear core size dependence on the ORR activity was observed as the temperature increased. The activity of Pt/Pd(2.3)/C was the lowest as compared to the other catalysts at 40 °C, and its plot showed a peak at 50 °C. Subsequently, the activity decreased at 60 °C, although Pt/Pd(2.3)/C had the highest k_{app} among the three catalysts. In addition, Pt/Pd(4.3)/C possessed the highest ORR activity among the catalysts at 50 °C, but it decreased at 60 °C. Moreover, Pt/Pd(8.0)/C started losing its activity at 40 °C, which was the lowest temperature among the catalysts and had the

lowest ORR activity at 60 °C. These results seem to be significant because the trends of ORR activity at 25 °C were opposite to those at 60 °C when Pt/Pd/C were used. ORR activity of Pt/Pd/C were also measured upon cooling from 60 to 25 °C, indicating that there is no significant loss of ORR activity after high temperature measurement in Figure 17. Each Pt/Pd/C still possessed activity close to the fresh sample even after measurement at 60 °C. Therefore, the activity decay of Pt/Pd/C is not caused by degradation at 60 °C.

To investigate the loss of k_{app} at elevated temperatures in the Pt/Pd/C, the coverage of oxide species was estimated through electrochemical measurements at different temperatures and potentials. As shown in Figure 18a, the coverage of the Pt/C increased over 0.8 V (vs. RHE) because of the formation of oxide species, which is consistent with previous reports^{50,51}. The coverage exceeds 1.0 over 1.0 V (vs. RHE) because the surface is almost fully covered with Pt-OH species and started to transform to Pt-O species^{50,51}, occupying the active sites on the Pt surface and prevent the ORR process. In the case of Pt/Pd/C in Figure 18b-d, the coverage of Pt/Pd/C was significantly smaller than Pt/C at 25 °C, over 0.8V. This suggested that there were less oxygen species which adsorbed on Pt active site in Pt/Pd/C than Pt/C. As the oxygen species adsorbed on Pt site hinders ORR, the higher activity can be expected in the smaller coverage^{10-15, 27, 28}. Therefore, a larger value of k_{app} in the Pt/Pd/C than Pt/C was obtained at 25 °C. However, the oxide coverage of Pt/Pd/C increased dramatically for the temperatures above 40 °C. Figure 18e shows a comparison of the oxide coverage among the Pt/C and Pt/Pd/C at 1.1 V (vs. RHE). This clearly illustrates that the coverage in the Pt/Pd/C are affected by temperature more than that in the Pt/C and that the adsorption of oxide species is enhanced by higher temperatures in Pt/Pd/C. At 60 °C, the least oxide coverage was Pt/Pd(2.3)/C while that of Pt/Pd(8.0)/C was dramatically increased showing the same value as Pt/C. These trends agreed with the behavior of the apparent rate constants in Figure 16. Therefore, it can be suggested that the increase of the oxide coverage caused the significant activity decrease of Pt/Pd/C.

2.3.3 *operando* XAS measurements

In order to observe the temperature dependence of the oxide coverage on Pt, *operando* measurements were conducted. *operando* Pt L_{III}-edge X-ray absorption near edge structures in Figures 19-22 show the oxidation states of Pt atoms in the Pt/C and

Pt/Pd/C. XANES white line area change (Δ XANES) compared at 0.5V for Pt/C and Pt/Pd/C catalyst at 25 °C and 60 °C shows in Figure 23. Δ XANES was calculated from the following equation

$$\Delta\text{XANES} = \text{Area of white line at } (0.5 \sim 1.1 \text{ V vs. RHE}) - \text{Area of white line at } 0.5 \text{ V (vs. RHE)} \quad \text{eq. 6}$$

Here, the white-line peak area increased with increasing temperature, revealing that the Pt shell on Pt/Pd/C shows much more adsorption of oxide species at 60 °C than 25 °C. This agrees with the oxide coverage measurements shown in Figure 18, indicating that the oxide species on the Pt shell could easily be influenced by temperature.

To understand the local structures, we fabricated Pt layer model on the Pd according to our previous report⁴¹ and calculated the phase shifts and the back-scattering factors with the FEFF code. The fitted parameters were also shown in Table 3-6.

As mentioned above, the Pt-Pt bond length dependence has been reported as an important factor which could reflect the *d*-band center status and be related to the ORR activity^{26, 29}. Figures 24a and 24b show the fitting results for the Pt-Pt bond distance of Pt shell on each Pt/Pd/C at 25 and 60 °C in the range of 0.5 to 1.0 V vs. RHE, while the Fourier transforms of EXAFS are shown in Figures 25-28. The coordination numbers of Pt-Pt and Pd-Pd about Pt/Pd/C and Pt/C catalyst showed in Table 3-6. The coordination numbers of Pt-Pt and Pd-Pd on Pt/Pd/C and Pt/C catalyst showed in Table 2-5. Pt-Pt coordination numbers were almost the same regardless of the temperature at 0.5 V both in Pt/Pd/C and Pt/C catalyst. The less Pt-Pt coordination numbers were observed at higher potential and temperature due to Pt-O bond formation.

In terms of bond distance, Pt/C showed a Pt-Pt bond of 2.743 (± 0.002 Å) at 0.5 V (vs. RHE), which is slightly shorter than that of Pt foil (2.757 Å) at 25 °C. At 60 °C, the Pt-Pt distance of the Pt/C was slightly extended to 2.749 (± 0.003 Å). In the case of the Pt/Pd/C at 25 °C, Pt/Pd(2.3)/C had a contraction Pt-Pt bond distance of 2.731 Å at 0.5 V (vs. RHE), which was shorter than that of Pt/Pd(4.3)/C and Pt/Pd(8.0)/C. As the lattice shrinkage of Pd nanoparticles was observed with decreasing particle size owing to the nano-size effect^[56], the lattice strain effect of Pt atoms on the surface varies depending on the core size. As suggested by Kaito et al.⁵⁷, the appropriate Pt-Pt bond

shrinkage is expected to change the status of the *d*-band center and enhance the ORR activity. Therefore, the appropriate Pt-Pt bond distance on Pt/Pd(8.0)/C led to the best ORR activity for the Pt/Pd/C at 25 °C. In the case of Pt/Pd/C at 60 °C (Figure 24b), the Pt-Pt bond distance of Pt/Pd/C was extended as compared at 25 °C. At 60 °C, Pt/Pd(2.3)/C still had the shortest Pt-Pt bond distance than the others. It can be expected that the activity of Pt/Pd(2.3)/C at 60 °C was improved thanks to the extension of the bond, which had shrunk too much at 25 °C. On the other hand, Pt/Pd(4.3)/C and Pt/Pd(8.0)/C suffered over an extended Pt-Pt bond because of the high-temperature environment at 60 °C. Therefore, we can conclude that the over-extended Pt-Pt bond leads to dramatic oxide adsorption at the active sites on the Pt surface, which is the main reason for the decrease of k_{app} in the Pt/Pd/C at 60 °C. Moreover, we expect that the over-extension of Pt-Pt bond distance at high temperatures on the Pd core surface should be the reason of the Pd atoms possess a higher thermal expansion coefficient than Pt atoms⁵⁸. The larger thermal expansion of Pd cores in Pt/Pd/C than Pt/C lead the larger Pt-Pt bond extension of Pt shell on the surface and causes a decrease in the ORR activity at 60 °C.

2.3.4 High temperature X-ray diffraction

The Pt-Pt bond length extension on the Pd surface is expected to be caused by the larger thermal expansion coefficient of Pd with respect to Pt. The extra thermal expansion of nanosized materials also might be expected to contribute to the Pd core expansion. The *in-situ* high temperature X-ray diffraction results in Figure 29 and Figure 30 confirmed a difference in thermal expansion of the Pt/C and various particle size Pd/C. The Pd/C (141.5, 33.7 ppm·K⁻¹) and Pt/C (17.2 ppm·K⁻¹) possess a larger thermal expansion coefficient than bulk Pd and Pt, respectively, as established by other group⁵⁹. The larger thermal expansion coefficient of Pd/C relative to Pt/C indicates that Pd core expansion will impose additional thermal expansion on the Pt shell in the Pt/Pd/C. Therefore, we assumed that this Pt-Pt bond length extension in the Pt/Pd/C at high temperature is caused by the difference in the thermal expansion coefficients between Pt and Pd as well as by the particle size effect.

In summary, the compressive strain on Pt/Pd(8.0)/C at 25 °C lead the shorter Pt-Pt bond distance than Pt/C catalyst, change the position of d-band center and improve the ORR activity. However, Pt/Pd(2.3)/C suffered over compressive strain effect and lead

slight decrease of ORR activity. At 60 °C, due to the more significant thermal expansion of Pd core in Pt/Pd/C than Pt/C, the Pt shell in Pt/Pd/C exhibited the higher Pt-Pt bond length extension than for Pt/C. The over expansion of Pt-Pt bond length in Pt shell on the Pt/Pd/C weaken the compressive strain effect, which caused a decrease in the ORR activity. evidenced by *operando* XAS and *in-situ* high temperature X-ray diffraction.

2.4 Conclusion

This study investigated the effect of temperature on the ORR activity of a Pt-shell Pd-core catalyst. The apparent rate constants (k_{app}), the coverage of oxide species, and the local structures were determined using electrochemical measurements and *operando* XAS. The apparent rate constant (k_{app}) in the Pt/Pd/C corresponded to a higher ORR activity than the Pt/C at 25 °C, but the ORR activity started to decrease at high temperature (50-60 °C). Pt/Pd/C with a smaller core possess the lower ORR activity than the a larger Pd core at 25 °C, but the ORR activity started to decrease at 60 °C. The coverage of Pt/Pd/C was much lower than that of Pt/C at 25 °C. However, it increased dramatically with the increasing temperature, and Pt/Pd/C with larger Pd core got more oxygen coverage increase from 25 °C to 60 °C, which could be a part reason of the decrease in the ORR activity. The *operando* XAS study showed that the Pt-Pt bond length of the Pt/Pd/C catalysts was shorter than that of the Pt/C due to the compressive surface strain on the Pd core. According to *operando* XAS and high temperature X-ray diffraction, the Pt-Pt bond length extension was more significant for Pt/Pd/C catalysts than for Pt/C at 60 °C. The most significant Pt-Pt bond distance extension occurred on Pt/Pd/C with a larger Pd core, which could be the reason of a decrease in the ORR activity. This structural change of the catalyst was determined by the different thermal expansion between Pd core material and Pt shell.

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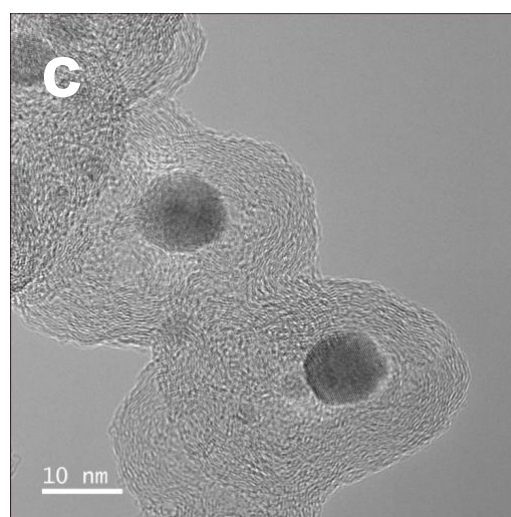
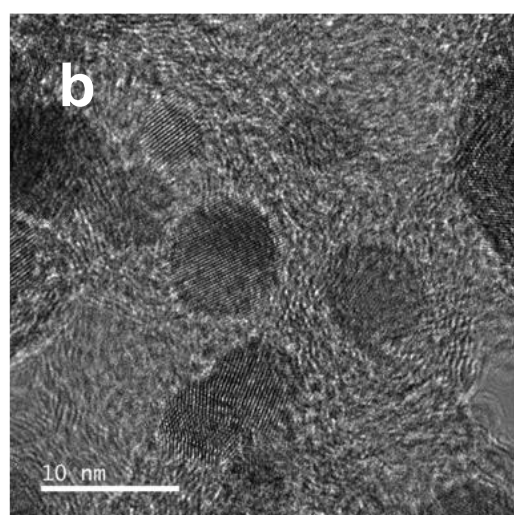
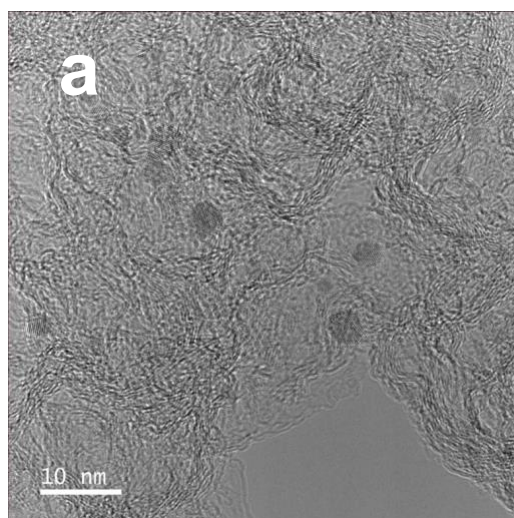


Figure 1. High resolution TEM image of Pt/Pd/C for the Pd core size of 2.3 nm(a), 4.3 nm(b), and 8.0 nm(c).

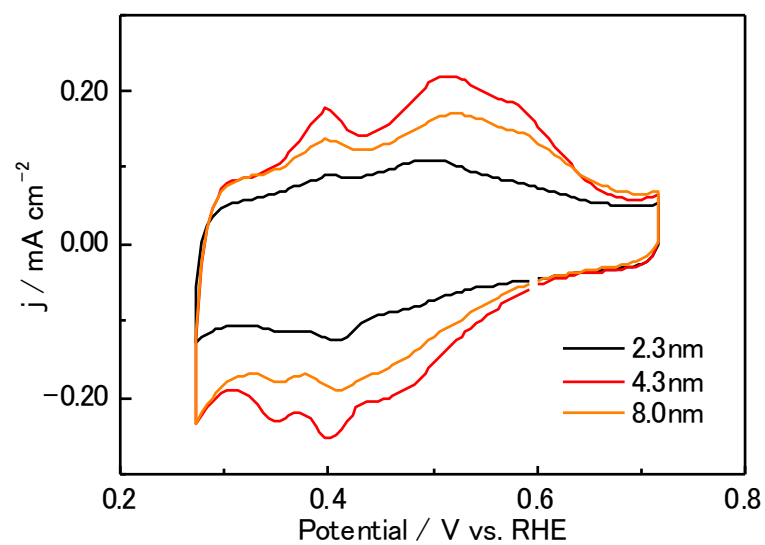


Figure 2. Cyclic voltammograms of Cu underpotential deposition on different particle size in N_2 -sat 0.1 M HClO_4 aq and 10 mM CuSO_4 .

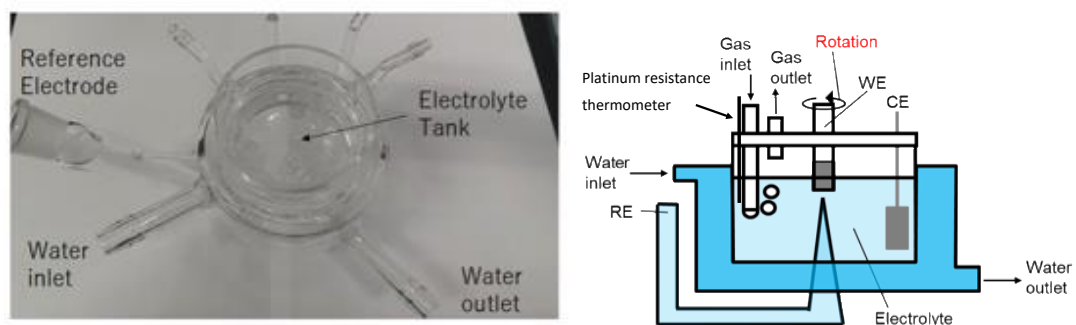


Figure 3. Photo (left) and illustration (right) of a three-electrode water-jacketed cell

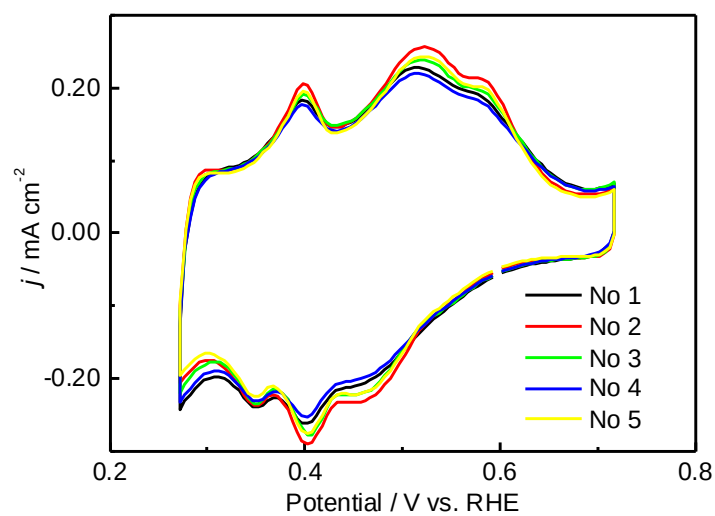


Figure 4. Cyclic voltammograms for Pt/Pd(4.3)/C Cu-UPD in 10 mM CuSO₄ + 0.1 M HClO₄ for 5 times of experiments.

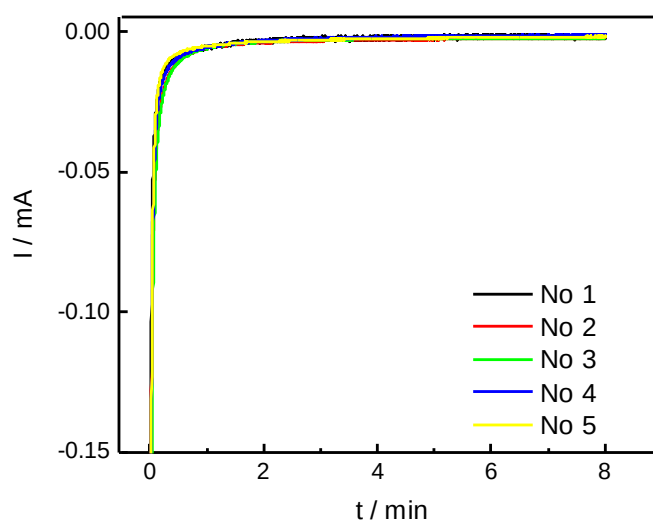


Figure 5. Chronoamperogram for 4.3nm diameter Pd/C in 10mM CuSO₄ + 0.1M HClO₄ for 5 times of experiments.

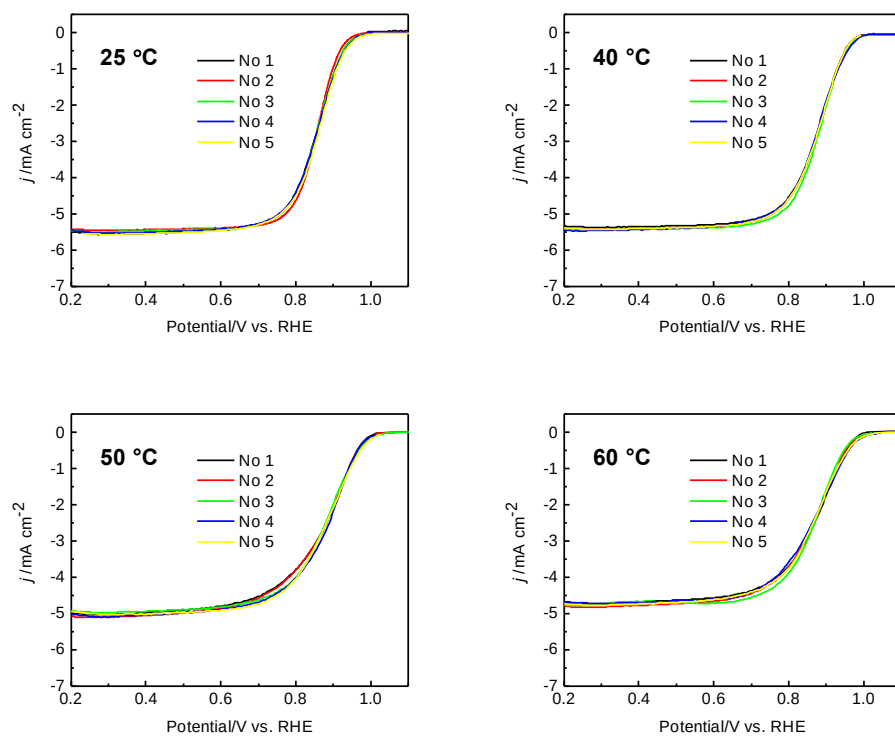


Figure 6. 5 times linear Sweep Voltammograms for Pt/C catalyst in O₂-saturated 0.1M HClO₄ at 25 °C, 40 °C, 50 °C and 60 °C (1600rpm).

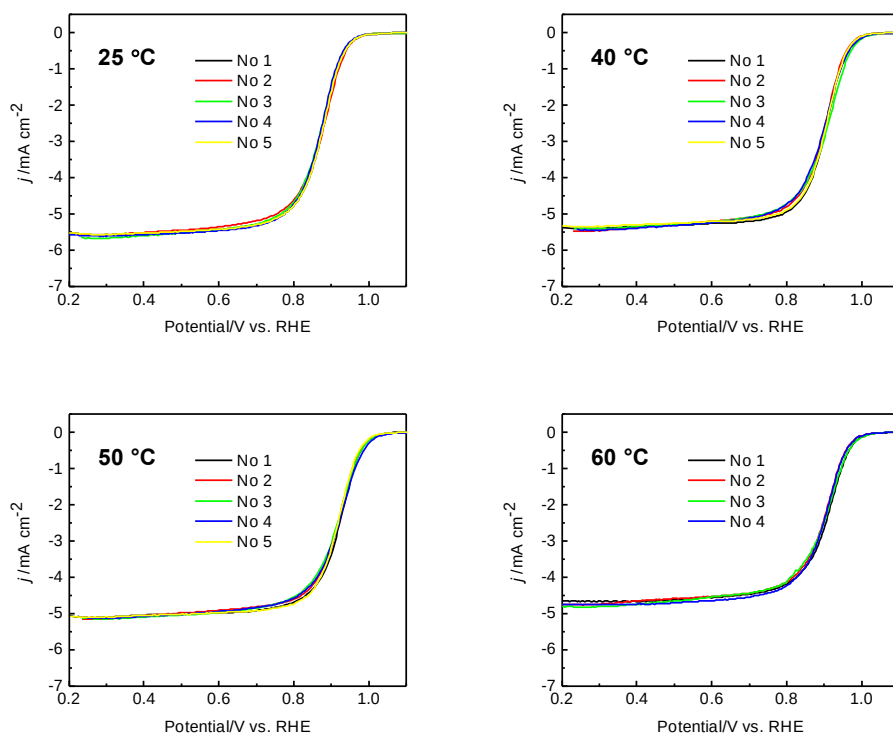


Figure 7. 4-5 times linear Sweep Voltammograms for Pt/Pd(4.3)/C catalyst in O₂-saturated 0.1M HClO₄ at 25 °C, 40 °C, 50 °C and 60 °C (1600rpm).

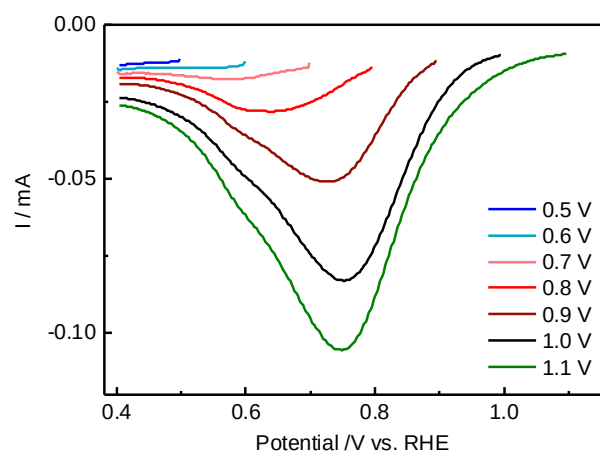


Figure 8. Reduction current of oxide species on Pt/C at 25 °C, holding potential from 0.5 -1.1 V vs. RHE.

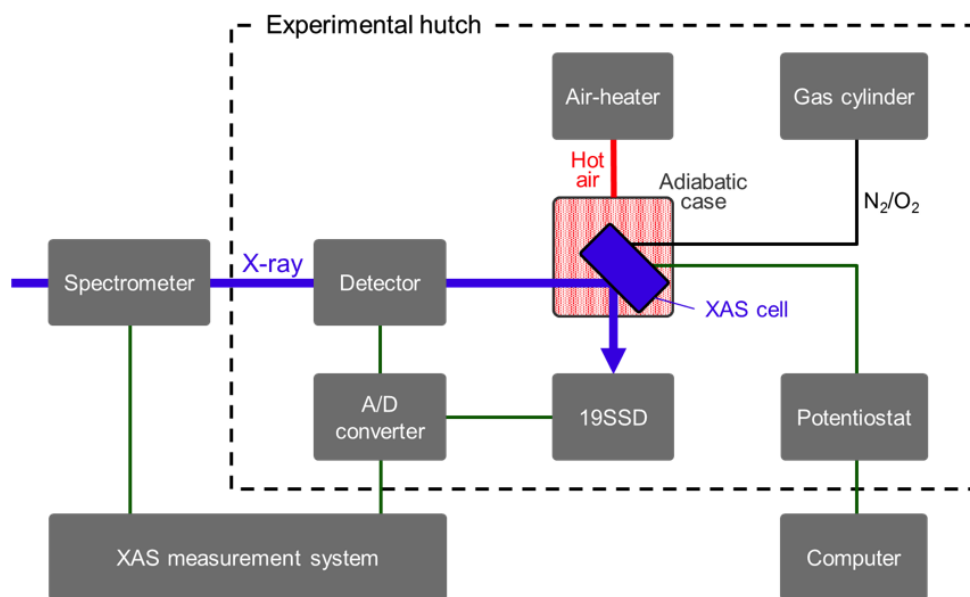


Figure 9. Measurement schematics for *operando* XAS measurement

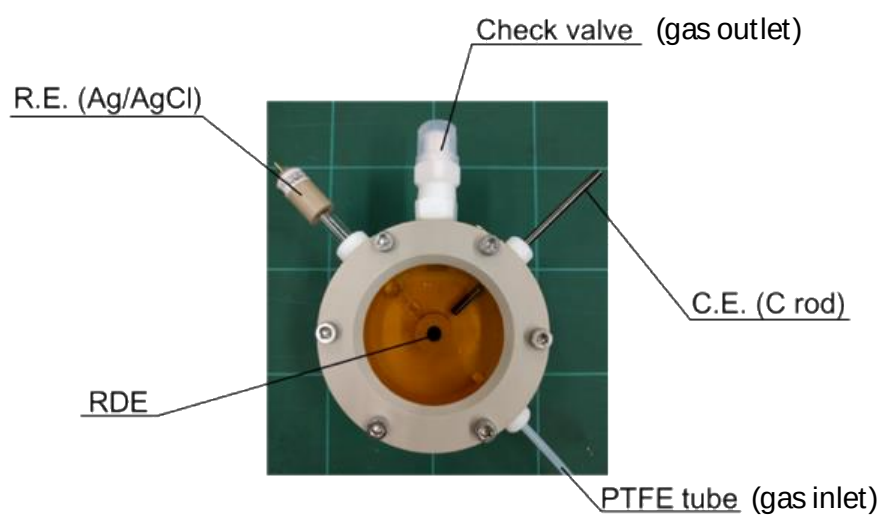


Figure 10. Assembled electrochemical cell for *operando* XAS measurement.

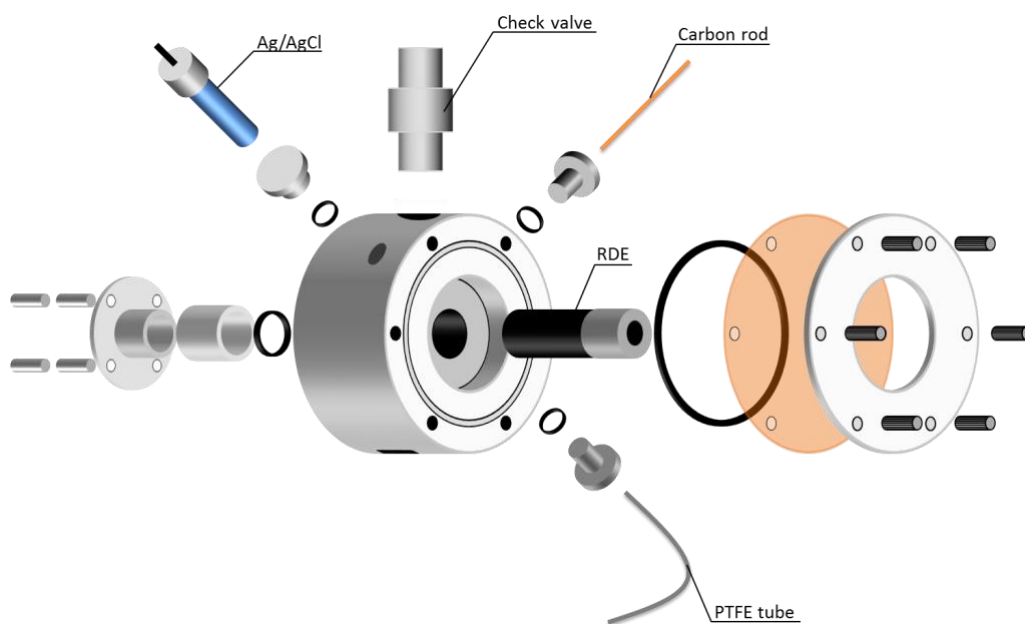


Figure 11. The structure of electrochemical cell for *operando* XAS measurement.

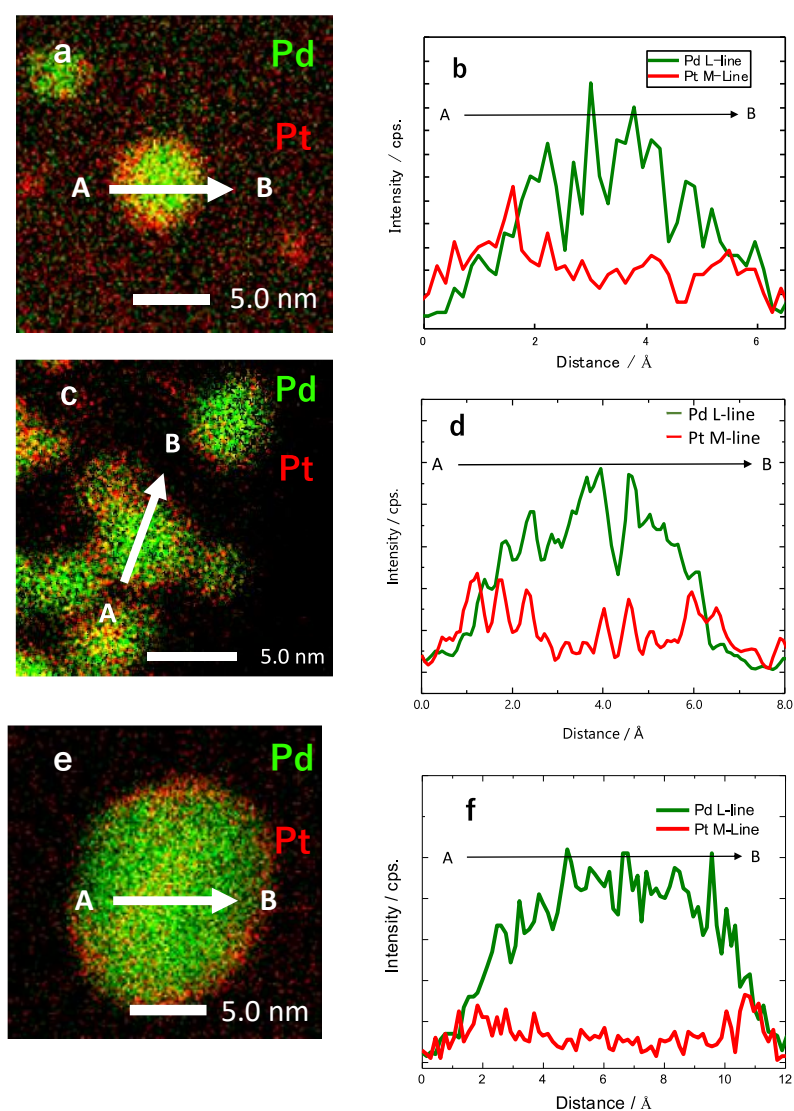
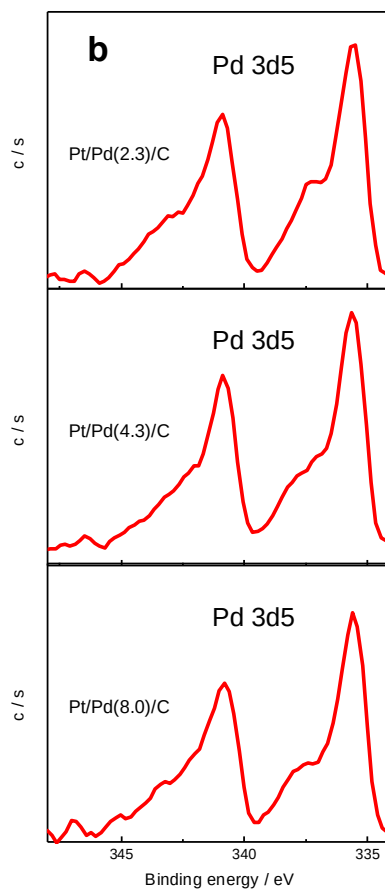
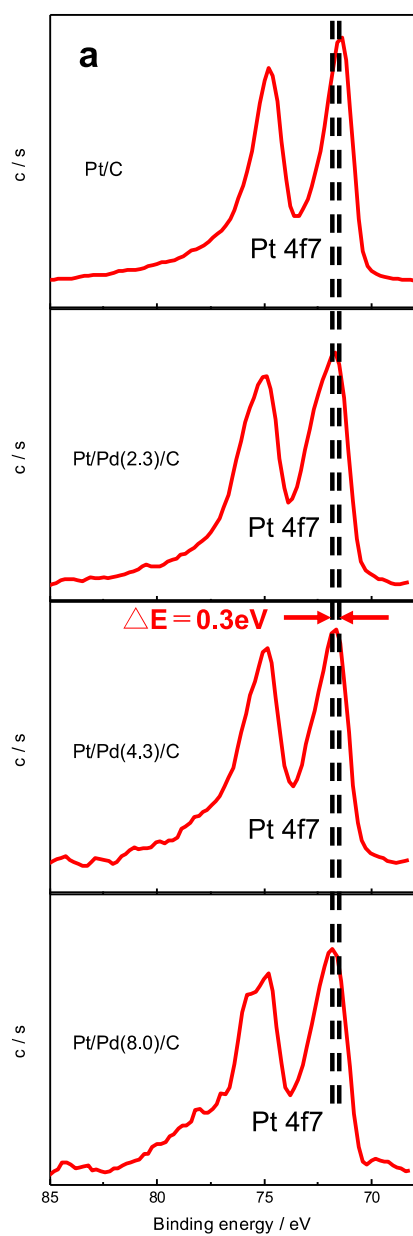


Figure 12. EDX elemental mappings and EDX line profiles of Pt/Pd/C: Pt and Pd EDX mappings of Pt/Pd(2.3)/C (a), Pt/Pd(4.3)/C (c), Pt/Pd(8.0)/C (e), showing arrow from A to B for collection of EDX line-profile data; (b, d, f) EDX line profile from A to B across the area indicated in (a, c, e).



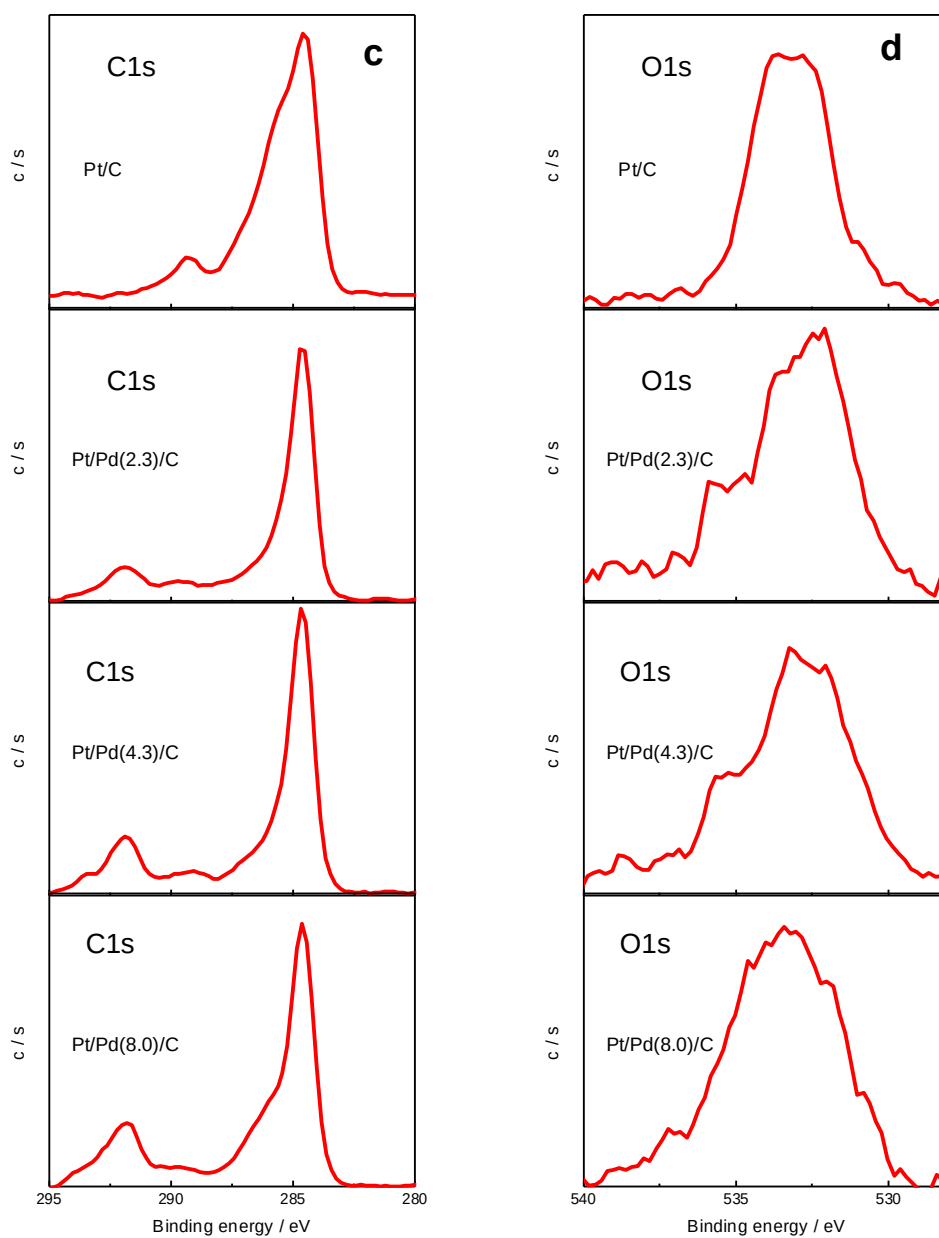


Figure 13. XPS spectra of (a) Pt 4f , (b) Pd3d, (c) C1s, (d) O1s in Pt/C and Pt/Pd(2.3)/C, Pt/Pd(4.3)/C, Pt/Pd(8.0)/C.

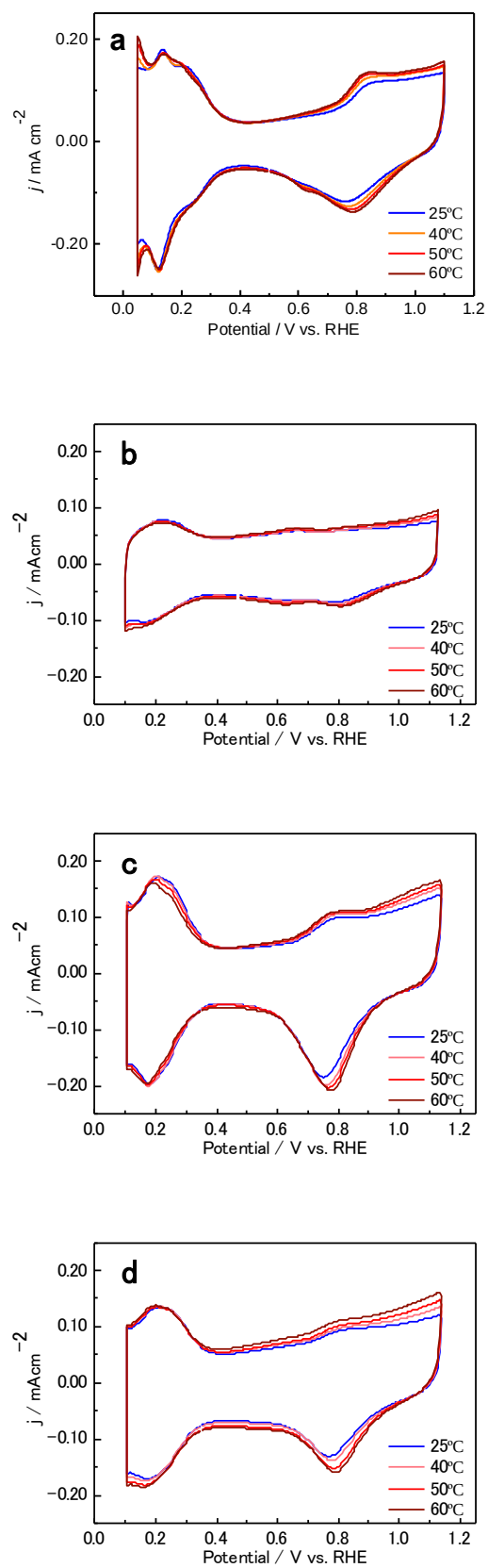


Figure 14. Cyclic Voltammograms for Pt/C (a), Pt/Pd(2.3)/C (b), Pt/Pd(4.3)/C (c),

Pt/Pd(4.3)/C (d) in N₂-saturated 0.1 M HClO₄ at various temperatures (25 - 60 °C).

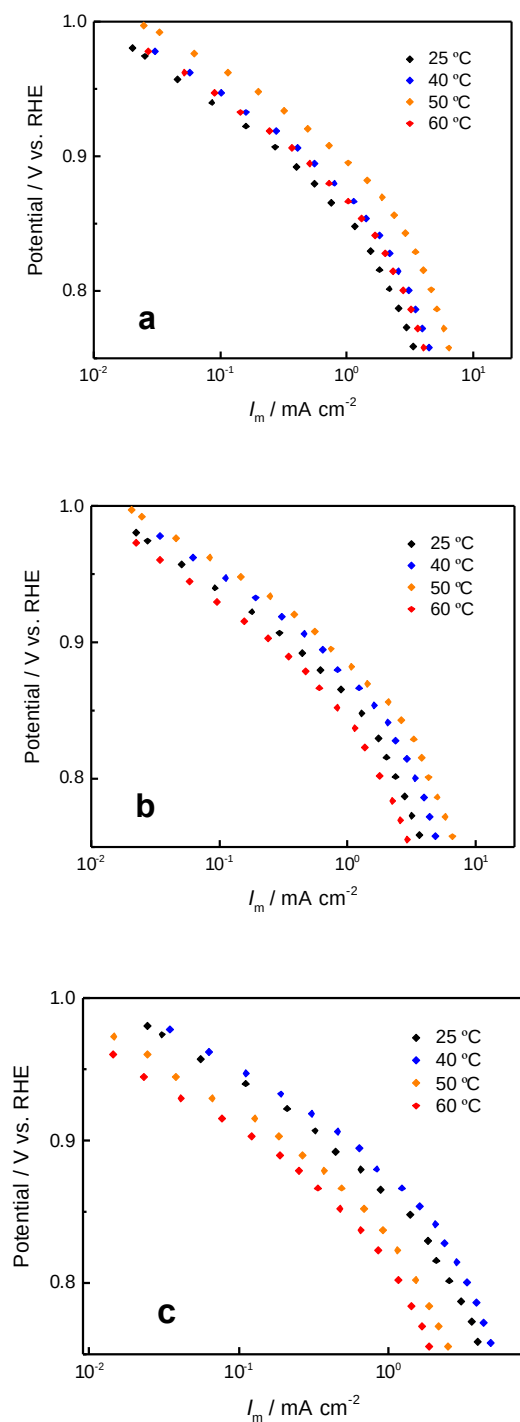


Figure 15. Tafel plots for the ORR about the Pt/Pd(2.3)/C (a), Pt/Pd(4.3)/C (b) Pt/Pd(8.0)/C (c) at 25 °C (black), 40 °C (blue), 50 °C (green) and 60 °C (red) at 1600 rpm.

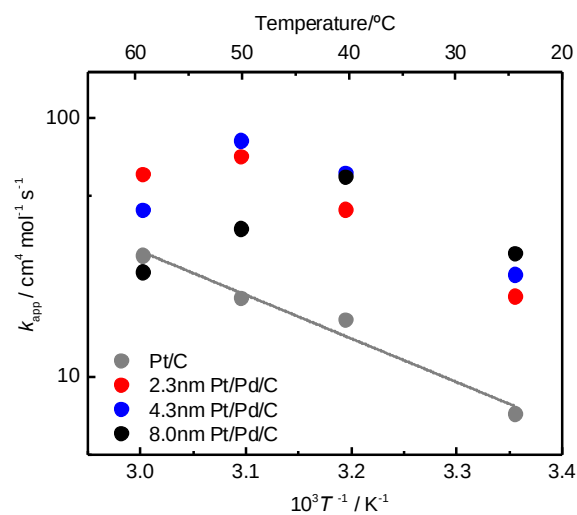


Figure 16. Arrhenius plots for the apparent rate constant k_{app} of Pt/Pd/C catalyst synthesized on 2.3 nm (red), 4.3 nm (blue), and 8.0 nm (black) diameter Pd core and Pt/C nanoparticle catalyst at 25, 40, 50, and 60 $^{\circ}\text{C}$, 0.90 V vs. RHE.

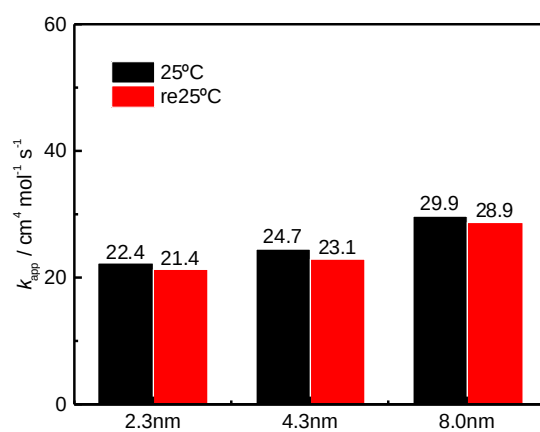


Figure 17. Comparison of apparent rate constant k_{app} for Pt/Pd(2.3)/C, Pt/Pd(4.3)/C and Pt/Pd(8.0)/C at 25°C (black bar) and 25°C after activity measurement at 60°C (red bar).

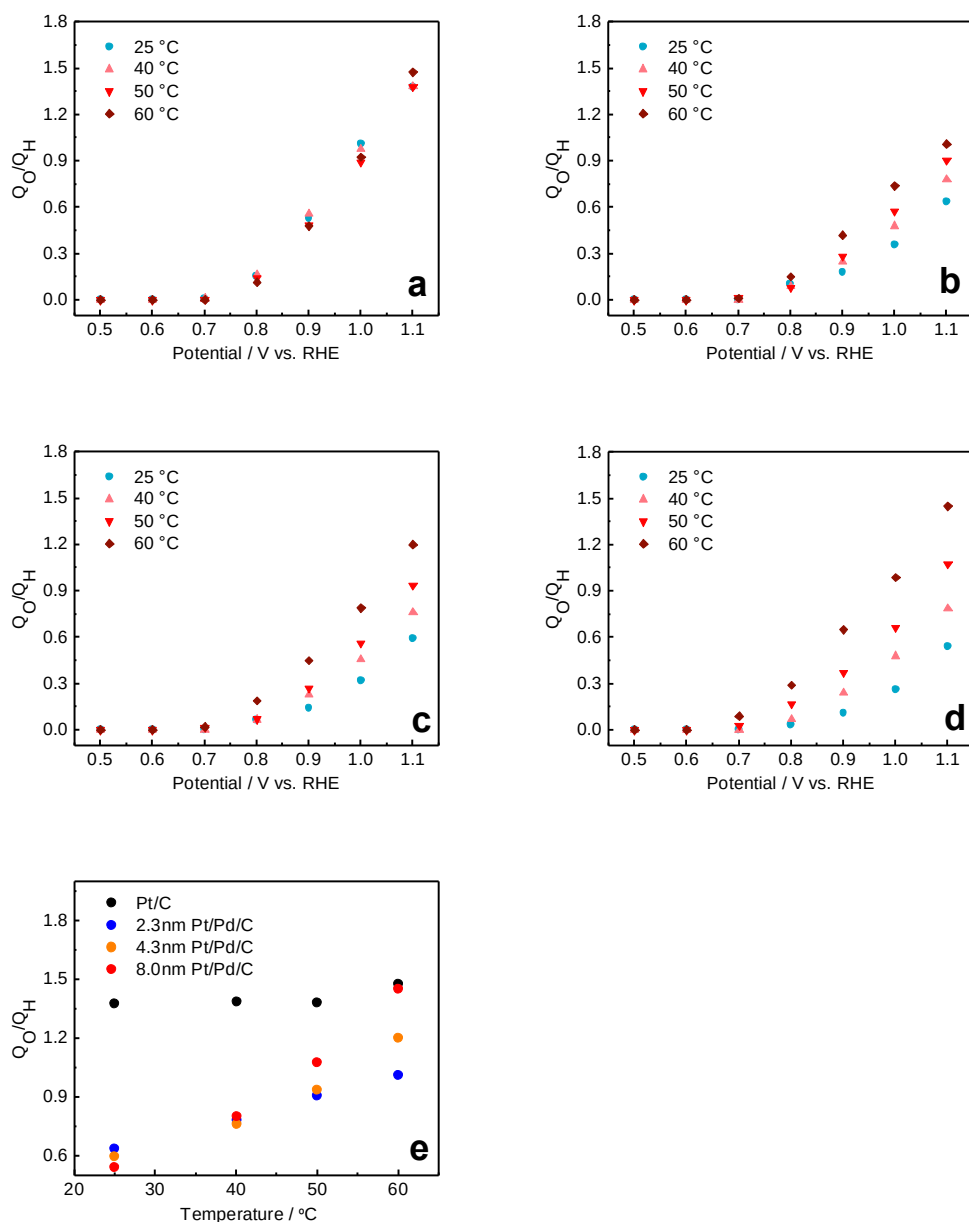


Figure 18. The oxide coverage of Pt/C catalyst (a) and Pt/Pd/C catalysts synthesized on 2.3 nm (b), 4.3 nm (c), 8.0 nm (d) at various potentials and temperatures (0.5 - 1.1 V, 25 - 60°C) and (e) the oxide coverage of the catalysts at 1.1 V vs. RHE.

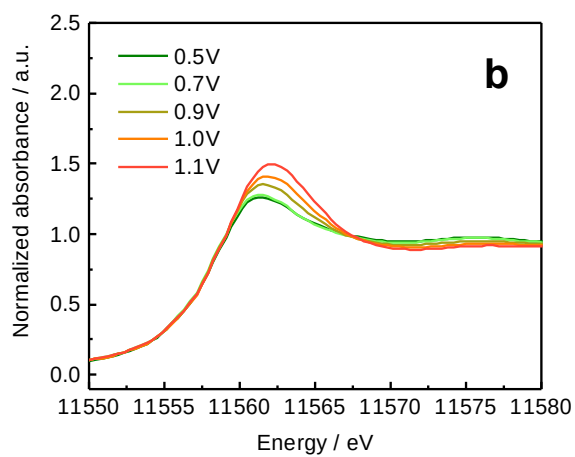
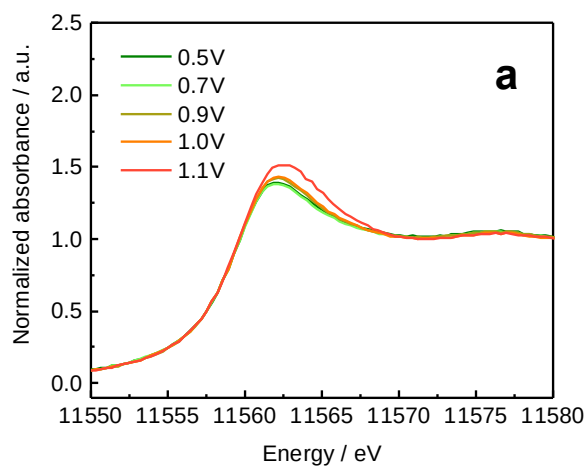


Figure 19. Normalized Pt L_{III} -edge XANES of Pt/C catalyst on GC at various potential (0.5V-1.1V) in O_2 -sat 0.1 M $HClO_4$ at 25 °C (a) and 60°C (b).

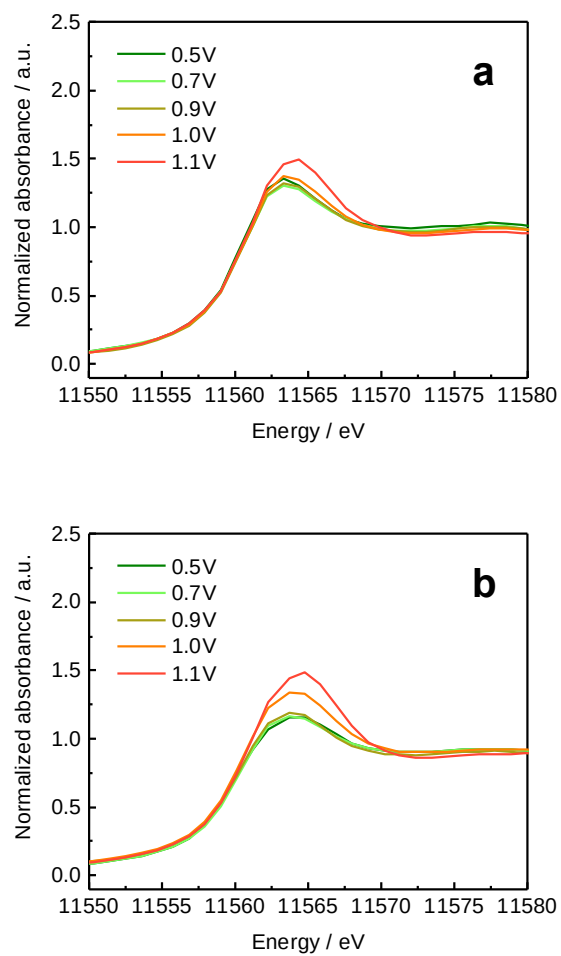


Figure 20. Normalized Pt L_{III} -edge XANES of Pt/Pd(2.3)/C on GC at various potential (0.5V-1.1V) in O₂-sat 0.1 M HClO₄ at 25 °C (a) and 60 °C (b).

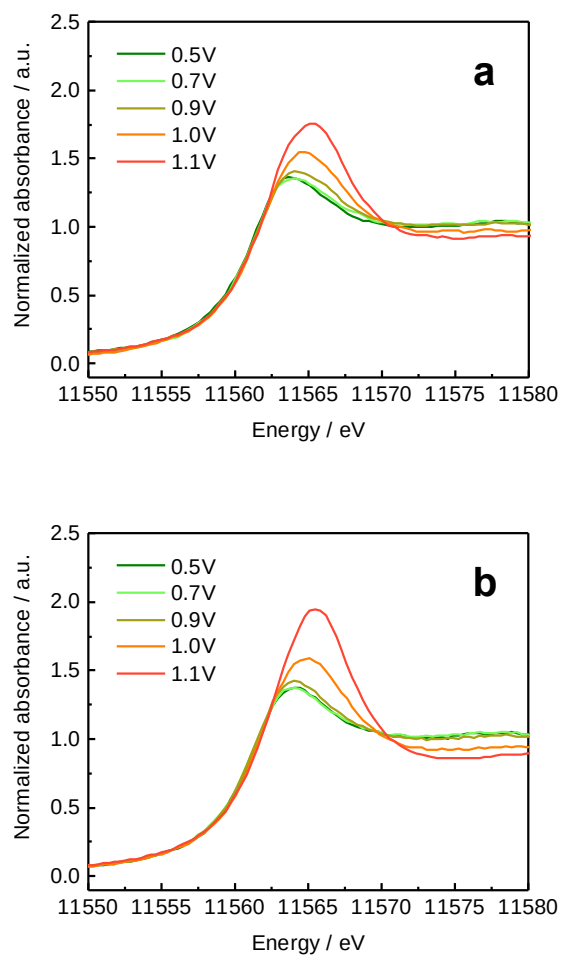


Figure 21. Normalized Pt L_{III} -edge XANES of Pt/Pd(4.3)/C on GC at various potential (0.5V-1.1V) in O_2 -sat 0.1 M $HClO_4$ at 25 °C (a) and 60°C (b).

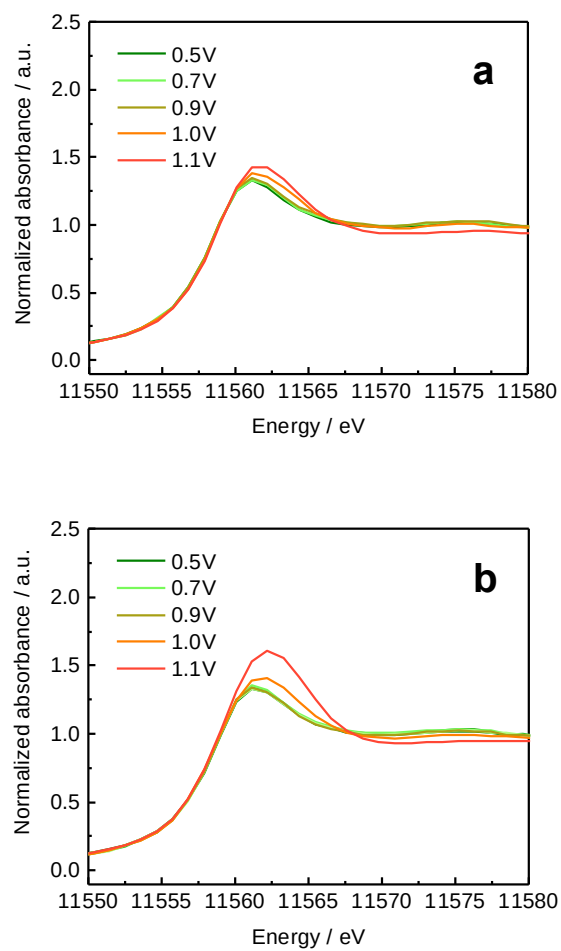


Figure 22. Normalized Pt L_{III} -edge XANES of /Pd(8.0)/C on GC at various potential (0.5V-1.1V) in O_2 -sat 0.1 M $HClO_4$ at 25 °C (a) and 60°C (b).

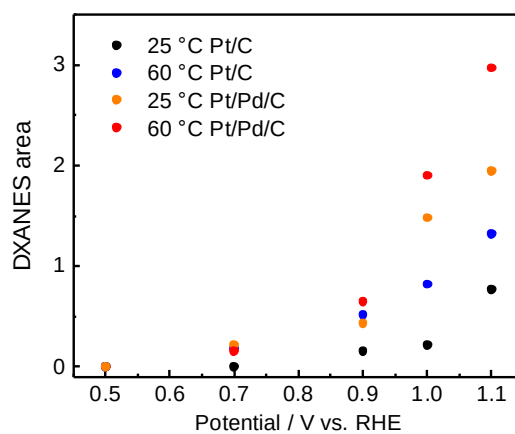


Figure 23. Change of XANES area compared with 0.5V of Pt/C catalyst at 25 °C (black points), 60 °C (blue points) and Pt/Pd(4.3)/C catalyst at 25 °C (orange points), 60 °C (red points).

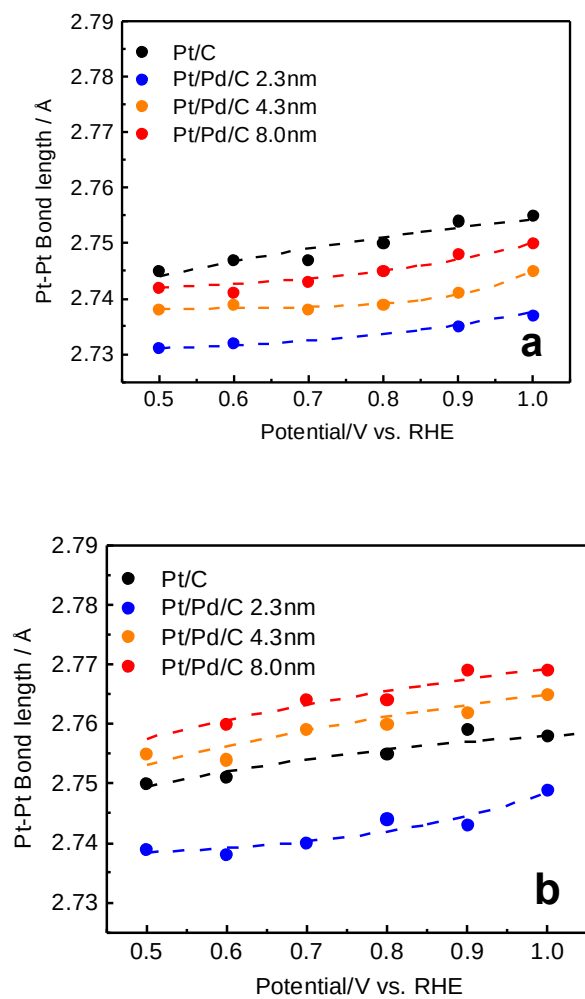


Figure 24. EXAFS fitting results for Pt-Pt bond distance of the nearest neighbors in Pt/C catalyst (black) Pt/Pd/C catalyst synthesized on 2.3 nm (blue), 4.3 nm (orange) and 8.0 nm (red) diameter Pd core fitted from the corresponding EXAFS at 25 °C (a) and 60 °C (b).

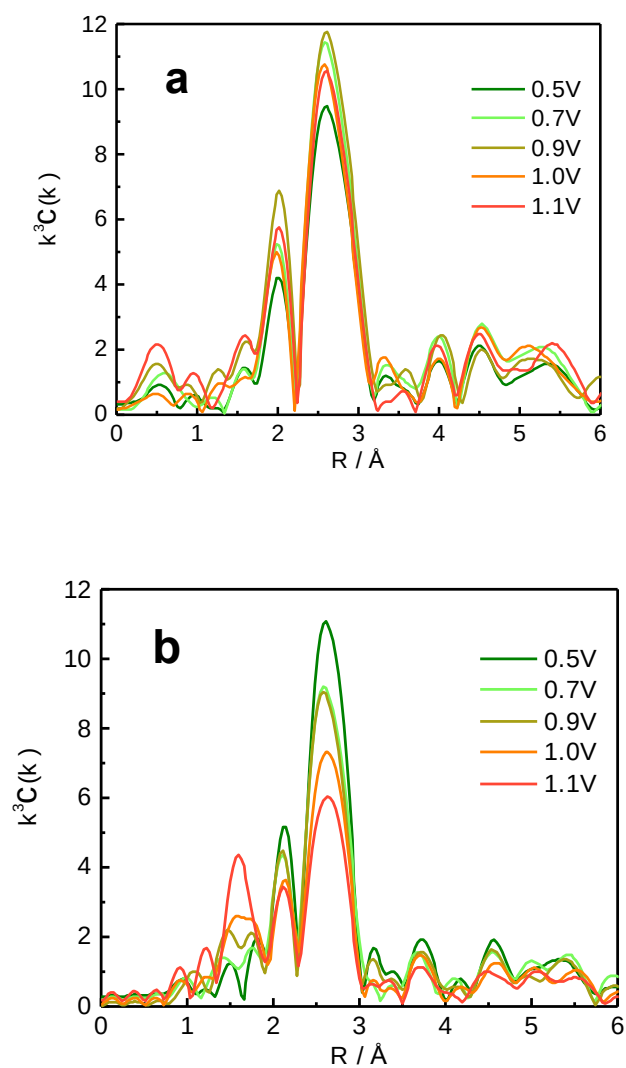


Figure 25. Fourier transforms for Pt/C catalyst at 25 °C (a) and 60 °C (b) in O₂-sat, 0.1M HClO₄ aq.

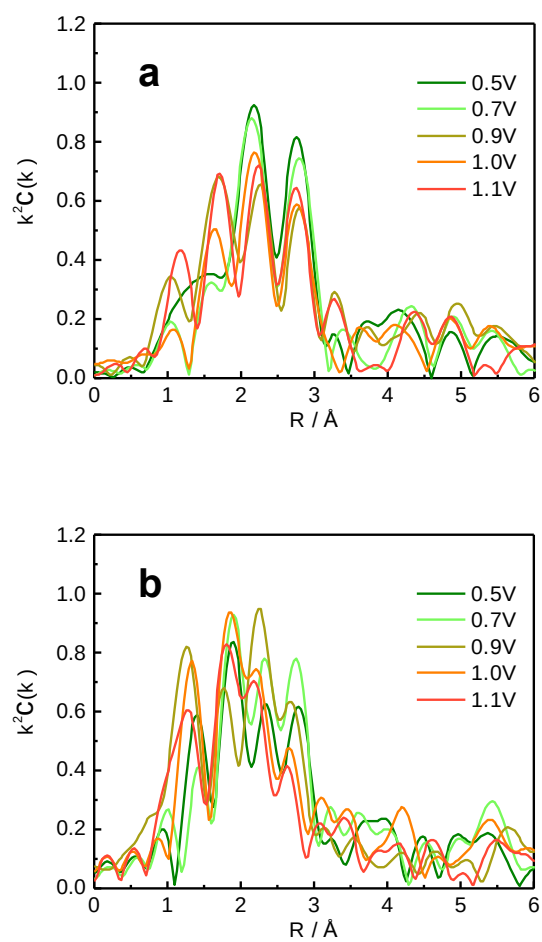


Figure 26. Fourier transforms for Pt/Pd(2.3)/C at 25 °C (a) and 60 °C (b) in O₂-sat, 0.1M HClO₄ aq.

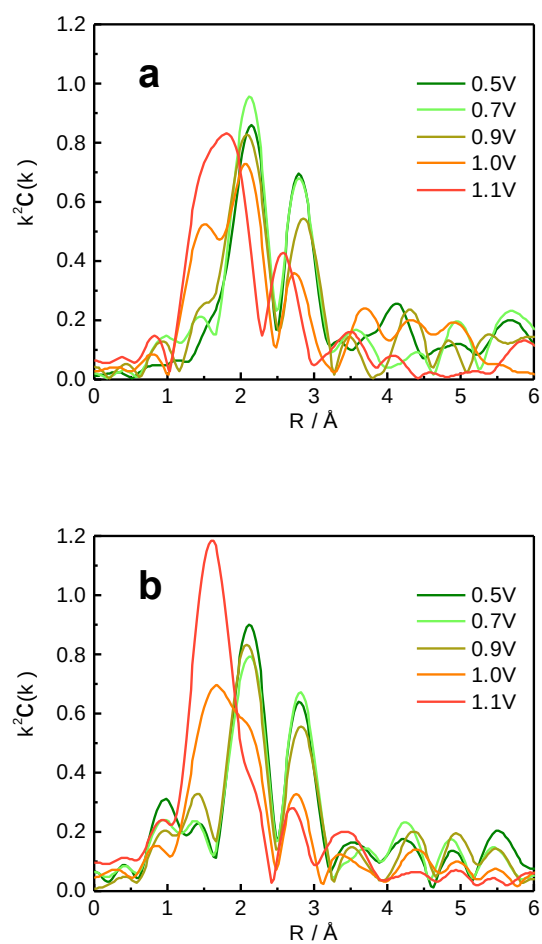


Figure 27. Fourier transforms for Pt/Pd(4.3)/C at 25 °C (a) and 60 °C (b) in O₂-sat, 0.1M HClO₄ aq.

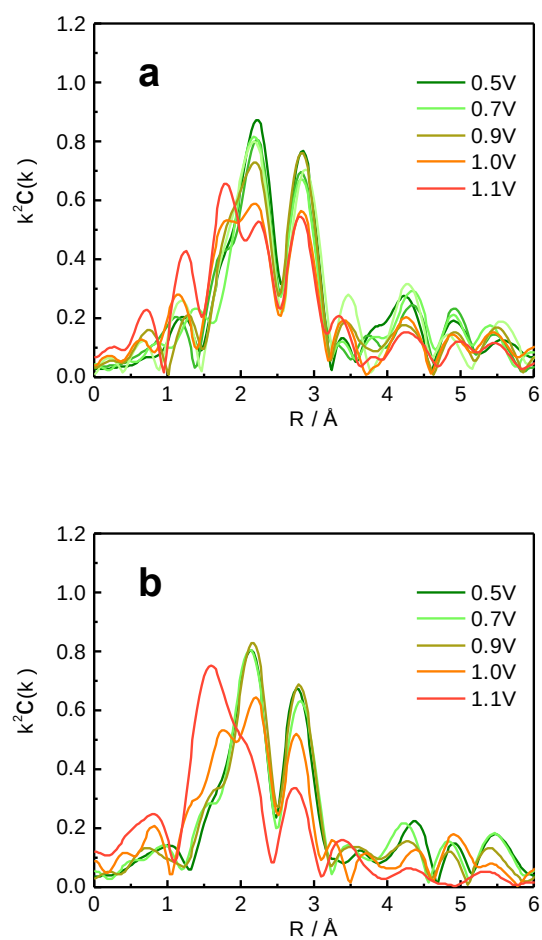


Figure 28. Fourier transforms for Pt/Pd(8.0)/C at 25 °C (a) and 60 °C (b) in O₂-sat, 0.1M HClO₄ aq.

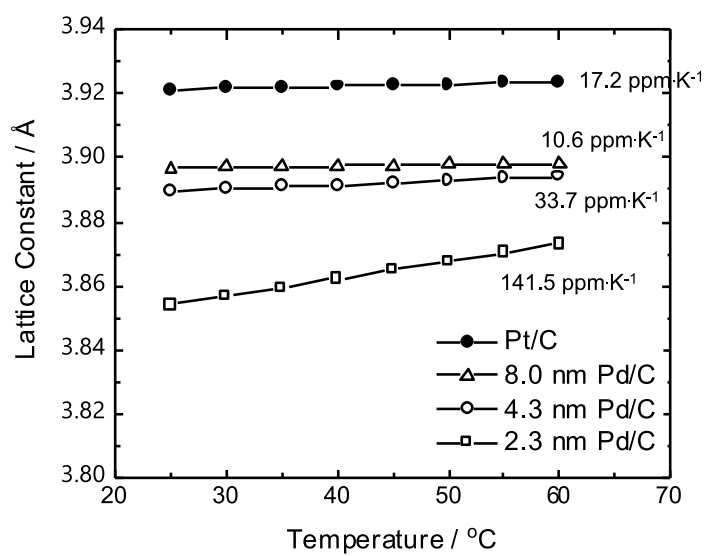


Figure 29. Lattice constant of Pt in Pt/C and 2.3nm, 4.3nm, 8.0nm diameter Pd nanoparticles in Pd/C from 25 °C to 80 °C, analyzed through *in-situ* HT-XRD. The slope of the line in the figure indicates thermal expansion coefficient for each material.

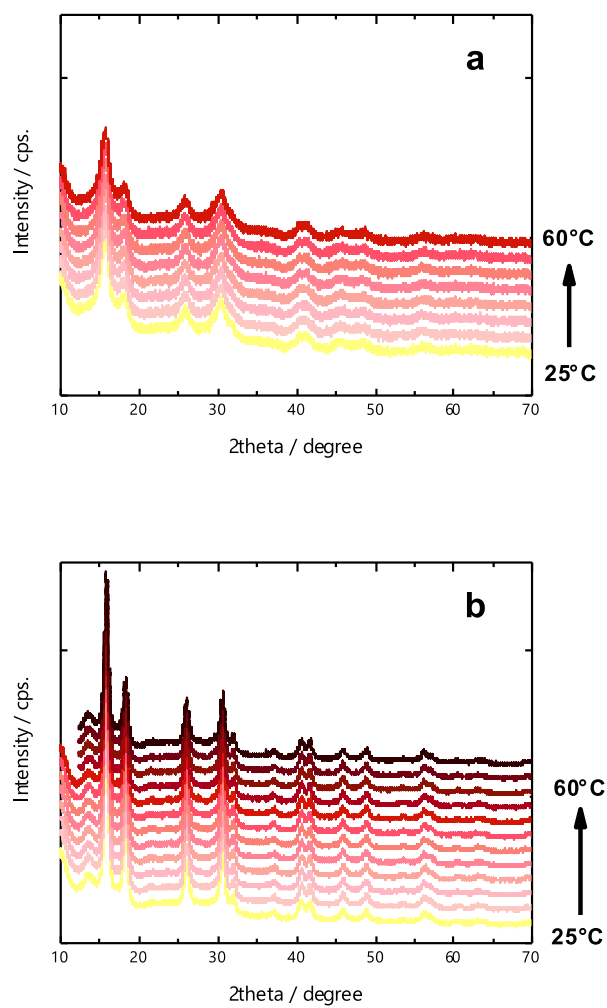


Figure 30. *in-situ* high temperature X-ray diffraction from 25 °C to 60 °C for (a) Pt/C and (b) 4.3nm Pd/C.

Table 1. Specific activity (SA) and mass activity (MA) of Pt/C and Pt/Pd/C core-shell catalysts with 2.3nm, 4.3nm, 8.0nm Pd core at 25 °C, 40 °C, 50 °C and 60 °C.

Temperature / °C	Pt/C		2.3nm Pt/Pd/C		4.3nm Pt/Pd/C		8.0nm Pt/Pd/C	
	SA($\mu\text{A}/\text{cm}^2_{\text{Pt}}$)	MA(A/g _{Pt})	SA($\mu\text{A}/\text{cm}^2_{\text{Pt}}$)	MA(A/g _{Pt})	SA($\mu\text{A}/\text{cm}^2_{\text{Pt}}$)	MA(A/g _{Pt})	SA($\mu\text{A}/\text{cm}^2_{\text{Pt}}$)	MA(A/g _{Pt})
25	169	219	394	465	478	575	577	694
40	239	353	530	545	736	756	712	731
50	232	342	692	664	795	762	361	346
60	252	369	512	518	374	378	213	214

Table 2. Oxygen concentration [O₂] calculated based on Henry's law.

T (°C)	[O ₂] (mM)
25	1.259
40	0.947
50	0.773
60	0.615

Table 3. Structure parameters of Pt/C fitted from the corresponding EXAFS. N is coordination number. R is bond distance. DW(Debye-Waller) is disorder factor. R-factor is fitting quality (residue).

Catalysts		Pt-Pt bond			Pt-O bond			R-factor/%
Temperature & potential		R(Å)	N	DW(Å ²)	R(Å)	N	DW(Å ²)	
Pt/C	25°C	0.5V	2.743±0.002	10.13±0.52	0.0014			0.37
		0.6V	2.745±0.002	10.43±0.42	0.0015			0.38
		0.7V	2.747±0.002	10.02±0.44	0.0011			0.34
		0.8V	2.755±0.003	9.28±0.61	0.0048	2.087±0.046	0.66±0.32	0.47
		0.9V	2.754±0.001	8.69±0.16	0.0018	2.083±0.006	0.88±0.11	0.41
		1.0V	2.755±0.001	8.96±0.33	0.0026	2.080±0.023	1.08±0.21	1.27
		1.1V	2.755±0.003	8.02±0.41	0.0034	2.083±0.043	1.13±0.31	1.18
		0.5V	2.748±0.003	8.79±0.37	0.0069			0.23
		0.6V	2.751±0.002	8.09±0.28	0.0066			1.15
		0.7V						
Pt/C	60°C	0.8V	2.755±0.001	8.70±0.19	0.0076	2.009±0.018	0.98±0.17	0.59
		0.9V	2.759±0.001	7.08±0.22	0.0068	2.001±0.021	1.09±0.22	1.26
		1.0V	2.758±0.003	6.64±0.32	0.0075	2.005±0.041	1.24±0.29	0.24
		1.1V	2.758±0.001	6.09±0.19	0.0080	1.991±0.014	1.31±0.11	0.95

Table 4. Structure parameters of the Nearest Neighbors of Pt-Pt bond, Pt-O bond of 2.3nm Pt/Pd/C core-shell catalyst in O₂-sat, 0.1M HClO₄ aq, fitted from the corresponding EXAFS using a general structural model of monolayer Pt atoms on Pd single crystal (111) facet⁴¹.

N is coordination number. R is bond distance. DW(Debye-Waller) is disorder factor. R-factor is fitting quality (residue).

Catalyst		Pt-Pt bond			Pt-O bond			Pt-Pd bond			C ₃	R-factor/%
Temperature & Potential		R(Å)	N	DW(Å ²)	R(Å)	N	DW(Å ²)	R(Å)	N	DW(Å ²)		
2.3nm	25°C	0.5V	2.731±0.001	8.88±0.05	0.0105			2.759±0.002	3.38±0.15	0.0053		1.97
		0.6V	2.732±0.002	8.73±0.15	0.0104			2.757±0.005	3.03±0.10	0.0052		2.35
		0.7V	2.737±0.003	5.27±0.10	0.0028			2.722±0.001	2.90±0.20	0.0026		2.72
		0.8V	2.738±0.004	5±0.10	0.0044	2.161±0.006	0.2±0.02	0.0077	2.743±0.002	3.08±0.15	0.0041	3.80
		0.9V	2.735±0.006	4.7±0.35	0.0027	2.002±0.023	0.3±0.11	0.0075	2.726±0.004	2.41±0.26	0.0072	8.67
		1.0V	2.737±0.003	4.3±0.11	0.0027	2.019±0.006	0.6±0.05	0.0050	2.740±0.006	2.05±0.21	0.0016	0.54
		1.1V	2.737±0.003	3.5±0.12	0.0096	2.036±0.012	0.82±0.12	0.0036	2.771±0.003	1.8±0.10	0.0019	1.20
	60°C	0.5V	2.739±0.004	4.87±0.05	0.0011			2.705±0.002	1.65±0.10	0.0013	0.00124	0.62
		0.6V	2.738±0.005	5.30±0.23	0.0010			2.711±0.004	1.81±0.14	0.0010	0.00135	5.51
		0.7V	2.740±0.003	6.22±0.22	0.0027			2.723±0.003	2.10±0.20	0.0025	0.00127	5.24
		0.8V	2.744±0.005	6.15±0.20	0.0060	2.196±0.011	0.3±0.16	0.0055	2.738±0.002	2.63±0.15	0.0044	2.53
		0.9V	2.743±0.004	5.39±0.23	0.0046	2.119±0.021	0.4±0.15	0.0102	2.746±0.004	1.54±0.11	0.0054	1.51
		1.0V	2.749±0.003	4.5±0.25	0.0020	1.996±0.014	0.7±0.11	0.0014	2.763±0.003	0.94±0.15	0.0021	2.65
		1.1V	2.765±0.002	2.7±0.29	0.0157	1.990±0.021	0.9±0.15	0.0043	2.760±0.005	0.56±0.25	0.0137	1.46

Table 5. Structure parameters of the Nearest Neighbors of Pt-Pt bond, Pt-O bond of 4.3nm Pt/Pd/C core-shell catalyst in O₂-sat, 0.1M HClO₄ aq, fitted from the corresponding EXAFS using a general structural model of monolayer Pt atoms on Pd single crystal (111) facet⁴¹.

N is coordination number. R is bond distance. DW(Debye-Waller) is disorder factor. R-factor is fitting quality (residue).

Catalyst		Pt-Pt bond			Pt-O bond			Pt-Pd bond			C ₃	R-factor/%
Temperature & Potential		R(Å)	N	DW(Å ²)	R(Å)	N	DW(Å ²)	R(Å)	N	DW(Å ²)		
4.3nm	25°C	0.5V	2.738±0.001	7.74±0.13	0.0085			2.747±0.002	3.71±0.17	0.0066		1.90
		0.6V	2.739±0.006	6.97±0.14	0.0058			2.722±0.005	3.56±0.10	0.0050		1.81
		0.7V	2.738±0.002	7.14±0.11	0.0052			2.730±0.001	3.02±0.12	0.0037		2.17
		0.8V	2.739±0.002	5.52±0.11	0.0034	1.993±0.006	0.4±0.08	0.0061	2.725±0.001	2.60±0.09	0.0020	2.47
		0.9V	2.741±0.008	6.20±0.25	0.0036	2.061±0.015	0.6±0.11	0.0016	2.714±0.004	1.72±0.25	0.0008	1.83
		1.0V	2.745±0.002	5.12±0.41	0.0063	2.017±0.021	1±0.24	0.0003	2.715±0.005	1.54±0.17	0.0020	8.69
		1.1V	2.743±0.003	0.89±0.33	0.0095	2.017±0.032	1.4±0.36	0.0020	2.638±0.005	0.375±0.21	0.0096	2.97
	60°C	0.5V	2.755±0.002	7.56±0.19	0.0071			2.732±0.002	3.09±0.18	0.0056	0.00026	2.55
		0.6V	2.754±0.002	7.46±0.29	0.0059			2.720±0.001	2.82±0.12	0.0052	0.00047	2.29
		0.7V	2.759±0.005	6.85±0.24	0.0054			2.711±0.007	3.67±0.22	0.0086	0.00061	1.32
		0.8V	2.760±0.003	4.49±0.33	0.0015	1.968±0.027	0.6±0.11	0.0118	2.704±0.005	2.5±0.18	0.0011	4.34
		0.9V	2.765±0.002	4.45±0.23	0.0082	2.026±0.015	1±0.14	0.0075	2.735±0.004	1.56±0.19	0.0066	4.08
		1.0V	2.765±0.002	3.5±0.29	0.0008	2.005±0.041	1.6±0.17	0.0020	2.674±0.017	1±0.25	0.0012	2.89
		1.1V	2.784±0.005	1.7±0.29	0.0013	1.978±0.021	2.1±0.21	0.0086	2.877±0.004	0.4±0.21	0.0063	1.23

Table 6. Structure parameters of the Nearest Neighbors of Pt-Pt bond, Pt-O bond of 8.0nm Pt/Pd/C core-shell catalyst in O₂-sat, 0.1M HClO₄ aq, fitted from the corresponding EXAFS using a general structural model of monolayer Pt atoms on Pd single crystal (111) facet ⁴¹.

N is coordination number. R is bond distance. DW(Debye-Waller) is disorder factor. R-factor is fitting quality (residue).

Catalyst		Pt-Pt bond			Pt-O bond			Pt-Pd bond			C ₃	R-factor/%	
Temperature & Potential		R(Å)	N	DW(Å ²)	R(Å)	N	DW(Å ²)	R(Å)	N	DW(Å ²)			
8.0nm	25°C	0.5V	2.740±0.001	6.44±0.05	0.0038				2.706±0.001	2.90±0.07	0.0069		1.74
		0.6V	2.741±0.002	7.72±0.15	0.0074				2.736±0.003	3.60±0.10	0.01145		1.82
		0.7V	2.743±0.001	6.53±0.19	0.0047				2.710±0.003	2.27±0.12	0.0044		0.41
		0.8V	2.745±0.005	5.69±0.11	0.0014	2.033±0.006	0.35±0.04	0.0017	2.702±0.004	2.28±0.15	0.0033		2.43
		0.9V	2.748±0.004	5.24±0.25	0.0059	2.103±0.021	0.65±0.11	0.0057	2.755±0.005	2.79±0.22	0.0131		1.23
		1.0V	2.750±0.002	5.12±0.21	0.0079	2.058±0.021	0.80±0.14	0.0023	2.765±0.005	2.34±0.11	0.0142		4.05
		1.1V	2.758±0.003	3.39±0.22	0.0017	2.039±0.012	1.5±0.25	0.0054	2.702±0.006	2.3±0.13	0.0098		6.12
	60°C	0.5V	2.760±0.002	7.83±0.05	0.0095				2.725±0.002	2.80±0.10	0.0106	0.00086	1.29
		0.6V	2.760±0.003	7.4±0.21	0.0068				2.729±0.003	2.82±0.14	0.0079	0.00031	0.18
		0.7V	2.764±0.005	6.72±0.20	0.0099				2.739±0.007	2.68±0.21	0.0016	0.00125	0.59
		0.8V	2.764±0.005	6.52±0.21	0.0044	1.987±0.013	0.7±0.21	0.0095	2.717±0.005	2.61±0.13	0.0045	0.00036	0.728
		0.9V	2.769±0.004	6.42±0.33	0.0021	2.084±0.012	1.3±0.14	0.0099	2.726±0.004	2.48±0.11	0.0052	0.00021	0.92
		1.0V	2.769±0.003	5.77±0.39	0.0069	2.012±0.011	1.4±0.11	0.0052	2.713±0.007	2.94±0.25	0.0162	0.00084	1.32
		1.1V	2.774±0.005	2.3±0.29	0.0169	2.007±0.031	1.8±0.15	0.0084	2.784±0.003	1.3±0.14	0.0065	0.00191	1.57

Chapter 3. *operando* X-ray absorption spectroscopic study on influence of specific adsorption of sulfo group in perfluorosulfonic acid ionomer on the oxygen reduction reaction activity of Pt/C catalyst

3.1 Introduction

Polymer electrolyte fuel cells (PEFCs) are clean energy devices with polymer electrolytes and are expected to play an important role for the development of a global renewable energy system and a pure hydrogen energy society in the future. PEFCs have already been applied for small-scale energy systems such as fuel cell vehicles (FCVs)¹⁻⁵. However, several challenges must be overcome to realize the widespread use of FCVs. For successful commercialization, a reduction in the usage and cost of Pt cathode catalysts is necessary. Pt-based catalysts are basically used due to the relatively inefficient reaction kinetics and catalyst degradation under strong acidic conditions during the oxygen reduction reaction (ORR). However, there are still many difficulties in realizing acceptable cost-effective FCVs^{6,7}. Therefore, a high ORR activity and reliable durability of the cathode catalyst layer are highly desirable for ensuring the widespread use of FCVs.

It is known that the ORR activity of Pt-based catalysts is reduced by specific adsorption of anionic species⁸. Perfluorosulfonic acid ionomers such as Nafion[®] are commonly included in the catalyst layers of PEFCs to provide protonic pathways for promoting the ORR^{9,10}. The loss in ORR activity of Nafion[®]-capped Pt single crystals was found to follow the order Pt (111) > (110) > (100). This trend is same as that on Nafion[®]-free surfaces in a sulfuric acid solution¹¹. Polycrystalline Pt and Pt alloy surfaces also show loss in activity when capped with Nafion[®]⁸. These reports suggested that the adsorption of sulfo group anion from the side chain of Nafion[®] blocked the active site of Pt¹². A similar behavior has been observed for Pt-based catalysts (Pt/C), but the extent of decrease in the ORR activity varies depending on the carbon structure¹³⁻¹⁸. The properties of the carbon support are crucial in reducing the poisoning effect of perfluorosulfonic acid ionomers and in improving the catalyst performance¹⁶⁻¹⁸. Catalysts prepared from porous carbons with 4–7 nm opening pores render excellent

ORR activities and transport properties¹⁸. Shinozaki et al. studied the impact of Nafion[®] on the ORR activities of Pt/C and Pt-alloy/C catalysts using a rotating disk electrode (RDE) and found that catalysts with high surface area of carbon could mitigate the loss in activity because Pt nanoparticles located inside the pores of the high-surface-area carbon inhibited the ionomer coverage¹⁹. These studies clearly indicate that quantification of the ionomer coverage is important for designing new catalysts.

An electrochemical method is an alternative method for estimating the ionomer coverage on Pt surfaces. In the CO displacement method, a constant potential was applied while introducing the CO gas^{11,20-23}. When CO displaced the adsorbing species on Pt, oxidation or reduction currents were generated depending on the displaced species, and the ionomer coverage was estimated based on this¹¹. Using this method, Takeshita et al. quantitatively determined the ionomer coverage and found that the ionomer coverage of a Pt catalyst on a porous carbon support was lower than that on a non-porous catalyst²⁴. While the CO displacement method is useful for determining the ionomer coverage, the potential range during measurement is limited, which is a drawback. Because the adsorbed CO molecules on the Pt surface is oxidized at ~0.6 V vs. RHE (reversible hydrogen electrode), the potential range from only 0.08–0.56 V vs. RHE could be used to evaluate the anion adsorption^{11,20-23,25}.

To observe the anion adsorption on Pt, spectroscopic methods such as X-ray absorption spectroscopy for single crystal Pt (111) electrode surfaces in H₂SO₄ solution have been developed²⁶⁻²⁸. Combining X-ray absorption near edge structure (XANES) and full-multiple scattering calculations using the FEFF8 code, it was concluded that specific anion adsorption occurred significantly in 1 M H₂SO₄ but did not occur in 1 M HClO₄²⁶. However, direct observation of anion adsorption on practical Pt nanoparticle/C catalysts for perfluorosulfonic acid ionomers using X-ray absorption spectroscopy (XAS) still has less report. In this paper, to achieve specific adsorption over a higher potential range that is at least equal to the ORR active potential (around 0.90 V vs. RHE), which cannot be measured by the CO displacement method, operando XAS measurements were performed; the electronic status and local structural change of Pt atoms induced by the specific adsorption of anions at any potential were observed. operando XAS measurement is a reliable method for observing the electronic status, detailed structure of the Pt surface^{29,30}, and the strain inducing compression/extension of the Pt-Pt bond length³¹. Here, we report operando fluorescence XAS measurements

to directly obtain the signal from the catalyst loaded on RDE with the exact same amount of loading as in the electrochemical measurement, to ensure accurate XAS spectra and ORR activity.

In this study, we evaluated the ORR activities of commercial Pt/C catalysts with various ionomer-to-carbon (I/C) weight ratios (0.0, 0.20, 0.50, 1.0). The morphology of the Pt/C catalyst covered with swollen ionomers was investigated by cryo-transmission electron microscopy (Cryo-TEM). CO stripping voltammetry measurements, operando X-ray absorption fine structure analysis, and analysis of 5d orbital vacancy were used to quantitatively assess the anion adsorption among Pt/C catalysts with various I/C ratios. The various adsorption species on the Pt surface in the low (0.02–0.50 V vs. RHE) and high (0.50–1.0 V vs. RHE) potential ranges have been discussed.

3.2 Experimental Methods

3.2.1 Electrochemical measurements

Pt/C (29.1 wt.%; TEC10V30E, average particle size of 3 nm, observed by TEM) catalyst supported was purchased from TKK Co. Ltd., Japan. The Pt/C catalyst ink contained water and 2-propanal in 3:2 ratio (99.99%, FUJIFILM Wako Pure Chemical Corporation, Japan), and the amount of Pt/C was adjusted to form a $20 \mu\text{g}_{\text{carbon}} \text{cm}^{-2}$ catalyst layer after dropping 10 μL on a glassy carbon RDE (GC RDE, HOKUTO DENKO, Japan; 0.196 cm^2 area). The ink on the RDE was dried at 700 rpm at room temperature. Nafion[®] solution (5 wt.%, Sigma-Aldrich Co. LLC, Japan) was employed to prepare Pt/C catalyst ink with I/C ranging from 0.0 to 1.0. The high purity HClO_4 (Kanto Chemical Co., Inc, Japan, purity: 60.0 wt%) was adopted to prepare the 0.1M HClO_4 electrolyte. The water used for preparing the electrolyte was from ultrapure water with electrical resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ or more (Milli-Q[®], Millipore A/S).

ORR activity measurements were carried out in a three-electrode cell at 25 °C. The counter electrode was a Pt mesh, and the reference electrode was RHE. Prior to catalyst activity measurements, the potential was cycled 50 times between 0.02 and 1.0 V (vs. RHE) at 200 mVs^{-1} to obtain a stable cyclic voltammogram (CV) in N_2 -saturated 0.1 M HClO_4 . The final CV was obtained at 50 mVs^{-1} . After the CV measurements, the electrolyte was saturated with O_2 . Then, hydrodynamic voltammograms were obtained between 0.2 and 1.2 V vs. RHE at 10 mVs^{-1} from 100 to 2500 rpm. The oxygen reduction data for all the catalysts were analyzed according to Koutechy-Levich

equation. The oxygen coverage was measured by linear sweep voltammetry in N₂-saturated 0.1 M HClO₄. The potential was swept from 0.40 V (vs. RHE) to the target potential (0.50 - 1.0 V vs. RHE) at 50 mV·s⁻¹, and then hold the potential for 5 mins to obtain a stable current. At last, the potential was swept to 0.40 V (vs. RHE). The oxygen coverage was calculated through the oxide reduction charge to hydrogen adsorption charge³². The integrated cathodic current was used to estimate the charge of oxide species based on the following reaction ($\text{Pt-OH} + \text{H}^+ + \text{e}^- \rightarrow \text{Pt} + \text{H}_2\text{O}$) also reports from other researcher³².

CO stripping voltammetry measurements were conducted in the same three-electrode cell at 25 °C. The potential was cycled 50 times between 0.02 and 1.0 V (vs. RHE) at 200 mVs⁻¹. The final CV was obtained with 50 mVs⁻¹. Then, the potential was held at 0.12-0.5 V (vs. RHE), with N₂ bubbling for 10 min until a stable current was obtained. After that, the gas was immediately switched to CO (99.9%, GL Sciences Inc.) for about 20 s to obtain a stable current, indicating complete CO adsorption. The bubbling gas was switched again to N₂ for 40 min for CO deaeration. Finally, CO stripping voltammetry was initiated in the range from 0.02 to 1.0 V (vs. RHE). The coverage of anions was estimated through 2 times of total CO displacement current divided by CO stripping charge.

3.2.2 TEM observations.

The specimens for TEM observation were prepared by drying sample inks on Cu grid. For I/C = 0.10, 0.20, 0.50, and 1.0 samples, specimens were kept at 60 °C and 80% of relative humidity for 5 minutes, then quickly frozen with liquid ethane using an EM GP2 plunge freezer (Leica Microsystems, Austria). The frozen specimens were transferred to TEM in liquid nitrogen by using of cryo-transfer holder. The cryo-TEM observation was carried out at about -175 °C on a JEM-F200 (JEOL Ltd., Japan) microscope operating at 200 kV. For I/C=0.0 sample, the conventional TEM observation was carried out on a JEM-F200 (JEOL Ltd., Japan) microscope operating at 200 kV. During Cryo-TEM observation, we observed the ionomer suffer the damage from the electron beam as shown in Figure 1. Therefore, the observation was conducted in short exposure time

3.2.2 *operando* XAS measurements

operando XAS measurements for Pt L_{III}-edge of Pt/C catalysts were carried out in fluorescence mode using synchrotron radiation at BL37XU of SPring-8, Hyogo, Japan. A pair of Si (111) monochromators and a total-reflection Rh mirror (4 mrad) were used to obtain collimated and monochromatic X-rays. Prior to the experiments, the samples were electrochemically cleaned by CV in the range 0.0–1.1 V (vs. RHE). The electrode potential was swept cathodically from 0.5 to 1.1 V (vs. RHE). Data were analyzed using ATHENA and ARTEMIS, a suite of the IFEFFIT software programs³³.

3.3 Results and discussions

3.3.1 TEM observations

Pt/C nanoparticles with various I/C ratio ink were observed by cryo-transmission electron microscope (TEM) as shown in Figure 2. Figure 2a shows the TEM image of Pt/C catalyst without ionomer (I/C = 0.0), showing typical morphologies of a carbon supported Pt catalyst. In I/C = 0.10, Pt/C catalyst surface was partly exposed as indicated by the arrows in Figure 2b and the observed thickness of the ionomer covering the catalyst was smaller than the samples of I/C = 0.20, 0.50 and 1.0. As far as judging from the TEM images, the catalyst particles were fully covered by the ionomer in I/C = 0.20 (Figure 2c). When the I/C was over 0.20, all the Pt/C catalyst were surrounded by ionomer as shown in Figures 2c, d and e. In addition, some isolated ionomer was found in I/C = 1.0 as indicated by the arrow in Figure 2e. The carbon aggregate and morphology of ionomers observed in this study has a good agreement with previous report³⁴.

3.3.2 Electrochemical measurements

Figure 3 shows the CVs of the Pt/C catalyst ink with I/C ratios from 0.0 to 1.0 and the enlarge of hydrogen UPD and oxide formation region were showed in Figure 4. No significant change in the voltammograms between 0.0 and 1.0 V (vs. RHE) was observed with changing I/C ratio. There found a slight onset potential shift with the increasing I/C ratio from 0.0 to 1.0 and a negative shift in the onset of hydrogen underpotential deposition current and slight shifts on the onset potential of oxide formation (Figure 4 (a),(b)). This tendency was identical to the results of Shinozaki et al.¹⁹, which used the low surface area carbon supported Pt catalyst as we are using Vulcan[®] as a carbon support. There is another researcher, Zhu et al., reported on the effect of specific

adsorption of Nafion's sulfo groups³⁵. They also evaluated the CV curves of Pt/C catalyst (TEC10E50E, TKK) with I/C ratio from 0 to 1.33. Their CV result using high surface area carbon supported Pt show a slight positive shift of onset potential of Pt oxidation was seen. Even with the same type of carbon support, the CV reported by Zhu et al. is less clear in the effect of the Nafion coating than the one reported by Shinozaki et al.

Although the effect of ionomer content on the Pt/C catalyst could be not clearly observed through CV measurements, we found that the catalyst activity, including specific activity, changed with varying I/C ratios. To illustrate the effect of ionomer on the catalyst activity at 0.90 V (vs. RHE) for various ionomer contents, the specific activity and electrochemical surface area (ECSA) were plotted against the I/C ratio in Figure 5 and the liner sweep voltammogram and Koutecky-Levich plot were shown in Figures 6-10. Pt/C catalyst had the highest specific activity at I/C = 0.0 (ionomer-free) and we could observe that the diffusion limit current is larger at low I/C ratio in Figure 11, suggesting a slight oxygen diffusion resistance in high I/C ratio. The catalyst activity began to decrease with increasing ionomer content, but the ECSA remained almost same as that for the ionomer-free system. These results were consistent with those of a previous study³⁶ and indicate that ionomer decreases Pt/C catalyst activity but at the same time, does not affect the ECSA. It was clear that the limiting current did not change in $I/C < 0.20$ and the ORR activity has already decrease in Figure 11. This phenomenon indicate that the decreasing activity are not caused by the oxygen concentration effect. From $I/C=0.50-1.0$, the limiting current was changed from that of $I/C = 0.0-0.20$, but as the ORR activity was estimated at charge transfer rate-determining potential (0.90 V vs. RHE), the oxygen concentration do not have an significant effect on the activity. The report from Zhu et al. indicates the liner sweep voltammogram of Pt/C catalyst with I/C from 0.0 to 1.33 also have been evaluated³⁵. They indicated that the limiting current density in the mass control region slightly decreased upon increasing I/C ratio, while the activity has no noticeable difference at the same time, which an agreement with our results. Here, we conjecture that the increased specific adsorption of the Pt/C catalyst contributed to the activity loss due to the higher ionomer content (higher I/C ratios).

To clarify the specific adsorption effect of ionomer at a high potential range (0.70–0.90 V vs. RHE), we first need to evaluate the oxygen coverage. The oxide reduction

profiles for Pt/C catalysts with I/C = 1.0 were shown in Figure 12 as an example. The oxygen coverage increased at higher potentials for all the I/C ratios (Figure 13); at the same time, the adsorption of oxide species increased, which was in an agreement with previously reported results³⁷. The oxygen coverage in the Pt/C catalyst was slightly increased in I/C = 0.0, which agrees with the CV results described in Figure 4. This indicates that oxygen coverage does not mainly contribute to the change in Pt/C catalyst activity when the I/C ratios are varied from 0.0 to 1.0. Here, we can reasonably speculate that the Pt/C catalyst activity decreases with increasing I/C ratio and is mainly affected by the specific adsorption species from the ionomer.

To quantitatively evaluate the specific adsorption species, we used CO stripping voltammetry, which measures the displacement charge from the adsorption species to CO. The charge during each exchange reaction, Pt-H at 0.12 V (vs. RHE), and the anion adsorption species on Pt at 0.40 V (vs. RHE) or more were calculated, as shown in Figure 14. The examples of CO exchange current profiles were shown in Figure 15. At 0.12 V (vs. RHE), the hydrogen adsorbed species show no obvious change, similar to that observed for the ECSA. In the potential range 0.40–0.50 V (vs. RHE), the CO displacement charge of the Pt/C catalyst with I/C = 1.0 was obviously higher than that of the ionomer-free sample at each potential, which is in agreement with the previous reports on ionomer or anion specific adsorption through CO displacement measurement^{32,38,39}. I/C = 0.10 showed the displacement charge between I/C = 0.0 and 1.0 from 0.40 to 0.50 V (vs. RHE). This result in I/C = 0.10 was consistent with the results in Cryo-TEM image as well as the specific activity. This result confirmed that the ionomer coverage is impacting the CO displacement charge. For the anion coverage based on the CO exchange current, we calculated the anion coverage by $2 \times (\text{CO displacement charge}) / (\text{CO stripping charge})$ and the CO stripping profile and the results were shown in Figure 16 and 17, respectively. Comparing with the report from Garrick et al.³⁸ which reported the anion coverage of Pt/C catalyst with and without the presence of H₂SO₄. The anion coverage of Pt/C with/without the presence of H₂SO₄ was 0.25/0.15 at 0.50 V (vs RHE), which tendency was consistent with our report on I/C = 0.0 and 1.0. These indicate that the amount of specific adsorption increases with increasing ionomer content. All the above observations lead to the conclusion that increasing amount of adsorption species in the ionomer-containing group is attributable to ionomer-specific adsorption, and this is suggested to be the primary reason for the

decreasing Pt/C catalyst activity with increasing ionomer contents.

3.3.3 *operando* XAS measurements.

Although ionomer adsorption may be one of the main reasons for the lower catalyst activity, as revealed by the CO displacement measurement, only the adsorption species at voltages lower than 0.60 V (vs. RHE) could be analyzed. To observe the adsorption species in the high potential region, where the ORR occurred, *operando* XAS measurements were conducted as shown in Figure 18-20. In this study, the number of 5d orbital vacancies in Pt was calculated from the XANES spectra of Pt L_{III}-edge and L_{II}-edge³⁹ (Figure 21), and the chemical state (oxidation state) of Pt was determined. The detail calculation method described in the supporting information. The 5d orbital vacancies in the Pt/C catalyst with I/C = 0.0 and 1.0 are shown in Figure 22. The calculation of 5d orbital vacancies was based on Mansour et al.⁴⁰ and the brief illustration of the procedure was shown Figure 23.

The 5d orbital vacancies increase with increasing potential for all the samples, suggesting an increased Pt-O bond formation. This trend is similar to that discussed above. By comparing the 5d orbital vacancies of the Pt/C catalysts with I/C = 0.0 and 1.0, it can be easily determined that the 5d orbital vacancies of the catalyst with I/C = 1.0 are more than those of the Nafion-free sample at 0.90 V (vs. RHE), where the ORR occurs. Although the sulfo group is a monobasic acid and cannot always be compared to the dibasic acid, these trends are consistent with previously reported results comparing in HClO₄ and H₂SO₄ solution²⁰. This is a significant evidence that the ionomer is involved in more specific adsorption on the Pt/C catalyst, changes the electric state of Pt atoms, and increases the 5d orbital vacancies. Since we already found that the Pt-O species or oxygen coverage did not change in the high potential region (0.50–1.0 V vs. RHE), the change in the electronic state of Pt atoms should be caused by the extra specific adsorption species from the ionomer coverage. Through this measurement technique, we have developed a new method to quantitatively investigate the specific adsorption through *operando* X-ray absorption fine structure analysis and 5d orbital vacancies in the high potential range, where the ORR occurs (0.70–0.90 V vs. RHE). In order to compare with the results of Teliska et al.²⁶, the $\Delta\mu$ spectra was obtained by $\Delta\mu = \mu(X \text{ V vs. RHE}) - \mu(0.50 \text{ V vs. RHE})$, where $\mu(X \text{ V vs. RHE})$ indicates the XANES spectra obtained at $X = 0.60\text{--}1.1 \text{ V (vs. RHE)}$. When it was

compared with their results (Figure 24), the behavior of $I/C=1.0$ along with the potential in terms of the peak at 9 eV was similar to that of Teliska et al., indicating that the specific adsorption of sulfo group also occurs in our study. In addition, the behavior of $I/C=0.0$ along with the potential was also similar to that of Teliska et al.. In particular, the peak appeared at 8 eV (1.0 V vs. RHE) was lower than that of $I/C=1.0$ and showed a slight positive shift at 1.1 V vs. RHE. According to these results, the specific adsorption of sulfo group in $I/C = 0.0$ and 1.0 can be observed from XANES and consistent with previous reports by Teliska et al. under HClO_4 and H_2SO_4 solution, respectively. These results indicate that in the high potential range, the Pt/C catalyst activity decreases with increasing ionomer content and specific adsorption species.

3.4 Conclusion

In this study, the impact of ionomer on the ORR of a carbon-supported Pt/C catalyst using a thin film RDE in 0.1 M HClO_4 was investigated. The specific activity decreased as the I/C ratio increased from 0.0 to 0.20. We utilized many methods to evaluate the adsorption species separately, including the measurements of ECSA and oxygen coverage, CO stripping voltammetry, *operando* X-ray absorption fine structure, and analysis of 5d orbital vacancy. The ECSA and oxygen coverage did not change with increasing ionomer content, indicating that the Pt/C catalyst activity was affected by other adsorption species. Comparison of the CO displacement charge and 5d orbital vacancies of the Pt/C catalysts with $I/C = 0.0$ and 1.0 suggests that the ionomer-specific adsorption increases when the I/C ratio of the Pt/C catalyst is 1.0; active sites on the surface of the Pt/C catalyst are occupied, resulting in a lower catalyst activity.

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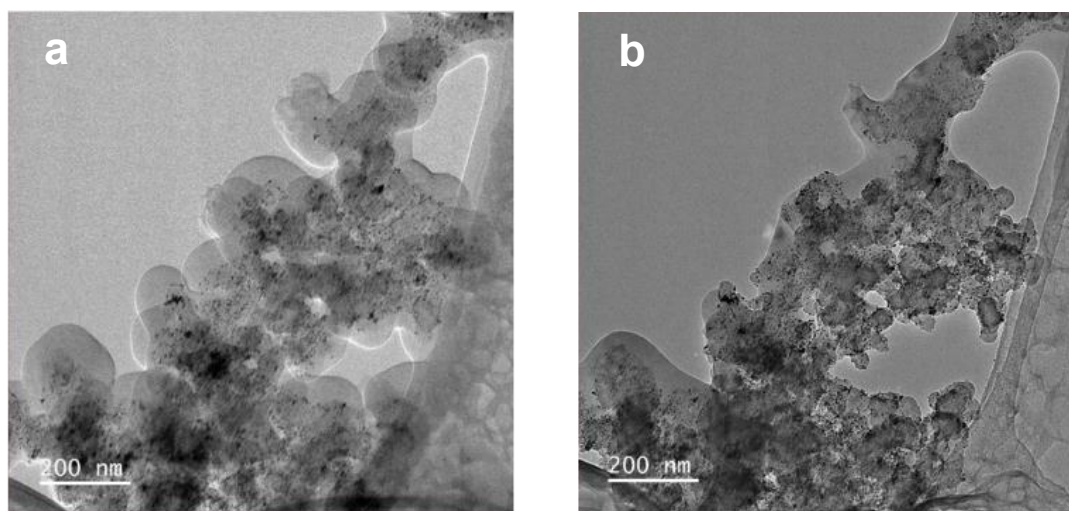


Figure 1. Cryo-TEM image of Pt/C catalyst with I/C = 0.20 before (a) and after (b) the 2 min exposure of electron beam.

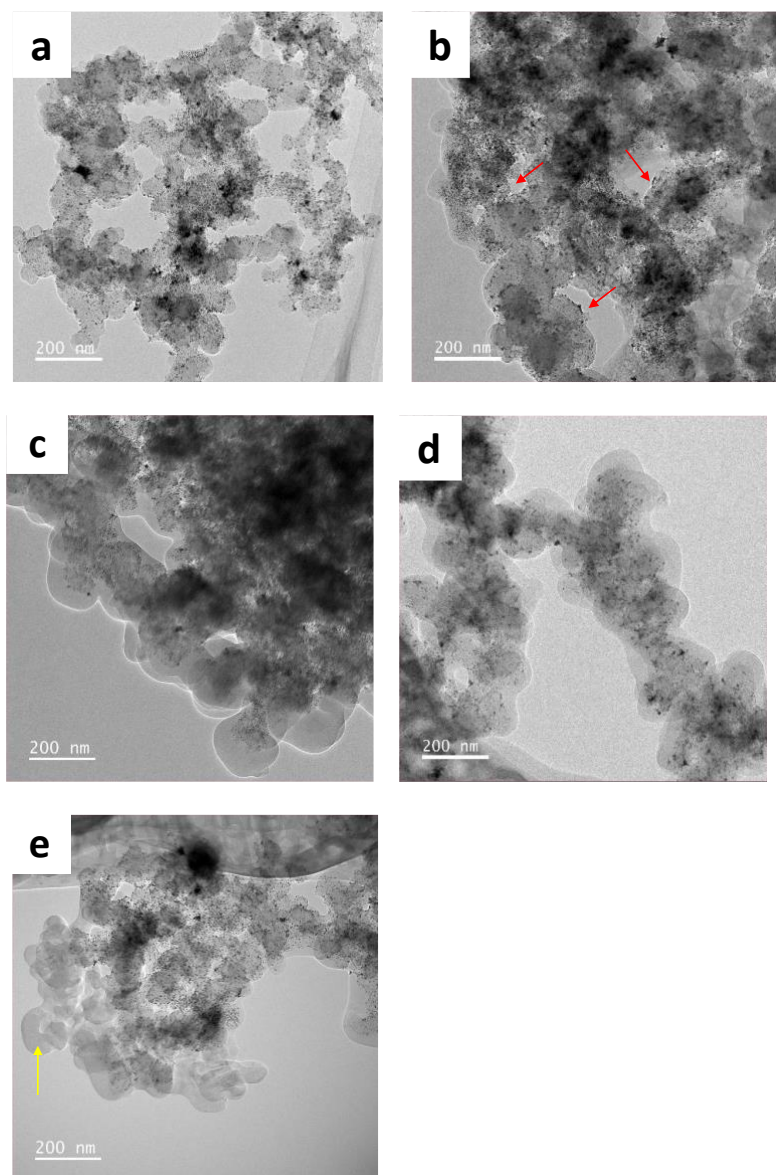


Figure 2. Transmission electron microscope (TEM) images of Pt/C catalyst at various I/C ratios. I/C = (a) 0.0, (b) 0.10, (c) 0.20, (d) 0.50 and (e) 1.0. Red arrows in (b) indicate the exposed surface of the catalyst. Yellow arrow in (e) shows the isolated ionomer.

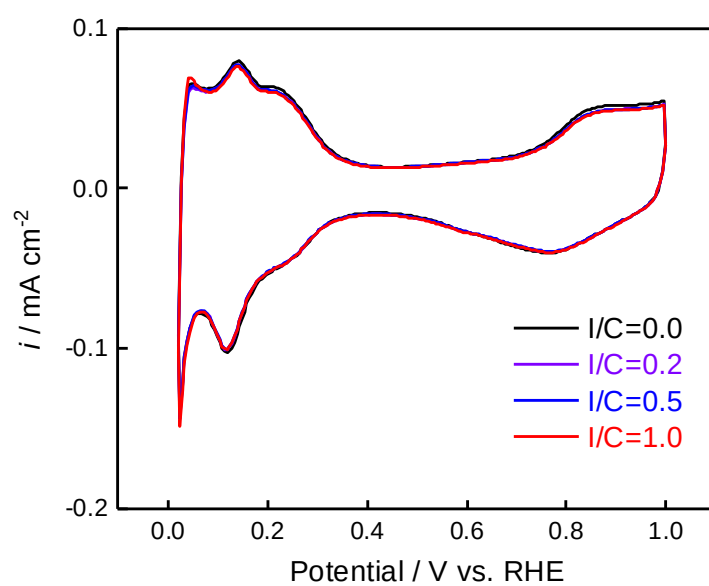
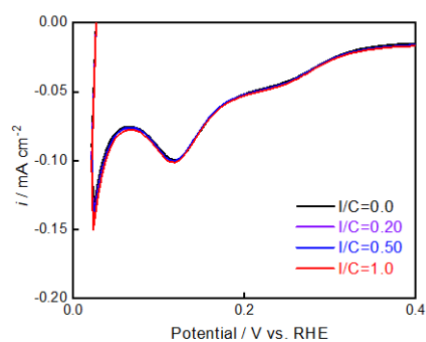


Figure 3. Cyclic voltammogram for Pt/C with varying I/C ratios.

(a)



(b)

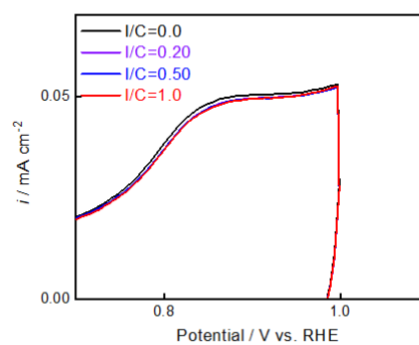


Figure 4. I/C dependence of cyclic voltammogram for Pt/C, enlarged figure (a) HUPD region and (b) oxide formation region

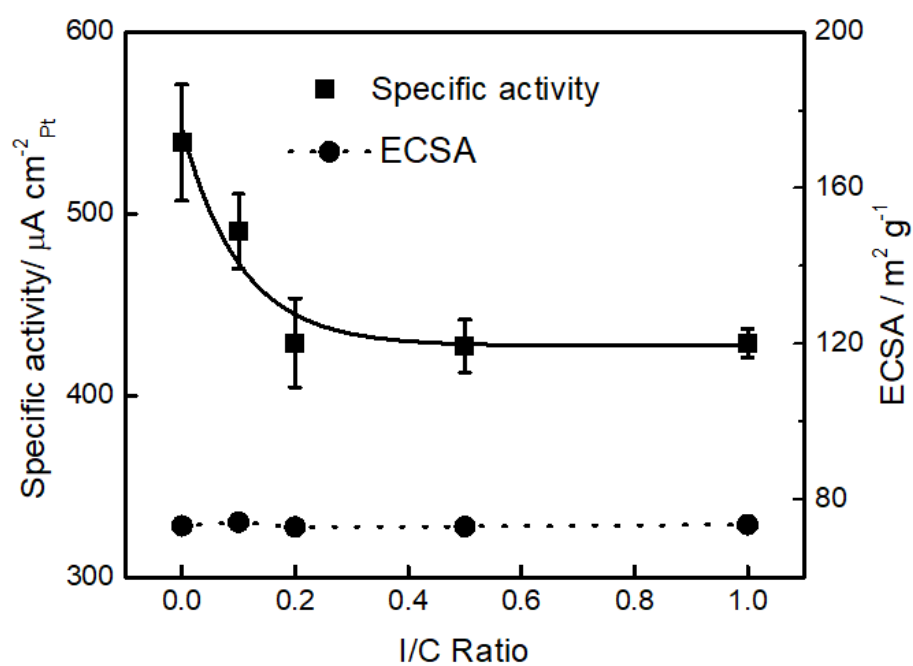


Figure 5. Influence of I/C ratio on the ECSA and specific activity of Pt/C at 0.90 V vs RHE.

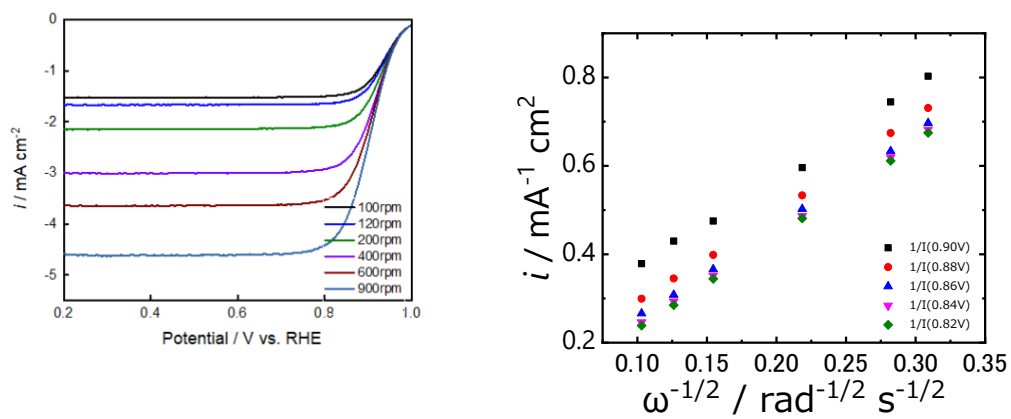


Figure 6. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pt/C catalyst with $I/C=0.0$.

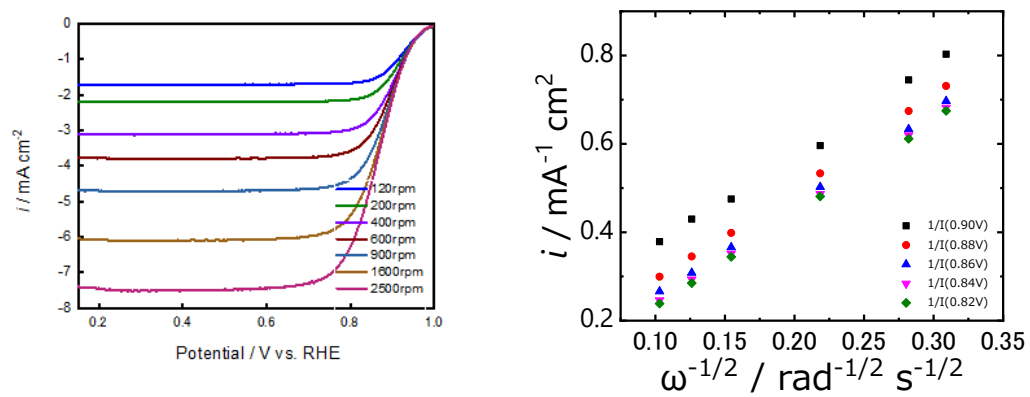


Figure 7. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pt/C catalyst with $I/C=0.10$.

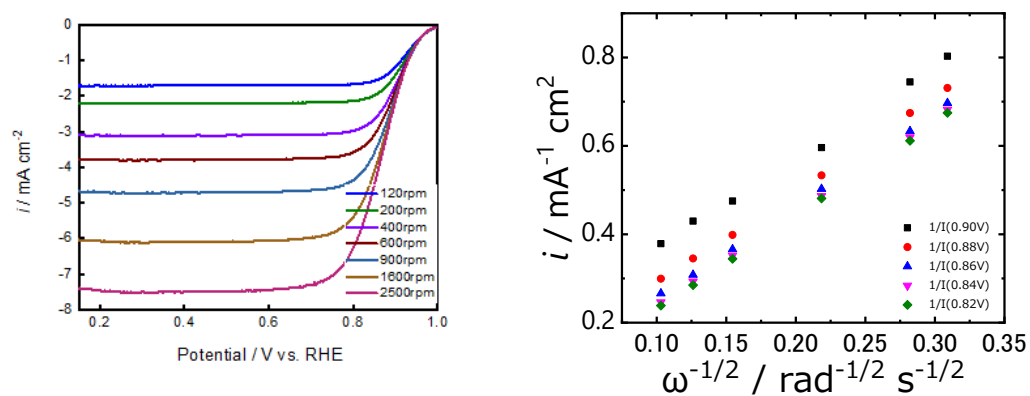


Figure 8. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pt/C catalyst with $I/C=0.20$.

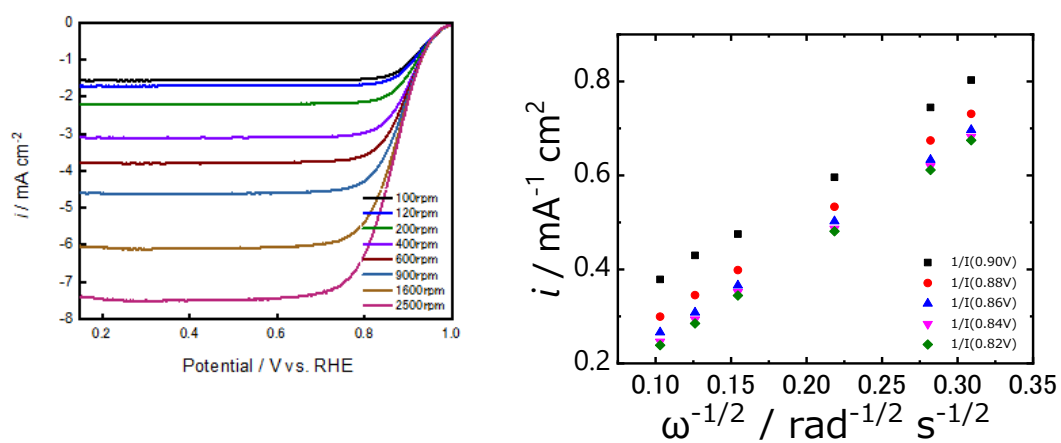


Figure 9. Liner sweep voltammogram (left) and Koutecky-Levich plot (right) for Pt/C catalyst with I/C=0.50.

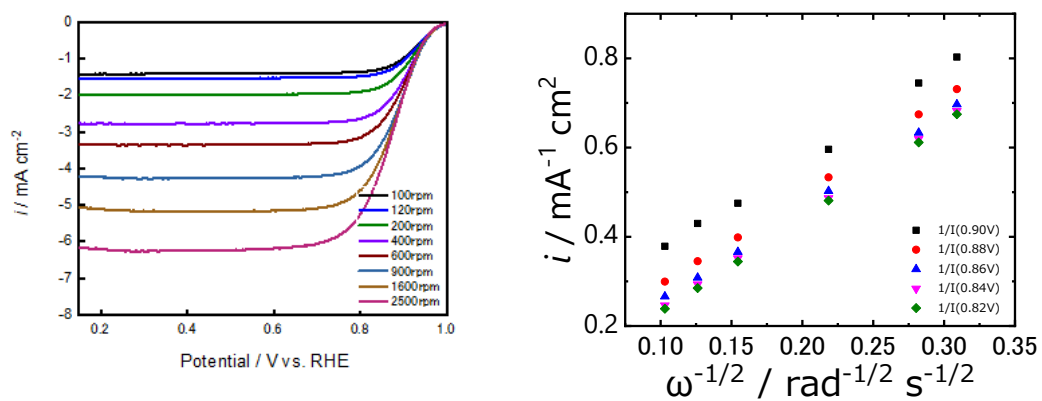


Figure 10. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pt/C catalyst with $I/C=1.0$.

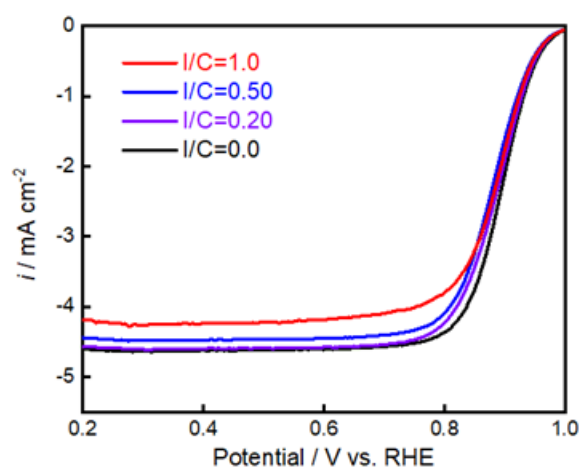


Figure 11. I/C dependence of linear sweep voltammogram for Pt/C

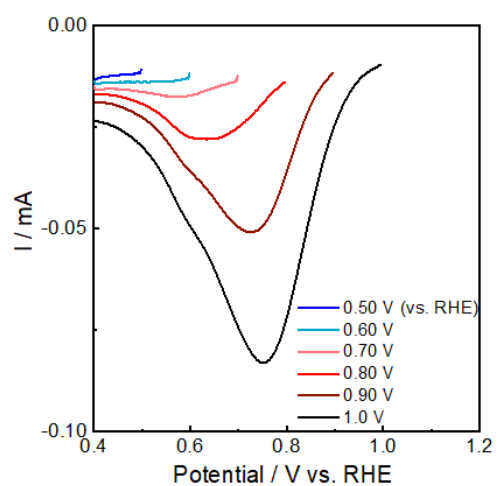


Figure 12. Reduction current profiles of oxide species on Pt/C catalyst with I/C=1.0 (0.50 -1.0 V (vs. RHE) indicates holding potential).

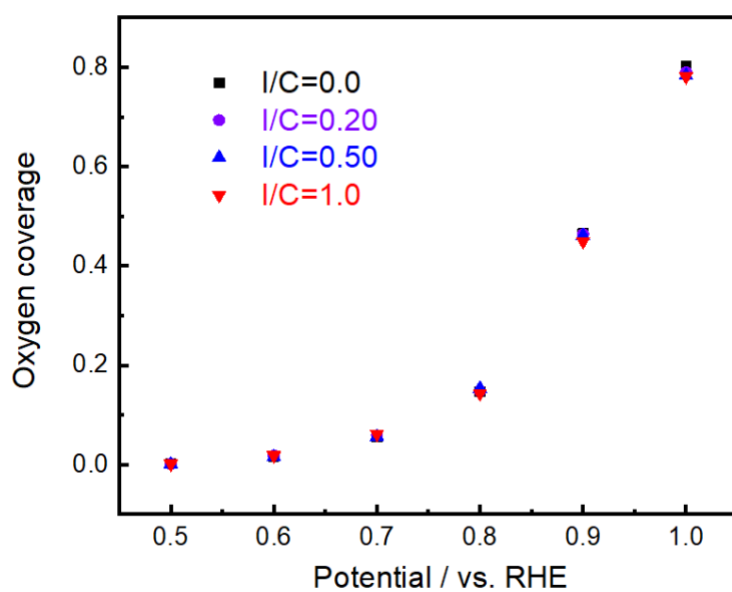


Figure 13. Dependence of I/C ratio on the oxygen coverage for Pt/C.

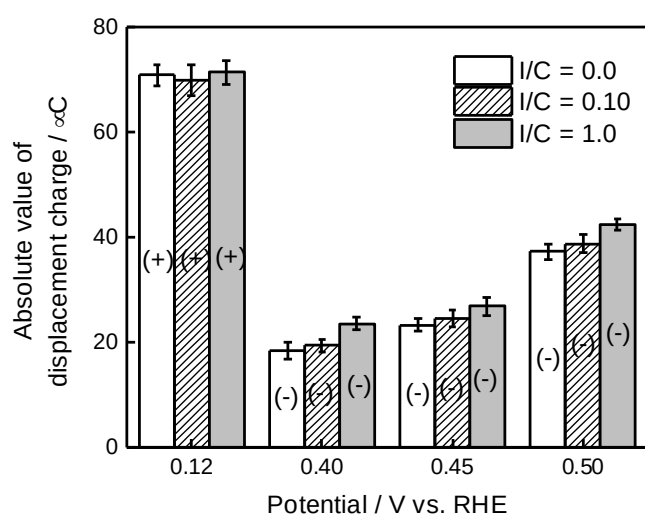


Figure 14. CO displacement charge measurements as a function of measurement potential for Pt/C with I/C = 0.0, 0.10 and 1.0. (+)/(-) indicates the polarity of the CO displacement charge.

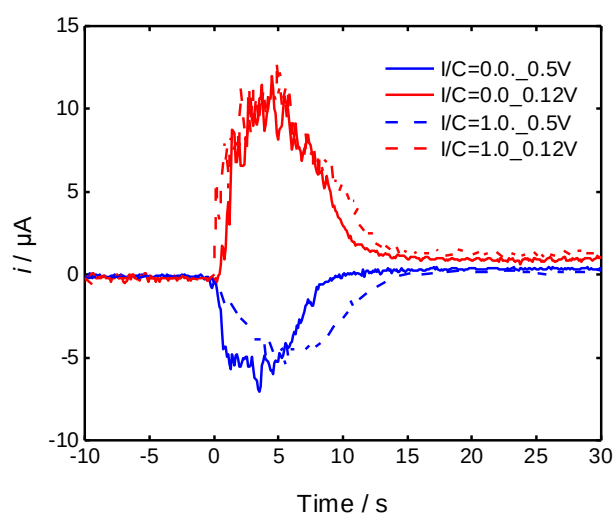


Figure 15. Current-time response of CO displacement charge experiments for Pt/C catalyst.

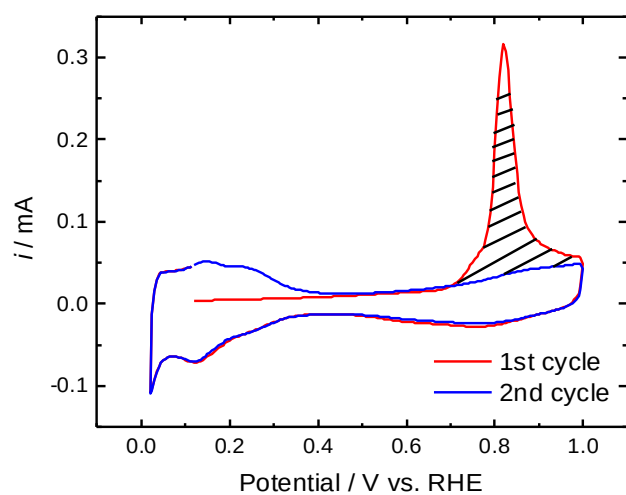


Figure 16. CO stripping voltammogram of Pt/C catalyst for I/C=0.0.

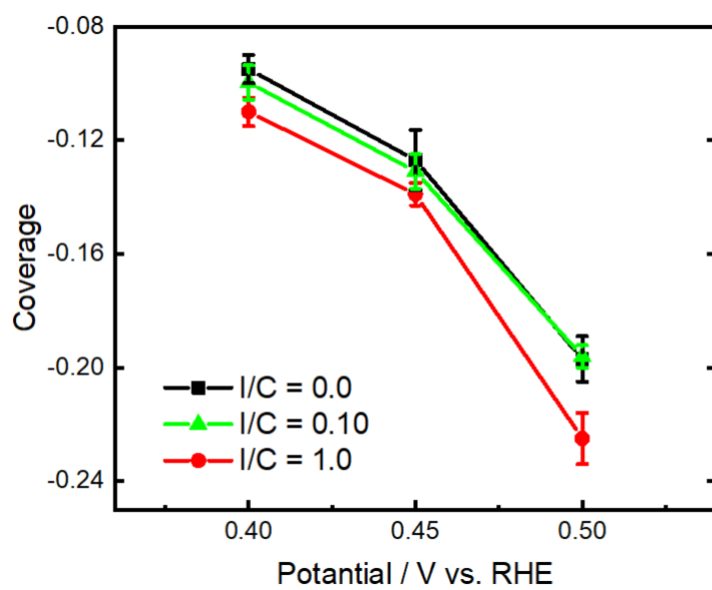


Figure 17. The anion coverage of for Pt/C catalyst with $I/C = 0.0, 0.10$ and 1.0 .

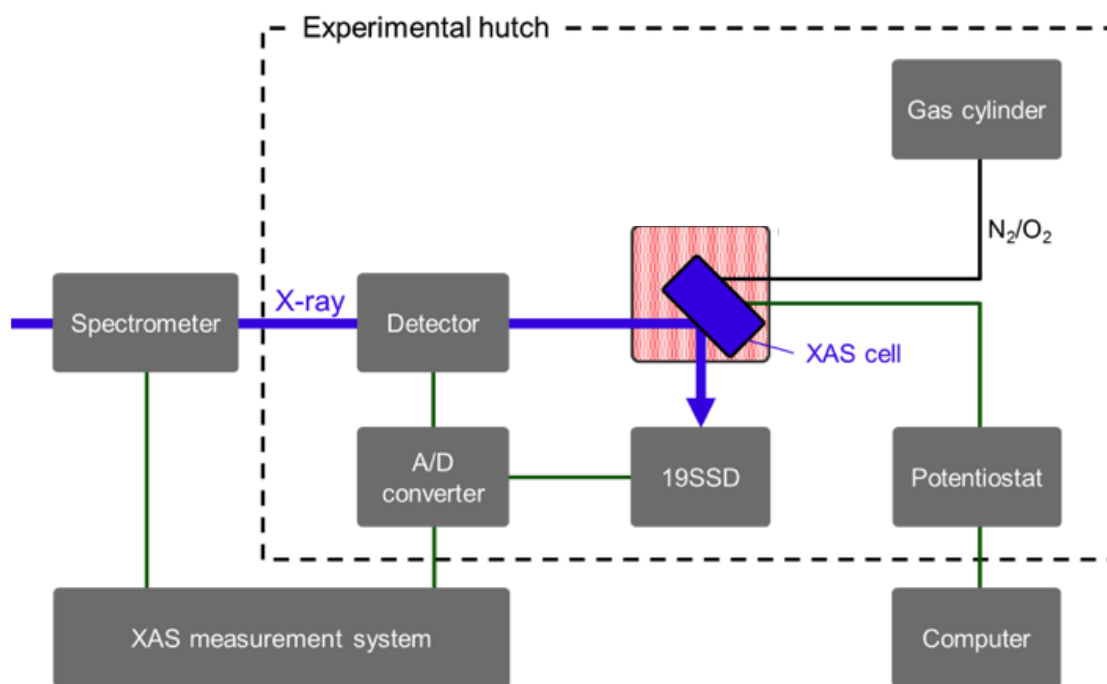


Figure 18. Measurement schematics for *operando* XAS measurement

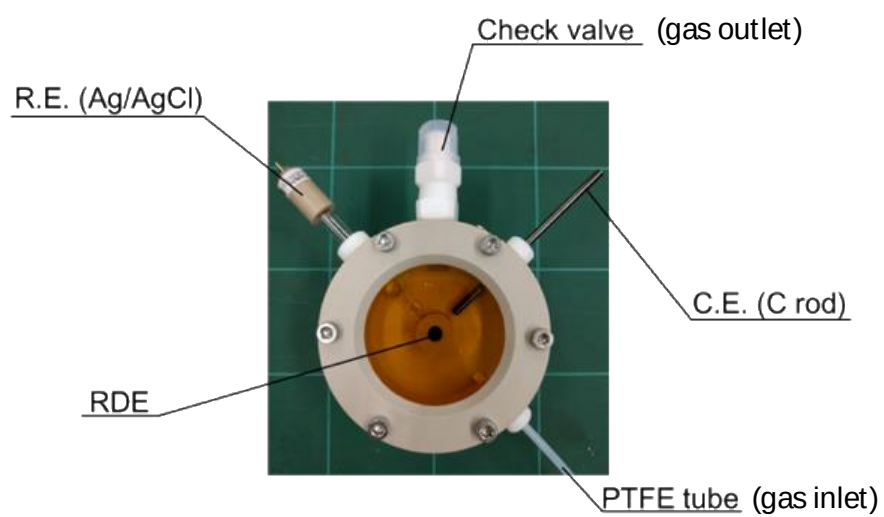


Figure 19. Assembled electrochemical cell for *operando* XAS measurement.

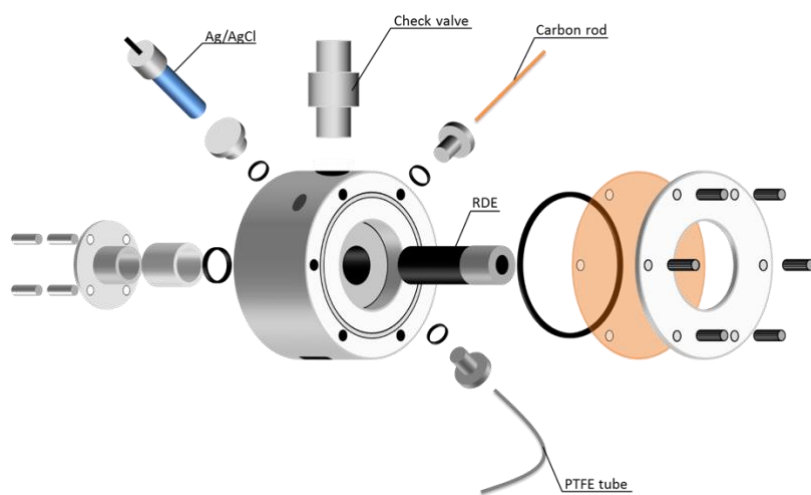


Figure 20. The structure of electrochemical cell for *operando* XAS measurement.

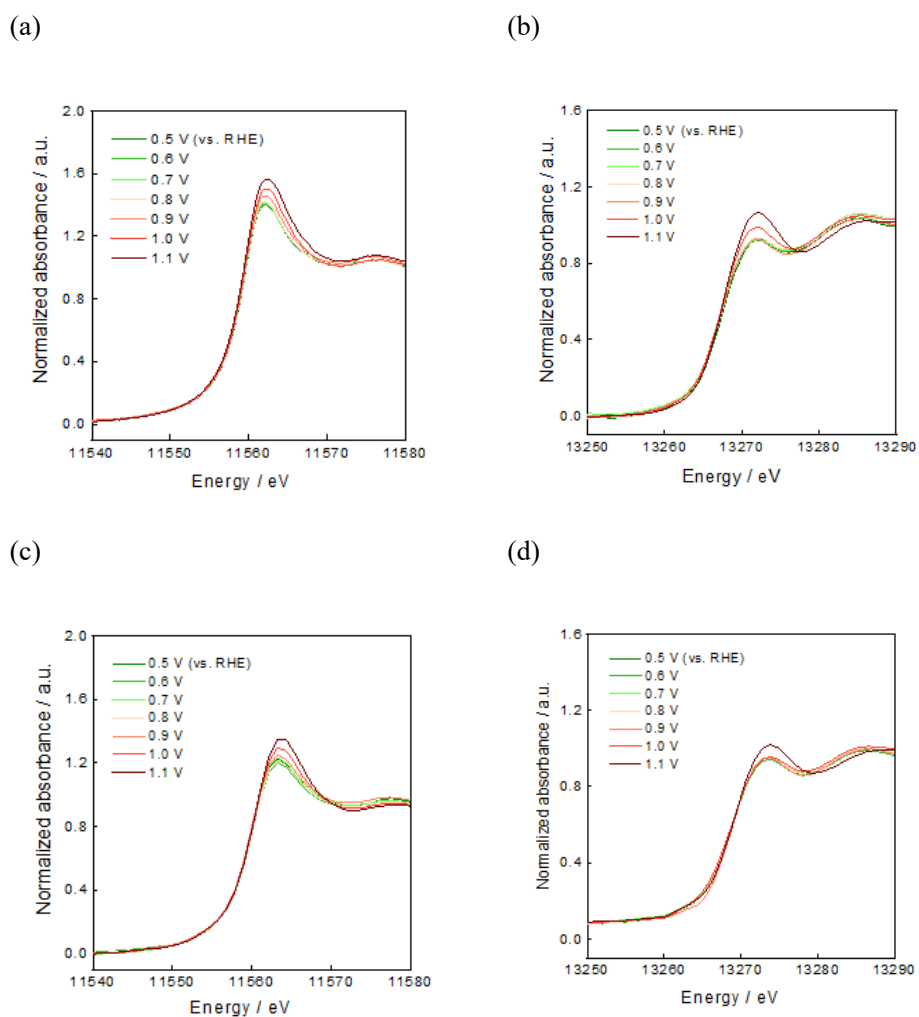


Figure 21. XANES spectra for (a) Pt L_{III}-edge and (b) Pt L_{II}-edge of I/C = 1.0 and (c) Pt L_{III}-edge and (d) Pt L_{II}-edge of I/C = 0.0.

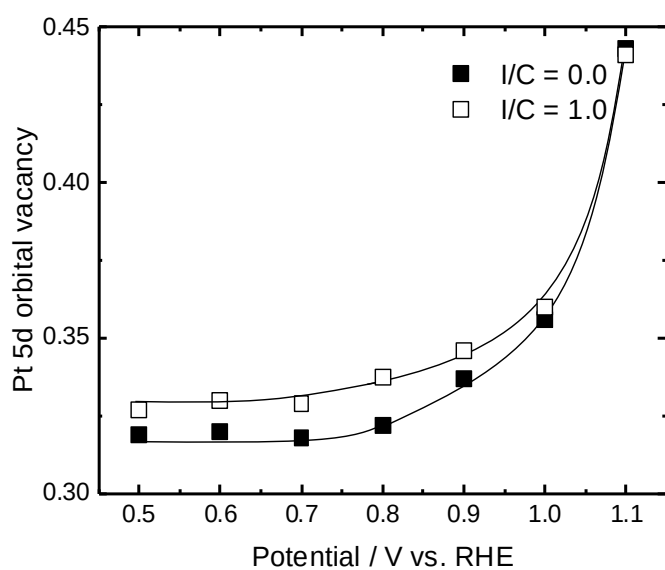


Figure 22. Change in 5d orbital vacancy of Pt/C catalysts with I/C = 0.0 and 1.0 from 0.5 to 1.1 V.

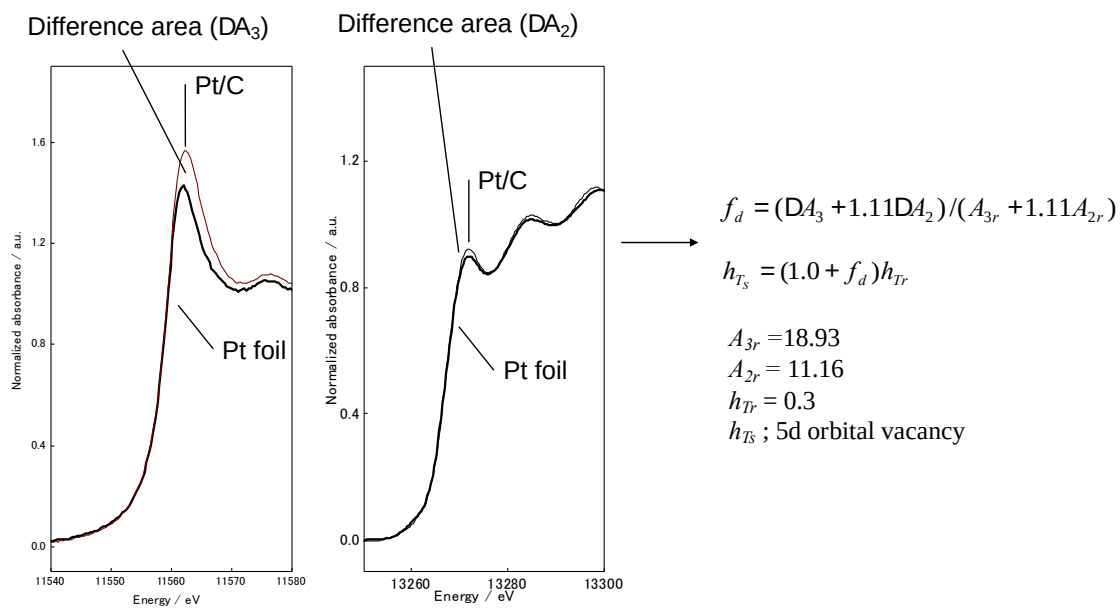
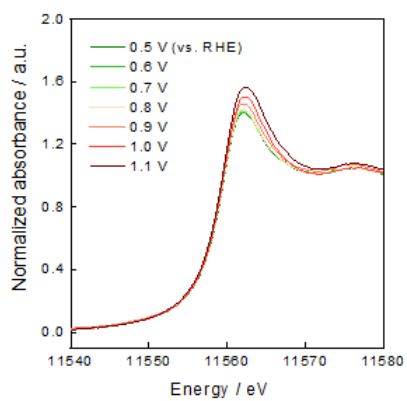
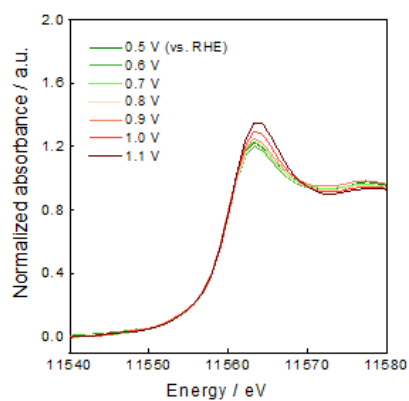


Figure 23. The brief illustration for calculating the 5d orbital vacancy from the XANES based on reference 40.

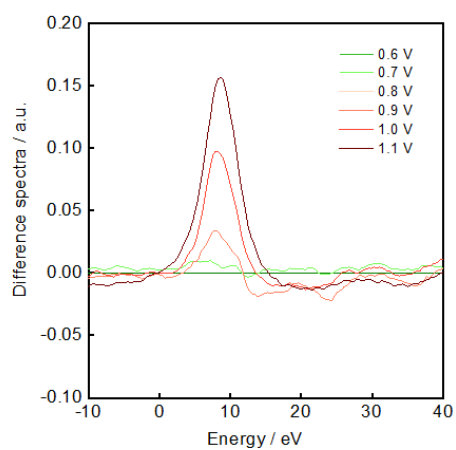
(a)



(b)



(c)



(d)

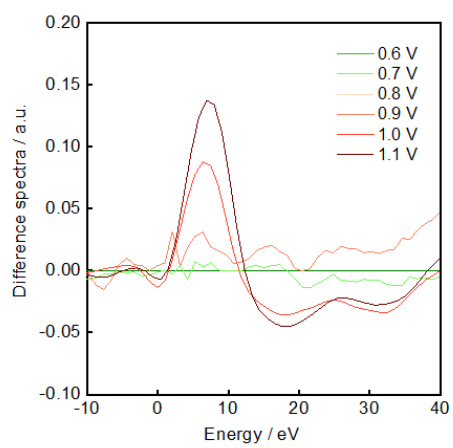


Figure 24. XANES spectra for Pt L_{III}-edge (a) I/C = 1.0 and (b) I/C = 0.0. $\Delta\mu$ spectra of Pt L_{III}-edge XANES (c) I/C = 1.0 and (d) I/C = 0.0.

Chapter 4. Specific Absorption Effect of Sulfo Group in Perfluorosulfonic Acid Ionomer on Pt-Pd Core-Shell Electrocatalysts for Oxygen Reduction Reaction by *operando* X-ray Absorption Spectroscopy

4.1 Introduction

Energy storage and conversion with high efficiency have a great impact on the sustainable development of the current society. Polymer electrolyte fuel cells (PEFCs) are expected to have an important role in near future to replace the traditional fossil fuels and apply in the hydrogen energy society. Currently, PEFCs are extensively studied for their use as stationary power sources and have already been applied for small-scale energy systems such as fuel cell vehicles (FCVs)¹⁻⁵. However, the high cost of PEFCs remains a major barrier that prevents the widespread applications of FCVs and the world-wide commercialization of PEFCs still need improvement. Due to the use of noble metals (platinum) as catalyst accounts for huge part of the PEFC manufacturing costs⁶, one of the most important issues is to reduce the cost and usage of Pt catalyst on the cathode. Pt-based catalysts are basically used due to the relatively inefficient reaction kinetics and catalyst degradation under strong acidic conditions during the oxygen reduction reaction (ORR)⁷⁻⁹. Therefore, high performance cathode catalyst with reliable ORR activity, durability and less cost are expected for the widespread application for PEFCs devices.

To improve the ORR activity and reduce the amount of Pt in the cathode, many researchers developed Pt-based catalyst through composition, morphology, and local structure¹⁰⁻¹⁶. Through morphology-controlling include nanowires¹² and nanoplates¹³ could provide a highly attractive approach to maintaining high Pt surface area and improve ORR activity. Pt-based core-shell structure catalyst also a type of catalyst has been focused which could possess lower Pt loading and provide higher ORR activity through the changing the electronic state of Pt atoms¹⁴⁻¹⁶. The activity of Pt-based catalysts has related with tensile or compressive substrate-induced strain in combination with the ligand effect^{17,18}. The status of *d*-band on the Pt surface layer, which is modified by ligand and strain effects, can influence the binding strength and

adsorption properties of oxide species.

The specific adsorption of anionic species on the Pt surface is well known as one reason inhibit the ORR activity of Pt-based catalysts⁹. Nafion[®] which is a type of perfluorosulfonic acid ionomers, usually adopted in the catalyst layer of PEFCs to provide the protonic pathway to the catalyst surface^{19,20}. However, the result for Nafion[®] covering Pt catalysts is active site loss through specific adsorption of the Nafion side-chain-bound sulfonate groups on the catalyst surface^{21,25,26}. Subbaraman et al. have found that the adsorption of oxide species at 0.8 V in 0.1 M HClO₄ on Pt(111) and Pt₃Ni(111) single crystal catalysts was dramatically affected by competing adsorption of anionic species from Nafion and cause about 25% activity loss⁹. Based on our previous study, the ORR activity of Pt/C catalysts decrease with increasing Nafion[®] content in the catalysts ink³⁹. The specific adsorption has been quantitatively evaluated through *operando* XAS methods at high potential region (0.6 -1.1 V vs. RHE) even though many Pt atoms in the bulk have not affected by specific adsorption from ionomer. Meanwhile, Tymoczko et al. demonstrated that Pt(top)/Cu(2nd-layer)/Pt (111) alloy single crystal have a weaker interaction between the top Pt layer and sulfonate groups of Nafion due to electronic effects from the Cu atoms in the second layer, which will act to minimize the impact of the interfacial ionomer²⁷. Through these results, it is necessary to observe the specific adsorption on the core-shell catalysts which might have different behavior suffered from the substrate metal.

CO displacement charge measurement is a typical method for evaluating the coverage of ionomer. The oxidation or reduction currents would be arisen during the displacement of adsorbing species by CO, and the coverage of ionomer could be evaluated by integrating CO displacement charge^{21, 29-31}. The successful quantitatively evaluation of the coverage of ionomer on Pt catalyst through CO displacement method has been reported³², but this method still remains limitation. The CO molecules adsorbed on the Pt surface would be oxidized around 0.60 V vs. RHE (reversible hydrogen electrode), the anion adsorption situation of Pt-based catalyst only has been evaluated from 0.08 to 0.56 V in previous reports^{21, 29-33}.

operando XAS (X-ray absorption spectroscopy) is reliable tool on evaluating the electronic status and detail structure on the Pt surface^{34, 35} as well as observing the anion adsorption on the Pt surface. The anion adsorption on the single crystal Pt (111) electrode surfaces in H₂SO₄ solution has been observed through the combination of X-

ray absorption near edge structure (XANES) and full-multiple scattering calculations using the FEFF8 code³⁶⁻³⁸. Our previous studies also achieved the detection of specific adsorption over a higher potential range that is at least equal to the ORR active potential (around 0.90 V vs. RHE) by *operando* XAS measurements, which cannot be measured by the CO displacement method. The quantitative detection of the specific adsorption was reported under the ORR potential by measuring Pt 5d orbital vacancy of the Pt/C catalyst using *operando* XAS³⁹. However, the effect of the electronic structure of the catalysts on the specific adsorption properties still has less report in supported catalysts. Therefore, Pd core-Pt shell catalyst, which is one of the typical highly active catalyst¹⁴⁻¹⁶, was selected as the material for investigation. At the same time, the core-shell structure is an advantage in achieving the clear observation of the specific adsorption by *operando* XAS measurement because all of the Pt exposed on the surface. In addition to XAS, in this study, the oxygen reduction reaction activities of Pd core-Pt shell catalysts with different ionomer-to-carbon weight ratios ($I/C = 0.0, 0.10, 0.20, 0.50, 1.0$) has been evaluated. The characterization of the catalysts covered by ionomers was investigated through cryo-transmission electron microscopy (Cryo-TEM). CO stripping voltammetry measurements and the analysis of 5d orbital vacancy have been carried out for quantitative evaluation of specific adsorption on the Pt shell of core-shell catalyst with various I/C ratios.

4.2 Experimental Methods

4.2.1 Synthesis of Pd core-Pt shell catalyst

The synthesis method of Pd nanoparticle was followed by our previous report⁴⁰. Briefly, 0.5 mmol palladium(II) acetate and 10.0 mmol OAm (oleylamine) were mixed at 50 °C. Then 10.0 mmol OAc (oleic acid) was added to the solution and stirred for 60 minutes at 50 °C. Then, 1.5 mmol TBAB (tetra-butylammonium borohydride) was dissolved in 2.0 mL chloroform and injected the solution into the mixed solution of palladium(II) acetate, OAm and OAc. They stirred again for 60 minutes at 50 °C. After cooling to the room temperature, Pd nanoparticles was precipitated with ethanol and centrifugated. The obtained Pd nanoparticles containing 0.50 mmol of Pd was mixed with 0.67 mmol of Pt precursor and 4.0 mmol of OAm. The solution was refluxed for 24 hours and Pd core-Pt shell nanoparticles precipitated by with ethanol and centrifugated. The precipitated Pd core-Pt shell nanoparticles were redispersed in

chloroform solution containing carbon support (Vulcan XC-72). After the filtration, the carbon supported Pd core-Pt shell catalyst were obtained by subsequent calcination at 300 °C for 30 min at oxygen atmosphere.

Pt/C (29.1 wt.%; TEC10V30E, Tanaka Kikinzoku Kogyo Co. Ltd., Japan.) catalyst was also used as the reference.

4.2.2 Electrochemical measurements

The catalyst ink contained ultrapure water (Milli-Q[®], Millipore A/S, United States, electrical resistivity of 18.2 MΩ·cm or more) and 2-propanal in 1:1 ratio (99.99%, FUJIFILM Wako Pure Chemical Corporation, Japan), and the amount of Pd core-Pt shell/C was adjusted to form a 20 μg_{carbon} cm⁻² catalyst layer after dropping 5 μL on a glassy carbon RDE (GC RDE, HOKUTO DENKO, Japan; 0.196 cm² area). The ink on the RDE was dried at 700 rpm at room temperature. Nafion[®] solution (5 wt.%, Sigma-Aldrich Co. LLC, Japan) was employed to prepare Pd core-Pt shell catalyst ink with I/C ranging from 0.0 to 1.0. The high purity HClO₄ (Kanto Chemical Co., Inc, Japan, purity: 60.0 wt%) was adopted to prepare the 0.1M HClO₄ electrolyte.

ORR activities were measured in three-electrode cell at 25 °C. The reference electrode was reversible hydrogen electrode (RHE). Counter electrode of the cell was Pt mesh. 50 cycles of potentials in N₂-saturated 0.1 M HClO₄ from 0.02 to 1.1V (vs. RHE) with 100 mVs⁻¹ before the active measurements to achieve a stable cyclic voltammogram (CV) curves. The final CV achieve at 50 mVs⁻¹ scan speed. Then the electrolyte bubbling with O₂ gas until saturated. Linear sweep voltammetry (LSV) from 0.2V to 1.2V vs. RHE by 10 mVs⁻¹ scan speed at rotating speed with 100, 400, 900, 1600, 2500rpm. The oxygen reduction data for all the catalysts were analyzed according to Koutechy-Levich equation. The oxygen coverage of the catalysts measured by LSV in N₂-saturated 0.1 M HClO₄. First the potential scan starts from 0.4V (vs. RHE), to the holding potential (0.5V, 0.6V, 0.7V, 0.8V, 0.9V, 1.0V, 1.1V vs. RHE) with 50 mV·s⁻¹ scan speed. Holding the potential for 5 minutes until a stable current and then scan back to 0.4V (vs. RHE) to obtain reduction current. The integrated cathodic current was used to estimate the charge of oxide species based on the following reaction (Pt-OH + H⁺ + e⁻ → Pt + H₂O) also reports from other researchers^{41,42}. The coverage of oxide species was estimated through dividing the charge of oxide species by the underpotential deposition charge of hydrogen^{41,42}.

CO stripping voltammetry were measured in the same cell at 25 °C. 50 cycles of potentials in N₂-saturated 0.1 M HClO₄ from 0.02 to 1.1V (vs. RHE) with 100 mVs⁻¹ before the active measurements to achieve a stable cyclic voltammogram (CV) curves. The final CV achieve at 50 mVs⁻¹ scan speed. Then, the holding potential at 0.12V, 0.40V, 0.45V, 0.50V (vs. RHE) until a stable current was obtained. Then CO gas (99.9%, GL Sciences Inc.) bubbling to the electrolyte until stable current, showed complete CO adsorption on the catalyst. Then switch bubbling gas to N₂ gas for 40 min for CO deaeration. Finally, CO stripping voltammetry was initiated in the range from 0.02 to 1.0 V (vs. RHE). The coverage of anions was estimated through integrating CO exchange current divided by CO stripping charge.

4.2.3 TEM observations

Drying sample inks on Cu grid were prepared for the specimens of cryo-TEM. Specimens kept at 80% humidity and 60 °C for sample with I/C from (0.10 to 1.0), and liquid ethane in EM GP2 plunge freezer (Leica Microsystems, Austria) were used to quickly froze the samples. Then the frozen specimens The frozen specimens were transferred to TEM in liquid nitrogen with cryo-transfer holder. The cryo-TEM observation was carried out at about -175 °C on a JEM-F200 (JEOL Ltd., Japan) microscope operating at 200 kV. For I/C=0.0 sample, the conventional TEM observation and elemental mapping images were carried out on a JEM-F200 (JEOL Ltd., Japan) microscope operating at 200 kV.

4.2.4 *operando* XAS measurements

operando XAS measurements for Pt L_{III}-edge of Pd core-Pt shell/C catalysts were carried out in fluorescence mode using synchrotron radiation at BL37XU of SPring-8, Hyogo, Japan. A pair of Si (111) monochromators and a total-reflection Rh mirror (4 mrad) were used to obtain collimated and monochromatic X-rays. The details of the measurements has already reported on our previous study³⁹. Briefly, the material for the main body of the *operando* cell is made of poly ether ether ketone (PEEK). The catalyst coated RDE can be set on the center of the cell as working electrode. Ag/AgCl electrode (RE-8, EC Frontier CO., LTD., Japan) and Pt mesh were used as reference and counter electrode, respectively. The polytetrafluoroethylene (PTFE) tube on the bottom right part is for the O₂ gas inlet to the 0.1 M HClO₄ electrolyte to control the gas atmosphere.

The check valve (MFTD-6V, AS ONE Corporation, Japan) is the gas outlet and also can prevent the internal pressure rise during bubbling the gas. Kapton® film of 25 μm was used as the X-ray window. Prior to the experiments, the samples were electrochemically cleaned by CV in the range 0.0–1.1 V (vs. RHE). The electrode potential was swept cathodically from 0.5 to 1.1 V (vs. RHE). Data were analyzed using ATHENA and ARTEMIS, a suite of the IFEFFIT software programs⁴³.

4.3 Results and discussions

4.3.1 TEM observations

The TEM images of the synthesized Pd nanoparticles was indicated in Figure 1a. The particle size of Pd nanoparticle was about 3.0 nm (Figure 1b). The atomic ratio of Pt/Pd = 0.61 was determined in Pd core-Pt shell catalyst through the evaluation of inductively coupled plasma mass spectrometry. Considering fcc structure of Pd, 923 of Pd atoms are included in 3 nm and 492 of Pt atoms are needed to form Pt monolayer on Pd surface, suggesting that the atomic ratio of Pt/Pd becomes 0.53. Therefore, it can be estimated that the synthesized Pd core-Pt shell catalyst has 1.1-Pt layer on Pd in average.

HAADF-STEM (high-angle annular dark-field scanning transmission electron microscope) image of Pd core-Pt shell catalyst and EDX (Energy dispersive X-ray spectroscopy) element maps of Pd and Pt were shown in Figure 2. The EDX element maps in Figure 2b and line profile in Figure 2e confirmed the Pd core-Pt shell structure of the catalyst, which consistent with other report⁴⁴.

Pd core-Pt shell catalyst with I/C from 0.0 to 1.0 were observed by cryo- TEM in Figure 3a-e. Figure 2a shows the TEM image of Pd core-Pt shell catalyst without ionomer (I/C = 0.0), showed typical image of a nanoparticle catalyst with carbon support. In Figure 3b, with I/C=0.10, the catalyst surface was partly exposed from ionomer as marked by red arrows. The carbon aggregate and morphology of ionomers observed in this study has a good agreement with previous report⁴⁵. Through the TEM images, all the particles were completely covered by ionomer over I/C=0.20 as shown in Figures 3c-e.

4.3.2 Electrochemical measurements

Figure 4 indicates the thermo-gravimetry curve for carbon supported Pd core Pt

shell catalyst after calcination at 300 °C. Even after calcination, the weight loss about 8% was observed, suggesting that the organic species from catalyst synthesis were remaining on the catalyst. Figure 5 shows the cyclic voltammograms of the Pd core-Pt shell catalyst during cleaning with I/C ratios from 0.0 to 1.0. For, the first cycle of the cleaning, Pt oxidation and hydrogen UPD was not clearly observed due to the remaining organic molecules from catalyst synthesis and the typical cyclic voltammograms was obtained at 40th cycle, suggesting that the surface was enough cleaned. After the cleaning, the electrolyte in the electrochemical cell was exchanged to new one to prevent the contamination. Figure 6 shows the cyclic voltammograms of the Pd core-Pt shell catalyst with I/C ratios from 0.0 to 1.0 and the enlarge of oxide formation region and hydrogen UPD region showed in Figure 7. The observable slight peak shift to the higher potential with increasing I/C ratios exhibits about onset potential of oxide formation. There is also slight peak shift to lower potential with increasing I/C ratios can be observed in the onset potential of hydrogen under-potential deposition current. These results are consistent to the report from Shinozaki et al²⁵. and our previous results about Pt/C catalysts³⁹.

However, it is not clear to illustrate the ionomer effect through the cyclic voltammetry curves. Through the specific activity evaluation about the Pd core-Pt shell catalyst with various I/C ratios, we found obvious decreasing specific activity with increasing I/C ratios showed in Figure 8a and the liner sweep voltammogram and Koutecky-Levich plot were shown in Figures 9-13. The catalysts possess highest activity at I/C = 0.0 (without ionomer) and decrease with higher I/C ratios while the electrochemical surface area (ECSA) still almost same compared with catalysts at each I/C ratios. These results were consistent with previous study⁴⁶ and determine that ionomer have inhibition effect on the activity of the Pd core-Pt shell catalyst but no obvious effect about the ECSA. There is about 63% specific activity loss from I/C = 0.0 for our Pd core-Pt shell catalysts, while Pt/C catalysts did about 80% in our previous report³⁹, showed in Figure 8b. Even though the Pd core-Pt shell catalyst still remain higher specific activity than that of Pt/C catalyst at I/C = 1.0, the results indicate that the Pt surface on the Pd core suffered electronic effect from substrate, cause more specific adsorption on the Pt surface. It is notable that there are less diffusion limit currents observed in high I/C ratio at 0.50 and 1.0) in Figure 14, indicated that higher I/C ratios cause slight oxygen diffusion resistance even though it has no significant

effect on the activity of catalysts. Same trend also has been observed from Zhu et al.⁴⁷, indicated that the main reason of decreasing activity with increasing I/C ratios belong to the specific adsorption of ionomer even though slight oxygen diffusion resistance also occurred during the increase of ionomer content.

The oxygen coverage of the Pd core-Pt shell catalyst with various I/C ratios have been evaluated to clarify the change of the oxygen species adsorption. The oxide reduction profiles for Pd core-Pt shell catalyst with I/C=1.0 ratios showed in Figure 15 as an example. The oxygen coverage increased with higher potentials shown in Figure 16, and no obvious change among different I/C ratios. The catalysts with I/C = 0.0, 0.10 possess slightly higher oxygen coverage which reach an agreement to the results from CV results in Figure 6. These tendencies consistent to the previous reports about the oxygen coverage about Pt/C catalysts^{39,41}, while Pd core-Pt shell shows lower oxygen coverage compared with Pt/C catalysts¹⁴, indicated that Pt surface on the Pd core have less oxygen species adsorption and improved the activity. Through the comparison of activity change between Pt/C and Pd core-Pt shell catalysts, it is reasonable to determine the different amount of specific adsorption from ionomer on these catalysts and oxide species did not played an main role while the decrease activity happened with increasing ionomer.

To quantitatively evaluate the specific adsorption species on the Pd core-Pt shell catalysts, we employed CO stripping voltammetry, which could measure the displacement charge about adsorption species and CO molecule. The charge of Pt-H at 0.12 V (vs. RHE) and adsorption species on Pt surface from 0.40 to 0.50 V (vs. RHE) at I/C ratio = 0.0, 0.10, 1.0 were showed in Figure 17 and the examples of CO exchange current profiles were shown in Figure 18. Similar to the results of H_{UPD} region in Figure 6 and electro-chemical surface area in Figure 8, the Pt-H charge at various I/C ratios have no obvious change. CO displacement charge in potential from 0.40 to 0.50 V (vs. RHE) at I/C = 1.0 is obviously higher than that at I/C = 0.0 and 0.10, indicated the increasing adsorption species with increasing I/C ratio, which belong to the specific adsorption from ionomer, and reach an agreement with other reports⁴⁸⁻⁵⁰. The displacement charge at I/C = 0.10 is lower than I/C = 1.0 and higher than 0.0, indicating that the same status of the amount of specific adsorption from ionomer, which consistent to our results about cryo-TEM in Figure 3 and specific activity in Figure 8. The anion coverage calculated through $2 \times (\text{CO displacement charge}) / (\text{CO stripping}$

charge) showed in Figure 19 and CO stripping profile example showed in Figure 20. The anion coverage at 0.50 V (vs. RHE) is around 0.16 in I/C = 0.0 and 0.25 in I/C = 1.0, showed similar tendency with the result from Garrick et al.⁴⁹, reported the anion coverage of Pt/C catalyst with and without the employment of H₂SO₄ in the electrolyte. Compared to our previous reported anion coverage of Pt/C catalysts with various I/C ratios, Pd core-Pt shell possess larger gap of the anion coverage between I/C = 0.0 and 1.0, indicates our Pd core-Pt shell catalysts suffer more specific adsorption from ionomer, compared with Pt/C catalysts. This result also suggested that the ionomer specific adsorption on the Pt surface is the primary reason for the decreasing catalyst activity with increasing ionomer contents.

4.3.3 *operando* XAS measurements.

As mentioned above, the main reason of Pd core-Pt shell catalyst activity loss with increasing ionomer content is considered as the increasing specific adsorption from ionomer, CO stripping voltammograms can only evaluate the adsorption species at voltages lower than 0.60 V (vs. RHE). To observe the adsorption species in the high potential region, where the ORR occurred, *operando* XAS measurements were employed. The 5d orbital vacancies in Pt which could present the electronic statement of Pt atoms was calculated from the XANES spectra of Pt L_{III}-edge and L_{II}-edge. In this study, the number of 5d orbital vacancies in Pt was calculated from the XANES spectra of Pt L_{III}-edge and L_{II}-edge (Figure 21), based on the method from Mansour et al.⁵¹. The 5d orbital vacancies of the Pd core-Pt shell catalyst with I/C = 0.0 and 1.0 are shown in Figure 22 and compared with our previous study about 5d orbital vacancies about Pt/C³⁹.

The increasing 5d orbital vacancies with higher potentials can be observed in both samples, which represent the formation of Pt-O bond and more oxide species adsorption on the Pt surface, which come an agreement with the result of oxygen coverage. Same as the oxide species adsorption, the specific adsorption of ionomer also has influence on the electronic structure of the Pt atoms and change the 5d orbital vacancies. Comparing with the 5d orbital vacancies of catalyst with I/C = 0.0 and 1.0, there is obviously gap between them at 0.90 V (vs. RHE) where oxygen reduction reaction occurs, also in the lower (0.50-0.80 V vs. RHE) and higher (1.0-1.1 V vs. RHE) potential region. Compared with our previous report about the 5d orbital vacancies of Pt/C

catalysts at $I/C = 0.0$ and 1.0 ³⁹, the amount of 5d orbital vacancies were entirely higher in Pd core-Pt shell catalyst, which agrees with other reports⁵². The electronic states of Pt atoms in the bulk of the Pt nanoparticles also been evaluated in the Pt/C catalysts, which cause the less information from the oxide species and ionomer adsorption on the outer monolayer and lead the less change in 5d orbital vacancies, which considered as the reason of the difference between Pt/C catalyst and Pd core-Pt shell catalyst. The ligand effect from substrate of the Pd core-Pt shell also another reason leads the differences. The 5d orbital vacancies of Pt shell on the core-shell catalyst could provide most information of the electronic states on the surface while Pt/C, with particle size of 3.0 nm, can only have about 30% Pt atoms on the surface. These results indicate that in the high potential range, the Pd core-Pt shell catalyst activity decreases with increasing ionomer content due to the specific adsorption species.

The local structure around Pt in Pt/Pd/C was investigated through extended X-ray absorption spectra (EXAFS). Figure 23 indicates Pt-Pt bond distance change of Pd core-Pt shell catalysts with $I/C = 0.0$ and 1.0 from 0.50 to 1.1 V (vs. RHE) from EXAFS analysis. The fitting results from EXAFS analyses of the data at each potential are presented in Table S1. The features at 0.50 V indicated the typical Pd core Pt-shell structure reported elsewhere including our previous studies^{16, 17, 39} regardless of the ionomer. The estimated Pt-Pt bond distance of $I/C = 1.0$ was relatively larger than that of $I/C = 0.0$ at any potential. This bond extension might be caused by the specific adsorption on the Pt surface and this compressive Pt-Pt bond-induced structure in $I/C=0.0$ had an advantage for the ORR kinetics. In other words, our results provide clear evidence that the specific adsorption on the Pt surface could influence Pt-Pd bond extension and reduced the ORR activity.

4.4 Conclusion

In this study, the influence of ionomer about the oxygen reduction reaction activity of Pd core-Pt shell catalyst with carbon supporting has been investigated. The specific activity decreased with the increasing ionomer content from I/C ratio 0.0 to 1.0. The more significant activity loss of Pd core-Pt shell catalyst compared with Pt/C catalyst in our previous work suggest that more specific adsorption occurred on the Pd core-Pt shell catalyst compared with Pt/C catalyst. Many methods has been employed to evaluate the adsorption species include the ECSA, oxygen coverage, CO stripping

voltammetry, *operando* X-ray absorption fine structure, and analysis of 5d orbital vacancy. ECSA and oxygen coverage have no obvious change with increasing I/C ratios, indicate that the catalyst activity was not influenced by hydrogen and oxide species adsorption. CO displacement charge at 0.40-0.50 V change from I/C = 0.0 to 1.0 indicated that the specific adsorption from ionomer increase with higher ionomer content and anion coverage shows Pd core-Pt shell catalyst suffer more specific adsorption from ionomer than Pt/C catalysts. 5d orbital vacancies shows obvious increase from I/C = 0.0 to 1.0 on Pd core-Pt shell catalyst, suggests the increasing ionomer-specific adsorption in I/C = 1.0 and success evaluation about specific adsorption only on the surface of the catalyst.

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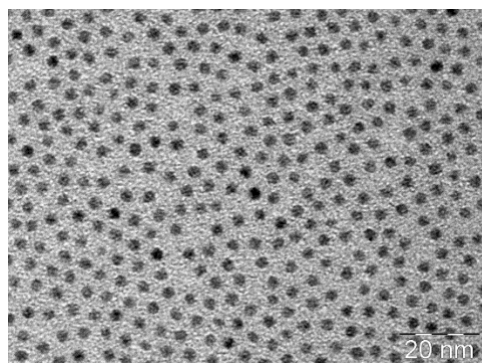
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a



b

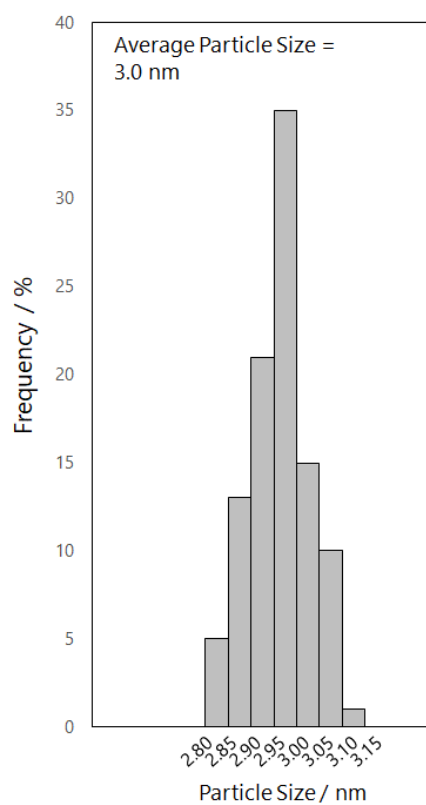


Figure 1. Transmission electron microscope images of (a) Pd nanoparticles (b) particle size distribution.

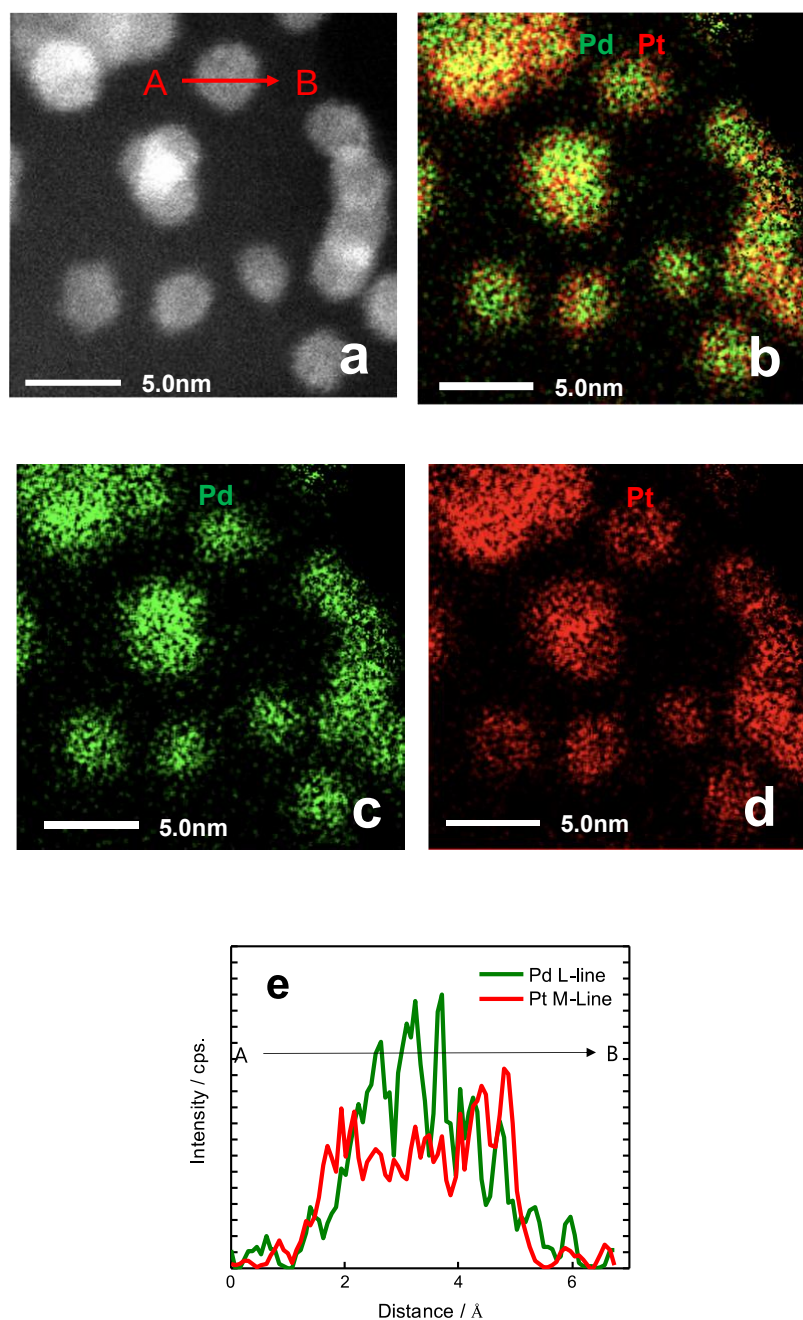


Figure 2. HAADF-STEM image (a), EDX elemental mappings of Pd core Pt shell catalyst. The combination of EDX map from Pd (c) and Pt (d) form the EDX map include Pt and Pd (b). EDX line profile (e) from A to B across the area indicated in (a).

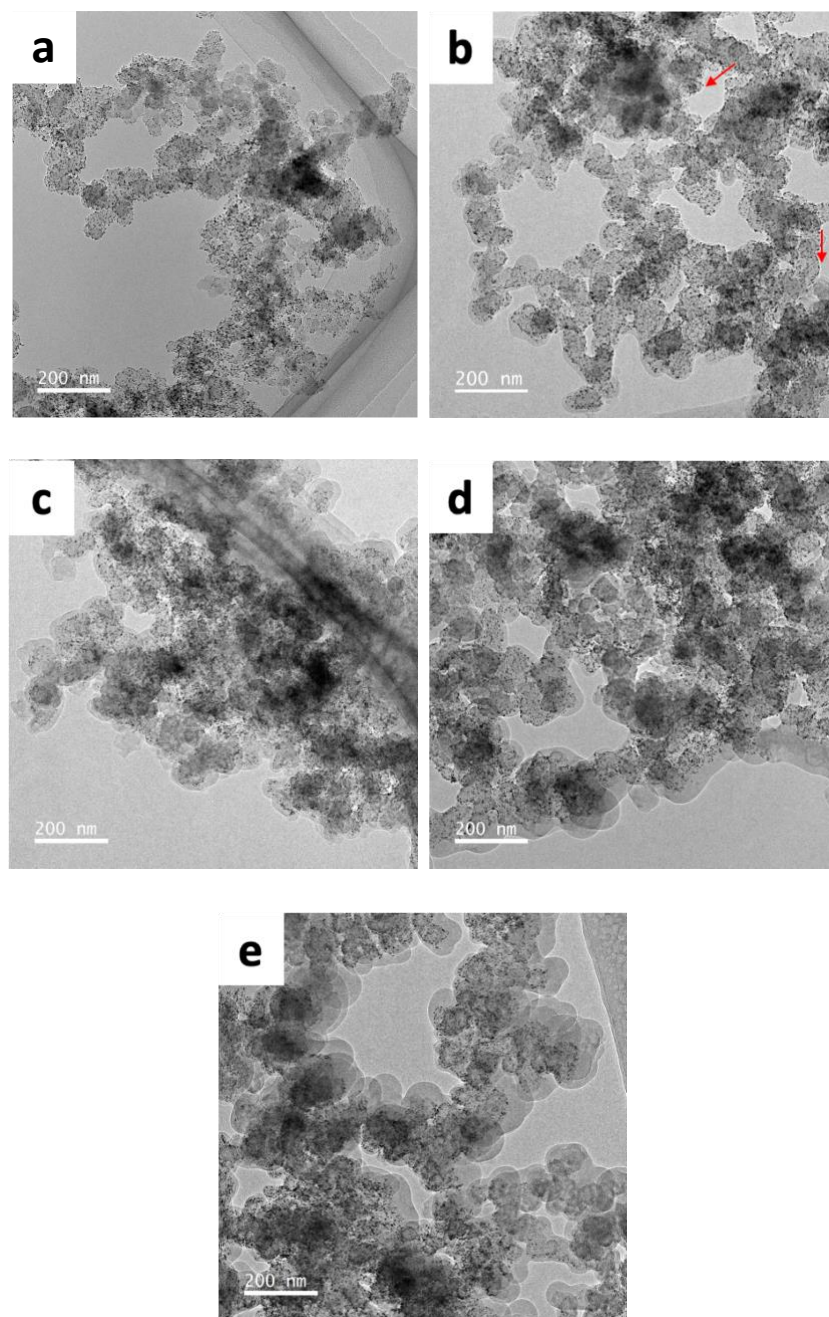


Figure 3. Cryo-transmission electron microscope (cryo-TEM) images of Pd core Pt shell catalyst at various I/C ratios ink. I/C = (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.5 and (e) 1.0.

Red arrows in (b) indicate the exposed surface of the catalyst.

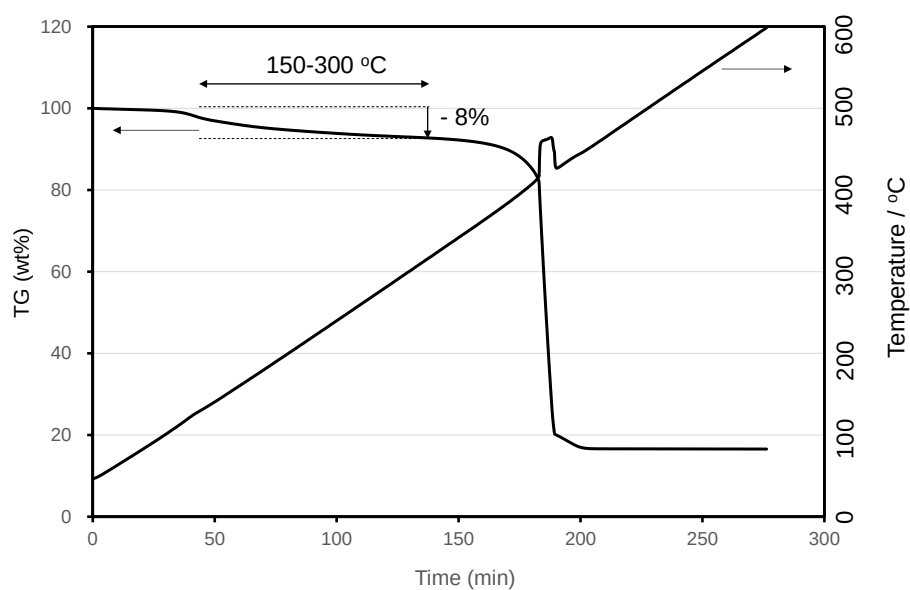
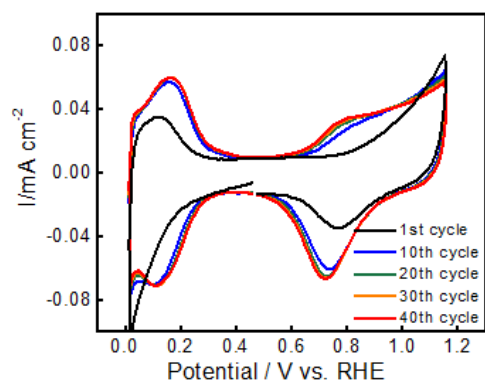
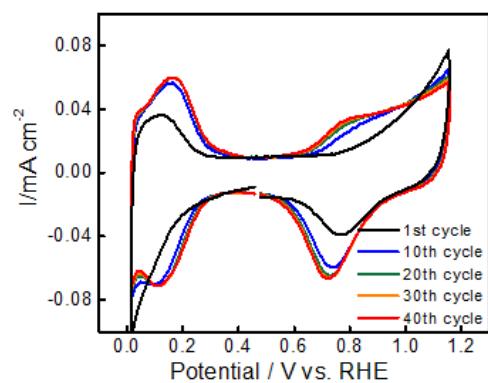


Figure 4. TG (Thermo-gravimetry) curves of carbon supported Pd core Pt shell catalyst after calcination at 300 °C for 30 min.

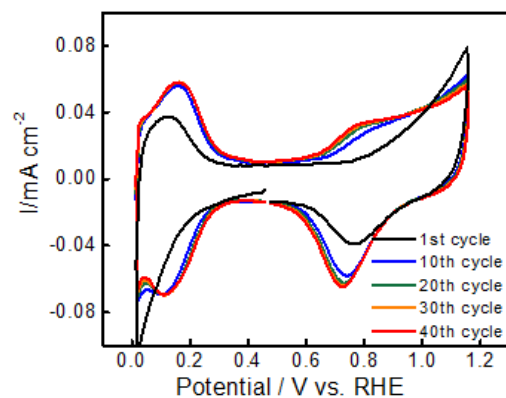
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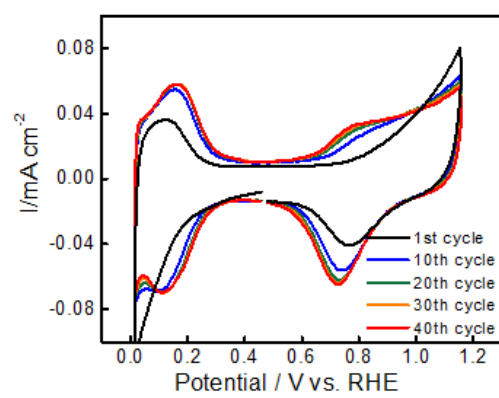
b



c



d



e

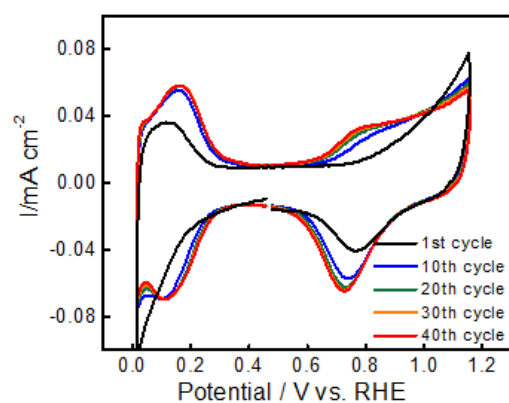


Figure 5. Cleaning CV from 1st to 40th cycles (a) $I/C = 0.0$, (b) $I/C = 0.10$, (c) $I/C =$

0.20, (d) $I/C = 0.50$, (e) $I/C = 1.0$

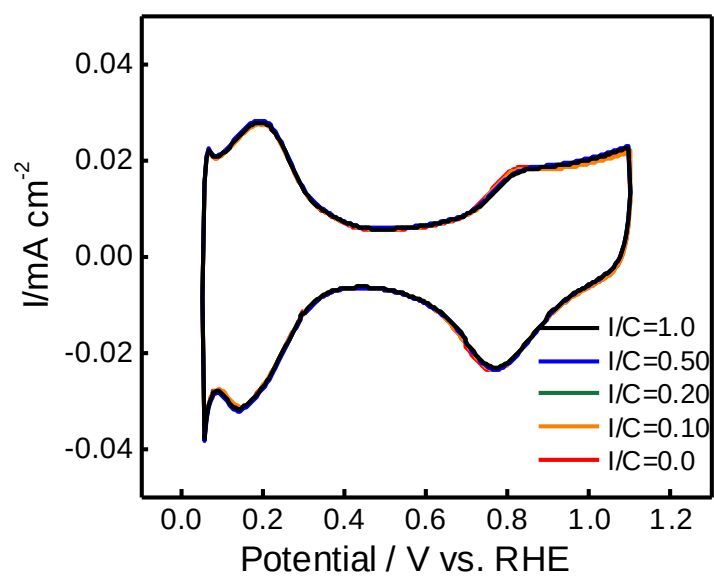


Figure 6. Cyclic voltammogram for Pd core-Pt shell catalyst with varying I/C ratios.

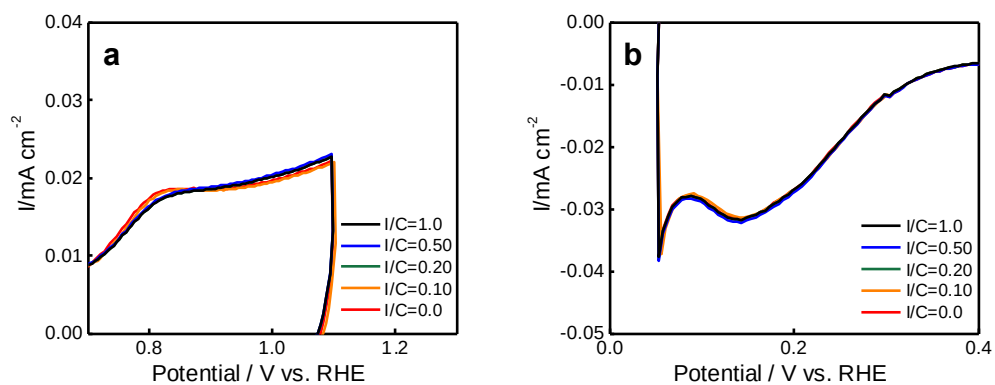


Figure 7. Cyclic voltammogram for Pd core-Pt shell catalyst with varying I/C ratios, enlarged in oxide formation region (a) and H_{UPD} region and (b).

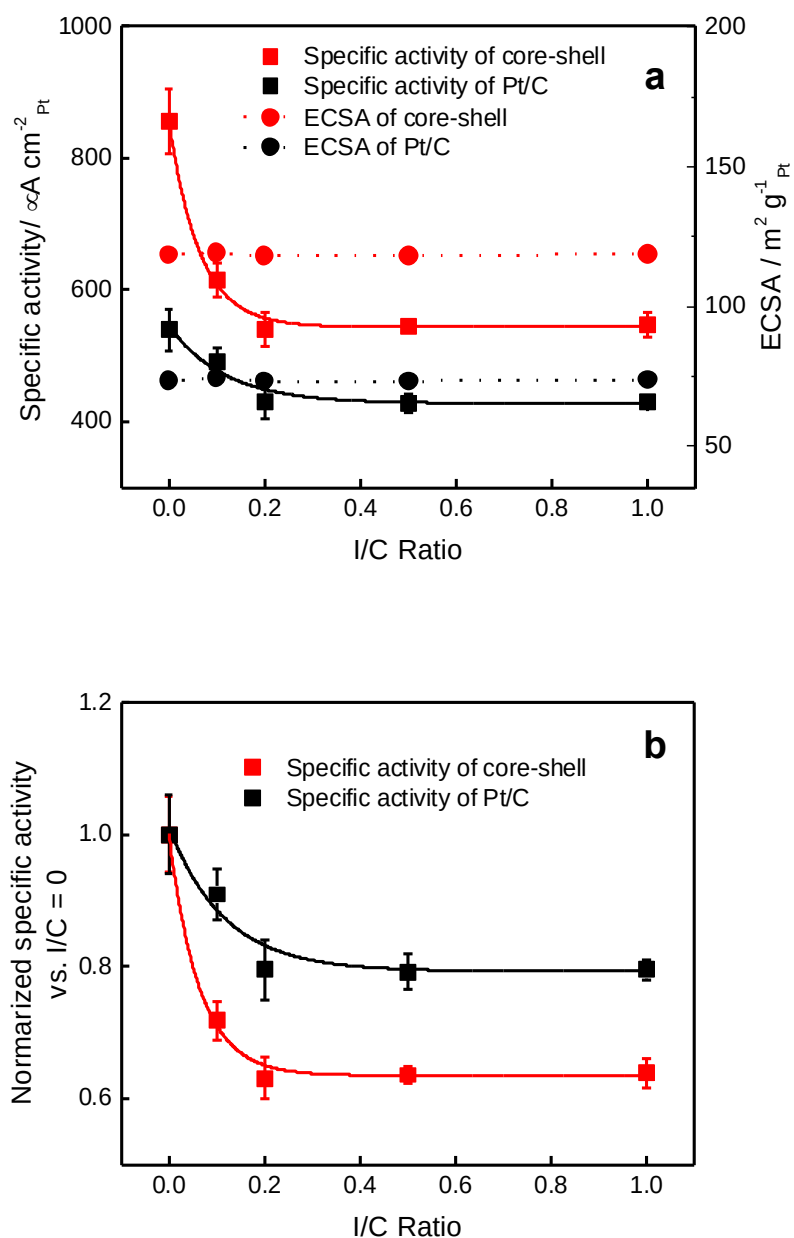


Figure 8. (a) Influence of I/C ratio on the ECSA, specific activity at 0.9 V vs RHE, and (b) normalized specific activity based on I / C = 0 of Pd core-Pt shell catalyst and Pt/C (TEC10V30E)³⁹.

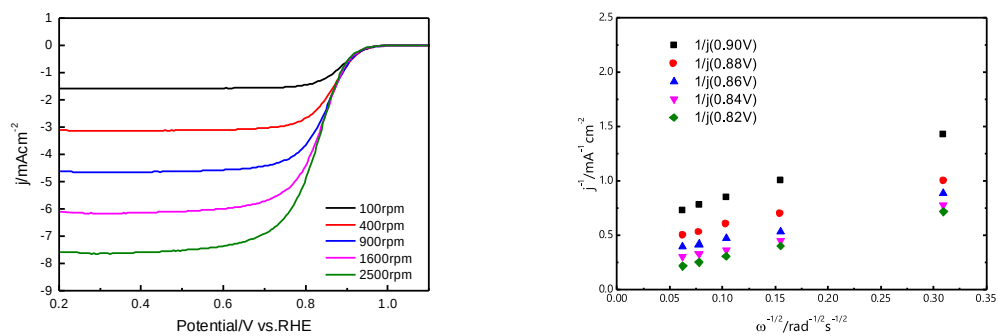


Figure 9. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pd core-Pt shell catalyst with $I/C=0.0$.

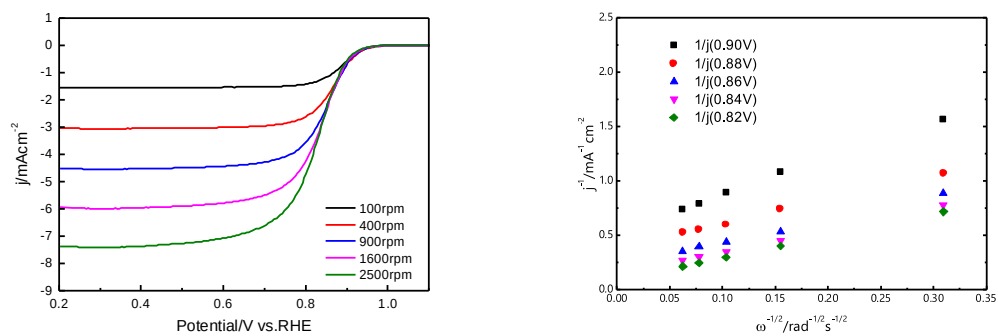


Figure 10. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pd core-Pt shell catalyst with $I/C=0.1$.

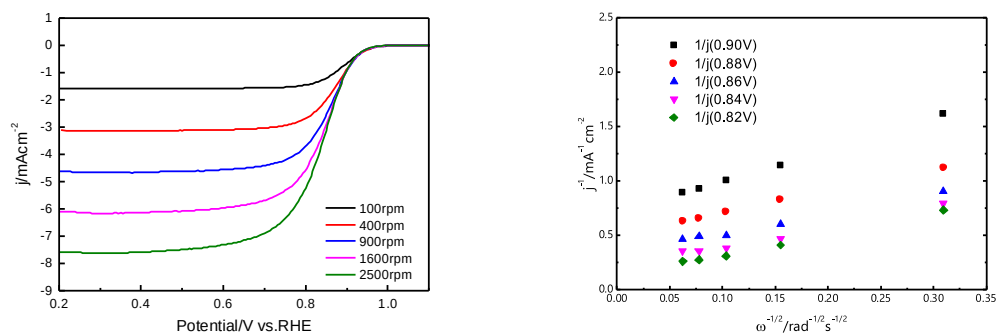


Figure 11. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pd core-Pt shell catalyst with $I/C=0.2$.

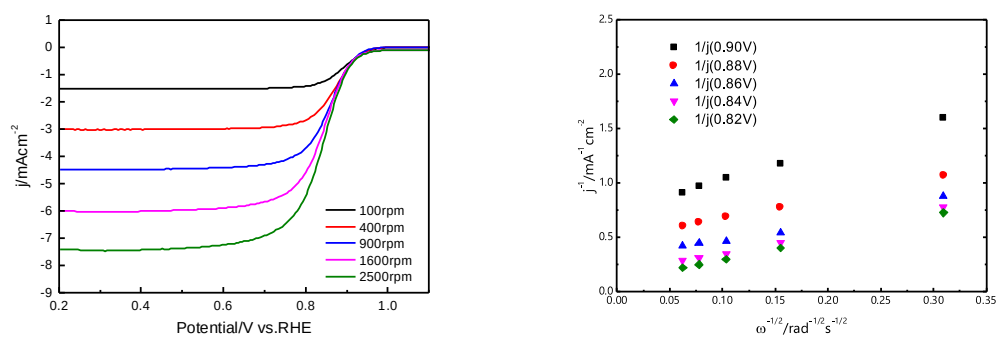


Figure 12. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pd core-Pt shell catalyst with $I/C=0.5$.

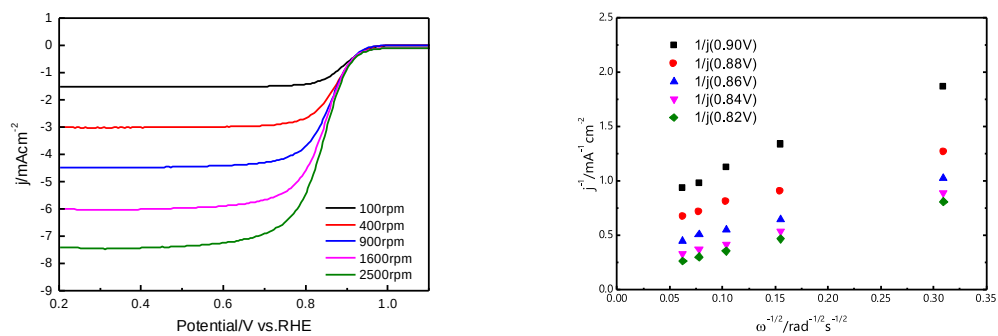


Figure 13. Linear sweep voltammogram (left) and Koutecky-Levich plot (right) for Pd core-Pt shell catalyst with $I/C=1.0$.

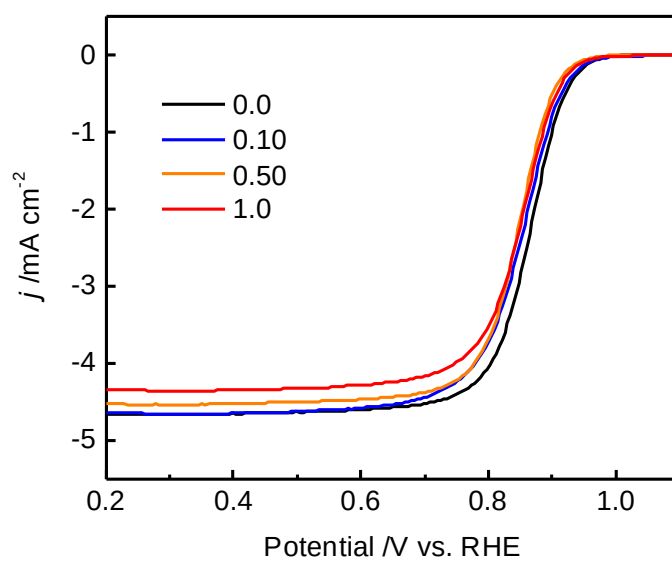


Figure 14. I/C dependence of liner sweep voltammogram for Pd core-Pt shell catalysts at 900 rpm.

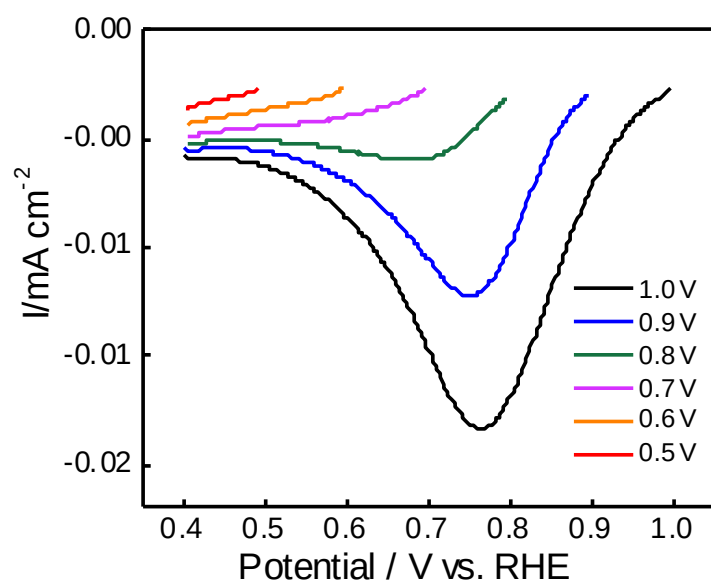


Figure 15. Reduction current profiles of oxide species on Pd core-Pt shell catalyst with I/C=1.0 (0.50 -1.0 V (vs. RHE) indicates holding potential).

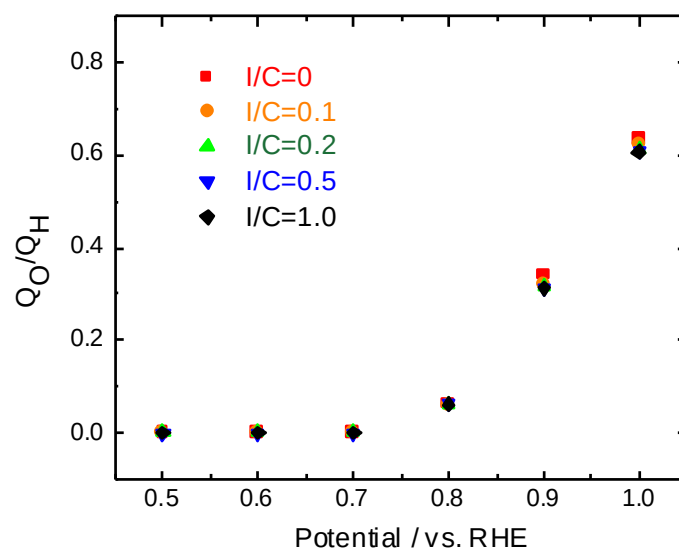


Figure 16. Dependence of I/C ratio on the oxygen coverage for Pd core-Pt shell catalyst.

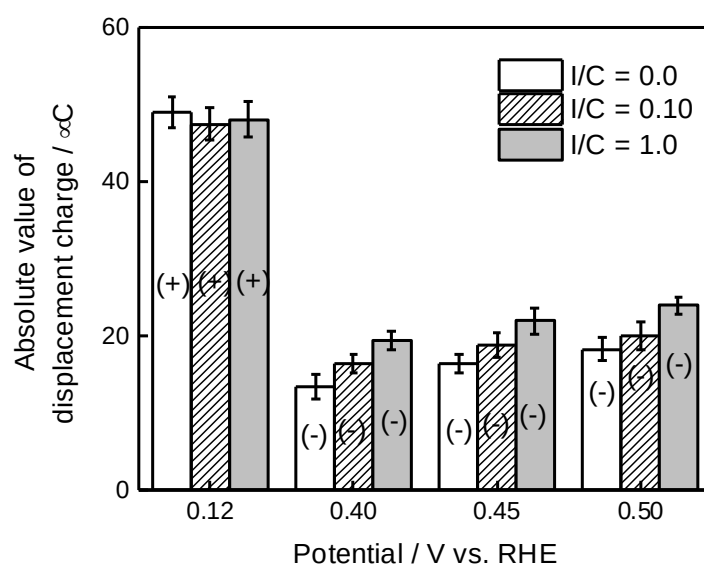


Figure 17. Absolute value of CO displacement charge as a function of measurement potential for Pd core-Pt shell catalyst with I/C = 0.0, 0.10 and 1.0. (+)/(-) indicates the polarity of the CO displacement charge.

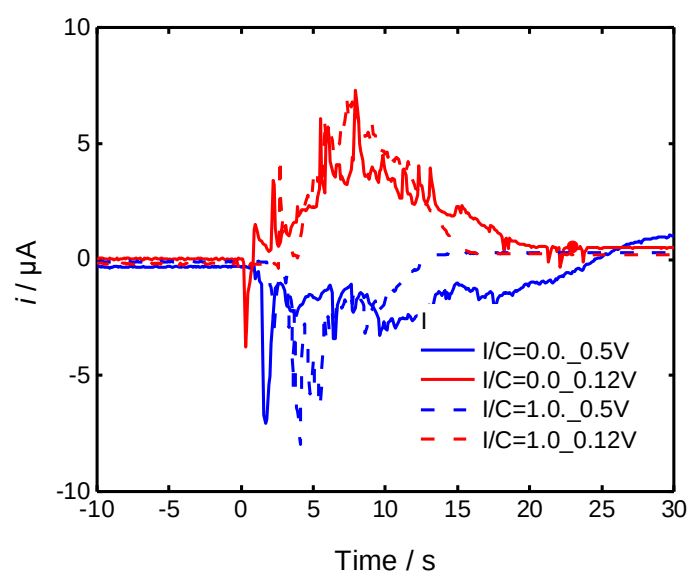


Figure 18. Current-time response of CO displacement charge experiments for Pd core-Pt shell catalyst.

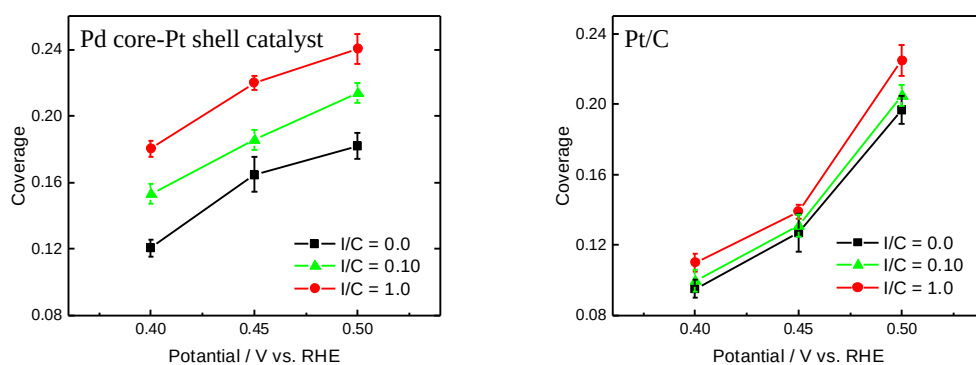


Figure 19. Effects of ionomer on anion coverage for Pd core-Pt shell catalyst and Pt/C catalyst at various potentials.

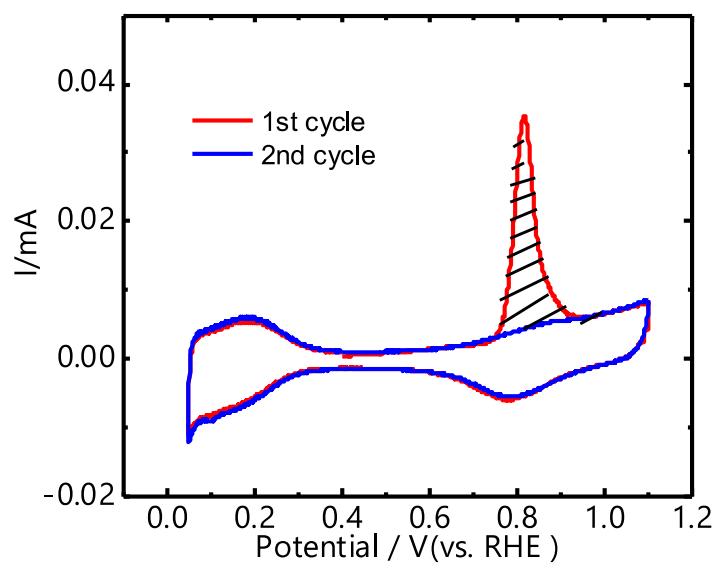


Figure 20 CO stripping voltammogram of Pd cpre-Pt shell catalyst for $I/C=0.0$.

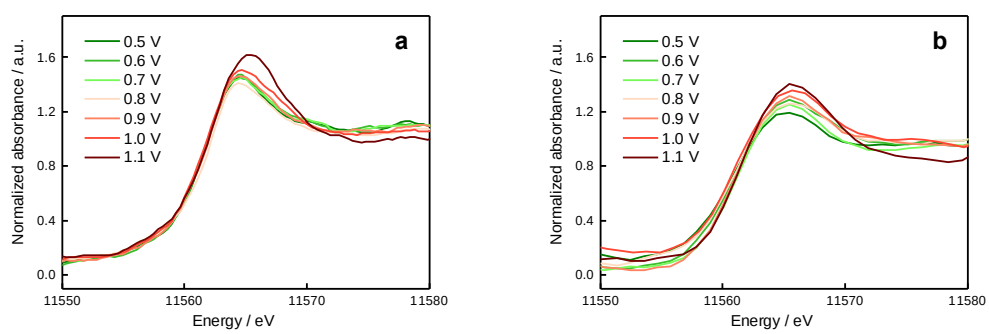


Figure 21. XANES spectra for Pt L_{III}-edge I/C = 1.0 (a) and I/C = 0.0 (b).

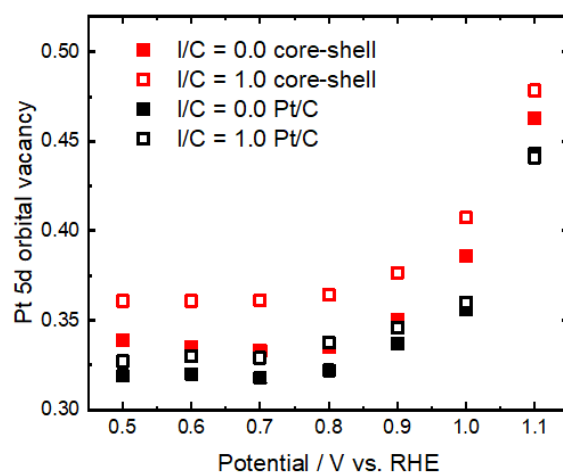


Figure 22. Change in 5d orbital vacancy of Pd core-Pt shell and Pt/C (TEC10V30E)³⁹ catalysts with I/C = 0.0 and 1.0 from 0.50 to 1.1 V (vs. RHE).

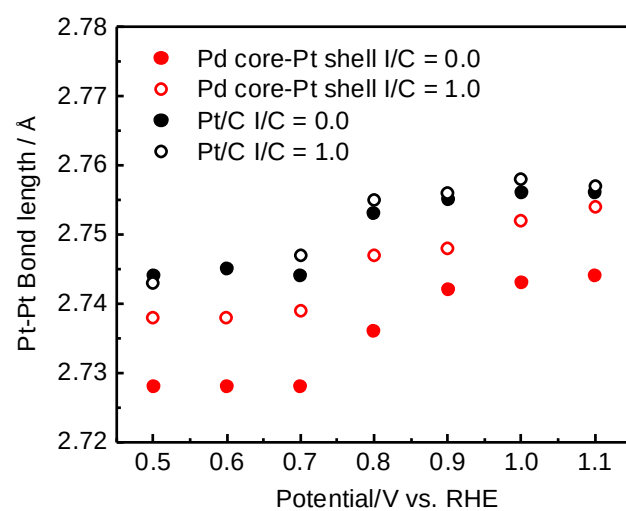


Figure 23. Pt-Pt bond distance change of Pd core-Pt shell catalysts and Pt/C catalysts with I/C = 0.0 and 1.0 from 0.50 to 1.1 V (vs. RHE).

Chapter 5. *operando* X-ray absorption spectroscopic study for specific absorption of ionomer on porous carbon supported platinum catalyst

5.1 Introduction

Polymer electrolyte fuel cells (PEFCs) are considered as important roles in the future hydrogen energy system, which is a highly expected way to solve energy storage and sustainable development of the world energy economic^{1,2}. The hydrogen energy system could replace the traditional fossil fuels and PEFCs are key devices to converse hydrogen energy to the electrical energy. Thanks to the employment of polymer electrolyte in PEFCs, they could be applied on small-scale power sources especially popular on the fuel cell vehicles (FCVs)³⁻⁷. Even though the PEFCs is already applied in some fields, the cost of PEFCs is still relatively high which is a major reason the prevent the wide-used of PEFCs products include FCVs which considered as one of the main devices to introduce the hydrogen energy to the world. Noble metals catalysts use on the anode and cathode accounts over 50% cost of PEFCs⁸ and it is important to reduce the usage and cost of catalysts. The Pt catalyst on the cathode take part in the oxygen reduction reaction (ORR) is relatively inefficient reaction kinetics and also influenced by the strong acid conditions and lead degradation effect⁹⁻¹¹. Therefore, cathode catalyst with high performance, durability and less cost is expected for the wide application of the PEFCs.

It is well known that the specific adsorption of anionic species on the Pt based catalyst surface is on of the reasons to prevent the ORR activity on the cathode¹¹. As a type of perfluorosulfonic acid ionomers, Nafion[®] usually employed in the catalyst layer of PEFCs, providing a pathway for ionic among the catalyst particles and enhance the ORR activity^{12,13}. The ORR activity inhibition effect of (bi)sulfate anion in the sulfuric acid solution has been observed on the Pt (111) and Pt (110) single crystals, and the same tendency has been found on the Nafion[®] capped Pt (111) and Pt (110) surface in the nonadsorbing supporting electrolyte (0.1M HClO₄)¹⁴. Similar results also found in Pt/C nanoparticle catalysts ink mix with Nafion on various type of supporting carbon¹⁵⁻¹⁸. These reports suggested that the less ORR activity in Pt-based catalyst capped with Nafion[®] could be respond by specific adsorption of sulfo group anion from the side

chain of Nafion[®], lead the active sites block on the Pt surface. The supporting carbon of Pt/C nanoparticle catalysts have surly influence the specific adsorption effect from Nafion[®] on the Pt surface and the ORR activity of the catalysts. Shinozaki et al. have evaluated the influence of the Pt-based catalyst ORR activity from various supporting carbon with different Nafion[®] contents¹⁸. The catalysts with high surface area carbon supporting suffer less activity loss with increasing Nafion[®] contents and this phenomenon can be observed in both Pt/C and Pt-based alloy/C catalysts. These results indicate that the Pt-based nanoparticles located in the pores of high surface area carbon could isolated from the ionomer coverage and save more active sites for ORR. Kamitaka et al. synthesized Mg-O templated mesoporous carbon CNovel[®] with various size microporous (3.5nm, 5.0nm and 10.0nm) as the supporting carbon for Pt/C nanoparticle catalysts¹⁵, found the Pt/C catalysts with mesoporous carbon CNovel[®] possess higher specific activity in MEA (membrane electrode assembly) than the Pt/C catalyst with non-porous supporting carbon, Vulcan[®]. Pt/CNovel[®] with various size microporous shows relatively less sulfonic adsorption in MEA at 0.4V compared with Pt/Vulcan[®]. Tough, there still less studies about the quantitatively specific activity change with various ionomer content on different size porous Pt/CNovel[®] and specific adsorption evaluation at higher potential region include where ORR occurs (0.45V-0.9V vs. RHE).

CO displacement charge measurement is a method to evaluate the specific adsorption quantitatively in common situation, through the introducing of CO gas during a constant potential holding. Oxidation or reduction currents would be rise during the displacement of adsorbing species by CO, and the coverage of ionomer could be evaluated through the different change of CO displacement charge¹⁹⁻²². The successful quantitatively evaluation of the coverage of ionomer on Pt catalyst through CO displacement method has been reported²³, but this method still remain limitation. The CO molecules adsorbed on the Pt surface would be oxidized around 0.6V. vs RHE (reversible hydrogen electrode), the anion adsorption situation of Pt-based catalyst only has been evaluated from 0.08V to 0.56V in previous reports¹⁹⁻²⁴.

operando XAS (X-ray absorption spectroscopy) is reliable tool on evaluating the electronic status and detail structure on of the Pt catalysts^{25, 26} as well as observing the specific adsorption on the Pt surface. The sulfonic adsorption on the single crystal Pt (111) electrode surfaces in H₂SO₄ solution has been observed through the combination

of X-ray absorption near edge structure (XANES) and full-multiple scattering calculations using the FEFF8 code²⁷⁻²⁹. Chapter 3 and chapter 4 have already achieved the evaluation of specific adsorption in the high potential region include ORR active potential (0.9V vs. RHE) by *operando* XAS measurements, which cannot be measured by the CO displacement method. The quantitative detection of the specific adsorption was reported under the ORR potential by measuring Pt 5d orbital vacancy of the Pt/C catalyst using *operando* XAS³⁰. However, there are still less report about the effect of porous supporting carbon towards the electronic structure and specific adsorption of the catalysts.

In this study, the oxygen reduction reaction activities of Pt/C catalysts with different size microporous supporting carbon and various ionomer/carbon (I/C) ratios (I/C = 0.0, 0.1, 0.2, 1.0) has been evaluated. The oxide species adsorption evaluated on the Pt surface at various potential ranges have been discussed and speculate the effect of specific adsorption from ionomer. CO stripping voltammetry measurements and the analysis of 5d orbital vacancy have been carried out for quantitative evaluation of specific adsorption on the catalysts with various I/C ratios.

5.2 Experimental Methods

5.2.1 Electrochemical measurements

Pt/C catalyst supported by porous carbon CNovel[®] with 3.5nm, 5.0nm and 10nm diameter microporous has been prepared and will be described as Pt/(3.5nm)CNovel[®], Pt/(5.0nm)CNovel[®] and Pt/(10.0nm)CNovel[®]. The catalyst ink contained ultrapure water (Milli-Q[®], Millipore A/S, United States, electrical resistivity of 18.2 MΩ·cm or more) and 2-propanal in 1:4 ratio (99.99%, FUJIFILM Wako Pure Chemical Corporation, Japan), and the amount of Pt/C was adjusted to form a 20 μg_{carbon} cm⁻² catalyst layer after dropping 5 μL on a glassy carbon RDE (GC RDE, HOKUTO DENKO, Japan; 0.196 cm² area). The ink on the RDE was dried at 700 rpm at room temperature. Nafion[®] solution (5 wt.%, Sigma-Aldrich Co. LLC, Japan) was employed to prepare Pt/C catalyst ink with I/C ranging from 0.0 to 1.0. The high purity HClO₄ (Kanto Chemical Co., Inc, Japan, purity: 60.0 wt%) was adopted to prepare the 0.1M HClO₄ electrolyte.

ORR activity measurements were carried out in a three-electrode cell at 25 °C. The counter electrode was a Pt mesh, and the reference electrode was reversible hydrogen

electrode (RHE). The RHE is prepared by immersing a Pt wire in the electrolyte in a glass tube equipped with inlet and outlet ports for H₂ gas. The RHE is inserted in the main electrochemical cell. Before activity measurements, 50 cycles between 0.02 and 1.1 V (vs. RHE) potential with 200 mVs⁻¹ to obtain a stable cyclic voltammogram (CV) in N₂-saturated 0.1 M HClO₄. The final CV was obtained at 50 mVs⁻¹. After the CV measurements, the electrolyte was saturated with O₂. Linear sweep voltammetry was obtained between 0.2 and 1.2 V vs. RHE at 10 mVs⁻¹ from 100 to 2500 rpm. The oxygen reduction data for all the catalysts were analyzed according to Koutechy-Levich equation. The coverage of oxide species was measured by linear sweep voltammetry in N₂-saturated 0.1 M HClO₄. The potential first swept from 0.4 V (vs. RHE) to the holding potential (0.5 - 1.1 V vs. RHE) at 50 mV·s⁻¹, and then the potential was maintained for approximately 5 min to obtain a stable current. Finally, the potential was again set to 0.4 V (vs. RHE). The integrated cathodic current was used to estimate the charge of oxide species based on the following reaction (Pt-OH + H⁺ + e⁻ → Pt + H₂O) also reports from other researchers^{31,32}. The coverage of oxide species was estimated through dividing the charge of oxide species by the underpotential deposition charge of hydrogen^{31,32}.

CO stripping voltammetry measurements were evaluated in the same three-electrode cell at 25 °C. The 50 cycles potential between 0.02 and 1.0 V (vs. RHE) at 200 mVs⁻¹. The final CV was obtained with 50 mVs⁻¹. Then, the potential was held at 0.12-0.5 V (vs. RHE), until a stable current was obtained. After that, the CO gas (99.9%, GL Sciences Inc.) bubbling to the electrolyte for about 20 s to obtain a stable current, indicating complete CO absorption. The bubbling gas was switched to N₂ for 40 min for CO deaeration. Finally, CO stripping voltammetry was initiated in the range from 0.02 to 1.0 V (vs. RHE). The coverage of anions was estimated through integrating CO exchange current divided by CO stripping charge.

5.2.2 *operando* XAS measurements

operando XAS measurements for Pt L_{III}-edge of Pd core-Pt shell/C catalysts were carried out in fluorescence mode using synchrotron radiation at BL37XU of SPring-8, Hyogo, Japan. A pair of Si (111) monochromators and a total-reflection Pt mirror (4 mrad) were used to obtain collimated and monochromatic X-rays. Prior to the experiments, the samples were electrochemically cleaned by CV in the range 0.0–1.1.

V (vs. RHE). The electrode potential was swept cathodically from 0.5 to 1.1 V (vs. RHE). Data were analyzed using ATHENA and ARTEMIS, a suite of the IFEFFIT software programs³³.

5.3 Results and discussions

5.3.1 Electrochemical measurements

Figure 1a-c shows the cyclic voltammetry curves of Pt/C catalysts with different size microporous supporting carbon and employed I/C ratios from 0 to 1.0. There is slight peak shift to higher potential with increasing I/C ratios about onset potential of oxide formation region in Figure 1a and 1c, indicated that ionomer possess slight influence on CV curves towards Pt/(3.5nm)CNovel[®] and Pt/(10.0nm)CNovel[®]. At the same time, there is less observable peak shift in oxide formation region in Figure 1b, represent that the ionomer has less effect to the Pt/(5.0nm)CNovel[®]. Here we estimate that the Pt/(3.5nm)CNovel[®] is hard to take part in the electrochemistry reaction through narrow pathways from the pores and only Pt on the surface of carbon could occur the reaction. On the other side, Pt nanoparticles in 10.0nm micropores could take part in electrochemistry reaction but also could suffer effect from ionomer at the same time. Here we indicate that the Pt nanoparticles in 5.0nm microporous could take part in the reaction and prevent the ionomer adsorption at the same time. These results are consistent to the report from Shinozaki et al¹⁸., showed low surface area carbon supported Pt/C catalysts have observable onset potential shift in oxide formation region while the high surface area carbon have less peak shift at the same time. Zhu et al³⁴. also reported that the CV curves of Pt/C with higher surface area carbon have no obvious change with increasing I/C ratios, come to an agreement with our results.

However, it is hard to do further discussion about the ionomer effect only by the cyclic voltammetry curves. Figure 2a shows the specific activity change of Pt/C catalysts on various supporting carbon with increasing I/C ratios and liner sweep voltammogram for Pt/C catalysts with various supporting carbon at 900rpm with 1.0 I/C ratios were showed in Figure 3. It is easy to find the activity of all kinds of catalysts decrease with increasing I/C ratios which could be responded by specific adsorption from ionomer. To investigate the activity dependence on I/C ratio and supported carbon further, the specific activity values were normalized using the value at I/C = 0 for each catalyst as shown in Figure 2b. The Pt/C catalyst on 5.0nm remains about 84% specific

activity at $I/C = 1.0$ compared with the activity at $I/C = 0$, while other catalysts only remained 73%~75% specific activity at the same condition. These results are come to similar tendency with other reports^{18,30}, indicated that 5.0nm micropores have better features to prevent the specific adsorption from ionomer and suffer less activity loss of Pt catalyst and reach an agreement with results from Figure 1.

Oxygen coverage of the Pt/C catalysts with various supporting carbon have been evaluated to clarify the change of the oxide species adsorption in various I/C ratios and the role in the changing ORR activity. The oxygen coverage of Pt catalysts increased with rising potentials showed in Figure 4. Pt/C catalysts with all kinds of supported carbon showed almost same oxygen coverage at each potential with various I/C ratios, indicate that oxide species adsorption have no obvious change with increasing ionomer contents, while ORR activity decreased at the same time. The oxygen coverage also have no obvious change among Pt/C catalysts on different supported carbon, means the Pt nanoparticles which could take part in the electrochemical reaction suffered almost same oxide species adsorption at the same condition and did not effected by the change of I/C ratios. These results indicated that the oxide species have not effected by changing I/C ratios and the specific adsorption from ionomer could be the main reason of the changing ORR activity. The supporting carbon influenced the specific adsorption from ionomer and effect the ORR activity of Pt/C catalysts at the same time.

To quantitatively evaluate the specific adsorption species on the Pt catalysts with various size microporous supporting carbon, CO stripping voltammetry has been adopted to measuring the displacement charge about adsorption species and CO molecule. The charge of Pt-H at 0.12V (vs. RHE) and adsorption species on Pt surface at 0.4V to 0.5V (vs. RHE) at I/C ratio = 0.0, 1.0 were showed in Figure 5. The CO displacement charge change from 0.4V to 0.5V (vs. RHE) at $I/C = 1.0$ of Pt/C catalysts with Pt/(3.5nm)CNovel[®] and Pt/(10.0nm)CNovel[®] is relatively higher than that at $I/C = 0.0$, indicated the increasing adsorption species while ionomer present in the catalysts ink, which close to the results from other reports^{30, 35-37}. On the other side, the CO displacement charge change from I/C 0.0 to 1.0 is obviously less in Pt/C catalyst with 5.0nm microporous supporting carbon showed in Figure 5b, compared with the Pt/(3.5nm)CNovel[®] and Pt/(10.0nm)CNovel[®] in Figure 5a and 5c. This phenomenon shows that the 5.0nm microporous supporting carbon lead less specific adsorption on the surface of Pt catalyst from ionomer. The anion coverage calculated through $2*(CO$

displacement charge)/(CO stripping charge) showed in Figure 6. The anion coverage at 0.4V (vs. RHE) without ionomer are all close to 0.1. which consist to other report³⁰. At 0.5V (vs. RHE), the anion coverage have around 0.06 increase from I/C 0.0 to 1.0 for Pt/C catalysts with Pt/(3.5nm)CNovel[®], showed similar tendency with Garrick et al.³⁶, while Pt/(5.0nm)CNovel[®] has 0.02 increase and 10.0nm has 0.05 increase. Compared to our previous reported anion coverage of Pt/Vulcan[®] catalyst with various I/C ratios³⁰, Pt/(3.5nm)CNovel[®] and Pt/(10.0nm)CNovel[®] possess similar anion coverage increase from I/C 0.0 to 1.0 at 0.5V (vs. RHE), while Pt/(5.0nm)CNovel[®] show obvious less anion coverage, means it suffer less specific adsorption from ionomer, compared with Pt/ Vulcan[®] and Pt/(3.5nm, 10.0nm)CNovel[®] catalysts. This result shows the reason why Pt/(5.0nm)CNovel[®] could remain more specific activity compared with other Pt/C catalysts, based on the less specific adsorption from ionomer.

5.3.2 *operando* XAS measurements.

Through the studies above, 5.0nm microporous CNovel[®] considered as one of the useful way to obtain less specific adsorption from ionomer and loss less specific activity at high ionomer contents at 0.5V (vs. RHE). To observe the adsorption species in the high potential region, at least the ORR occurred (0.6V~1.1V vs. RHE), *operando* XAS measurements were conducted and the 5d orbital vacancies in Pt which could present the electronic statement of Pt atoms was calculated from the XANES spectra of Pt L_{III}-edge and L_{II}-edge. In this study, the number of 5d orbital vacancies in Pt from Pt/(3.5nm)CNovel[®] and Pt/(5.0nm)CNovel[®] was calculated from the XANES spectra of Pt L_{III}-edge and L_{II}-edge (Figure 7 and 8), based on the method from Mansour et al.³⁸. The 5d orbital vacancies of the catalysts with I/C = 0.0 and 1.0 are shown in Figure 9 and the difference between I/C = 0.0 and 1.0 were calculated in Figure 10.

The 5d orbital vacancies increase with higher potentials in both samples, which shows the tendency of Pt-O bond formation and more oxide species adsorbed on the surface of Pt, which come an agreement with the result of oxygen coverage. The specific adsorption of ionomer is similar with the oxide species adsorption, also has influence on the electronic statement of the Pt atoms and lead the increase of the 5d orbital vacancies. Through the Figure 10, calculate the 5d orbital vacancies difference between I/C = 0.0 and 1.0, there is obviously gap between them at 0.9V (vs. RHE) where oxygen reduction reaction occurs, also in the lower (0.5-0.8V vs. RHE) and

higher (1.0-1.1V vs. RHE) potential region. Compare with the 5d orbital vacancies gap from $I/C = 0.0$ and 1.0 in Pt/(3.5nm)CNovel[®] and Pt/(5.0nm)CNovel[®], there are obvious difference can be observed. The increased 5d orbital vacancies gap is more in Pt/(3.5nm)CNovel[®] than Pt/(5.0nm)CNovel[®] in all potential regions and we can evaluate that the Pt/(5.0nm)CNovel[®] suffer about half specific adsorption from ionomer compared with Pt/(3.5nm)CNovel[®], come to an agreement with the CO displacement charge results. As we estimated, the Pt nanoparticles in 5.0nm microporous suffer less specific adsorption for the reason of less Nafion[®] molecular could get in to the 5.0nm microporous and adsorb on the Pt nanoparticles. In the case of 3.5nm microporous supporting carbon, might less Pt nanoparticles exist in the microporous, cause the 5d orbital vacancies gap from I/C 0.0 to 1.0 are more than 5.0nm one. The 5d orbital vacancies gap of Pt/(3.5nm)CNovel[®] are smaller that Pt/Vulcan[®] in our previous study³⁰, also consist with the estimate. At the same time, the over narrow 3.5nm microporous lead the slow material transport on the Pt nanoparticles and contribute less activities even though they are suffer less specific adsorption from ionomer.

5.4 Conclusion

In this study, the influence of ionomer about the oxygen reduction reaction activity of Pt/C catalyst with various size micropores supporting carbon has been investigated. The specific activity decreased with increasing ionomer content but Pt/C catalysts on 5.0nm microporous supported carbon suffer less ORR activity loss compared with Pt/C catalysts on other supporting carbons. Oxygen coverage evaluation indicated that the oxide species adsorption have no obvious change at various I/C ratios and various supporting carbons, which proved that the oxide species is not responsible to the decreased activity with increasing I/C ratios and also the different level of activity loss of Pt/C catalysts in various supported carbon. CO displacement charge at 0.4-0.5V change from $I/C = 0.0$ to 1.0 indicated that the specific adsorption from ionomer increase with higher ionomer content and anion coverage shows Pt/C catalysts with 3.5nm and 10.0nm microporous supporting carbon suffer more specific adsorption from ionomer compares with Pt/C catalyst with 5.0nm microporous. 5d orbital vacancies shows less gap from $I/C = 0.0$ to 1.0 on Pt/C catalyst with 5.0nm microporous supporting carbon, compared with Pt/C catalyst with 3.5nm microporous supporting carbon, suggests the 5.0nm microporous could prevent more specific adsorption from

ionomer. These results suggested that the Pt nanoparticles in 3.5nm micropores is hard to take part in the oxygen reduction reaction through narrow pathways in the micropores and only Pt on the surface of carbon could occur the reaction. Pt nanoparticles in 10.0nm micropores could take part in the reaction but also could suffer effect from ionomer at the same time. The Pt nanoparticles in 5.0nm micropores which considered as relatively appropriate diameter could take part in the reaction and prevent the ionomer adsorption at the same time.

Polymer electrolyte fuel cells (PEFCs) are considered as important roles in the future hydrogen energy system, which is a highly expected way to solve energy storage and sustainable development of the world energy economic. The hydrogen energy system could replace the traditional fossil fuels and PEFCs are key device to converse hydrogen energy to the electrical energy. Thanks to the employment of polymer electrolyte in PEFCs, they could be applied on small-scale power sources especially popular on the fuel cell vehicles (FCVs)¹⁻⁵. Even though the PEFCs is already applied in some fields, the cost of PEFCs is still relatively high which is a major reason the prevent the wide-used of PEFCs products include FCVs which considered as one of the main devices to introduce the hydrogen energy to the world. Noble metals catalysts uses on the anode and cathode accounts over 50% cost of PEFCs⁶ and it is important to reduce the usage and cost of catalysts. The Pt catalyst on the cathode take part in the oxygen reduction reaction (ORR) is relatively inefficient reaction kinetics and also influenced by the strong acid conditions and lead degradation effect⁷⁻⁹. Therefore, cathode catalyst with high performance, durability and less cost is expected for the wide application of the PEFCs.

It is well known that the specific adsorption of anionic species on the Pt based catalyst surface is on of the reasons to prevent the ORR activity on the cathode⁹. As a type of perfluorosulfonic acid ionomers, Nafion[®] usually employed in the catalyst layer of PEFCs, providing a pathway for ionic among the catalyst particles and enhance the ORR activity^{10,11}. The ORR activity inhibition effect of (bi)sulfate anion in the sulfuric acid solution has been observed on the Pt (111) and Pt (110) single crystals, and the same tendency has been found on the Nafion[®] capped Pt (111) and Pt (110) surface in the nonadsorbing supporting electrolyte (0.1M HClO₄)¹². Similar results also found in Pt/C nanoparticle catalysts ink mix with Nafion on various type of supporting carbon¹³⁻¹⁶. These reports suggested that the less ORR activity in Pt-based catalyst capped with Nafion[®] could be respond by specific adsorption of sulfo group anion from the side chain of Nafion[®], lead the active sites block on the Pt surface. The supporting carbon of Pt/C nanoparticle catalysts have surly influence to the specific adsorption effect from Nafion[®] on the Pt surface and the ORR activity of the catalysts. Shinozaki et al. have evaluated the influence of the Pt-based catalyst ORR activity from various supporting carbon with different Nafion[®] contents¹⁶. The catalysts with high surface area carbon

supporting suffer less activity loss with increasing Nafion[®] contents and this phenomenon can be observed in both Pt/C and Pt-based alloy/C catalysts. These results indicate that the Pt-based nanoparticles located in the pores of high surface area carbon could be isolated from the ionomer coverage and save more active sites for ORR. Among these reports, there are still less studies about the effect of the size of micropores in the supporting carbon towards the specific adsorption effect from ionomer.

In this study, the oxygen reduction reaction activities of Pt/C catalysts with different size micropores supporting carbon and various ionomer/carbon (I/C) ratios (I/C = 0.0, 0.1, 0.2, 1.0) has been evaluated. The oxide species adsorption evaluated on the Pt surface at various potential ranges have been discussed and speculate the effect of specific adsorption from ionomer.

5.2 Experimental Methods

Pt/C catalyst supported by porous carbon with 3.5nm, 5.0nm and 10nm diameter micropores has been prepared. The catalyst ink contained ultrapure water (Milli-Q[®], Millipore A/S, United States, electrical resistivity of 18.2 MΩ·cm or more) and 2-propanal in 1:4 ratio (99.99%, FUJIFILM Wako Pure Chemical Corporation, Japan), and the amount of Pt/C was adjusted to form a 20 μg_{carbon} cm⁻² catalyst layer after dropping 5 μL on a glassy carbon RDE (GC RDE, HOKUTO DENKO, Japan; 0.196 cm² area). The ink on the RDE was dried at 700 rpm at room temperature. Nafion[®] solution (5 wt.%, Sigma-Aldrich Co. LLC, Japan) was employed to prepare Pt/C catalyst ink with I/C ranging from 0.0 to 1.0. The high purity HClO₄ (Kanto Chemical Co., Inc, Japan, purity: 60.0 wt%) was adopted to prepare the 0.1M HClO₄ electrolyte.

ORR activity measurements were carried out in a three-electrode cell at 25 °C. The counter electrode was a Pt mesh, and the reference electrode was reversible hydrogen electrode (RHE). The RHE is prepared by immersing a Pt wire in the electrolyte in a glass tube equipped with inlet and outlet ports for H₂ gas. The RHE is inserted in the main electrochemical cell. Before activity measurements, 50 cycles between 0.02 and 1.1 V (vs. RHE) potential with 200 mVs⁻¹ to obtain a stable cyclic voltammogram (CV) in N₂-saturated 0.1 M HClO₄. The final CV was obtained at 50 mVs⁻¹. After the CV measurements, the electrolyte was saturated with O₂. Linear sweep voltammetry was obtained between 0.2 and 1.2 V vs. RHE at 10 mVs⁻¹ from 100 to 2500 rpm. The oxygen reduction data for all the catalysts were analyzed according to Koutechy-Levich

equation. The coverage of oxide species was measured by linear sweep voltammetry in N₂-saturated 0.1 M HClO₄. The potential first swept from 0.4 V (vs. RHE) to the holding potential (0.5 - 1.1 V vs. RHE) at 50 mV·s⁻¹, and then the potential was maintained for approximately 5 min to obtain a stable current. Finally, the potential was again set to 0.4 V (vs. RHE). The integrated cathodic current was used to estimate the charge of oxide species based on the following reaction ($\text{Pt-OH} + \text{H}^+ + \text{e}^- \rightarrow \text{Pt} + \text{H}_2\text{O}$) also reports from other researchers^{17,18}. The coverage of oxide species was estimated through dividing the charge of oxide species by the underpotential deposition charge of hydrogen^{17,18}.

5.3 Results and discussions

Figure 1a-c shows the cyclic voltammetry curves of Pt/C catalysts with different supporting carbon and employed I/C ratios from 0 to 1.0. There is slight peak shift to higher potential with increasing I/C ratios about onset potential of oxide formation region in Figure 1a and 1c, indicated that ionomer possess slight influence on CV curves towards Pt/C catalysts with 3.5nm and 10.0nm diameter micropores supporting carbon. At the same time, there is no observable peak shift in oxide formation region in Figure 1b, represent that the ionomer has less effect to the Pt/C catalysts with 5.0 micropores supporting carbon. Here we estimate that the Pt nanoparticles in 3.5nm micropores is hard to take part in the electrochemistry reaction through narrow pathways from the pores and only Pt on the surface of carbon could occur the reaction. On the other side, Pt nanoparticles in 10.0nm micropores could take part in electrochemistry reaction but also could suffer effect from ionomer at the same time. Here we indicate that the Pt nanoparticles in 5.0nm micropores could take part in the reaction and prevent the ionomer adsorption at the same time. These results are consistent to the report from Shinozaki et al¹⁶., showed low surface area carbon supported Pt/C catalysts have observable onset potential shift in oxide formation region while the high surface area carbon have less peak shift at the same time. Zhu et al¹⁹. also reported that the CV curves of Pt/C with higher surface area carbon have no obvious change with increasing I/C ratios, come to an agreement with our results.

However, it is hard to do further discussion about the ionomer effect only by the cyclic voltammetry curves. Figure 2a shows the specific activity change of Pt/C catalysts on various supporting carbon with increasing I/C ratios and liner sweep

voltammogram for Pt/C catalysts with various supporting carbon at 900rpm with 1.0 I/C ratios were showed in Figure 3. It is easy to find the activity of all kinds of catalysts decrease with increasing I/C ratios which could be responded by specific adsorption from ionomer. To investigate the activity dependence on I/C ratio and supported carbon further, the specific activity values were normalized using the value at $I/C = 0$ for each catalyst as shown in Figure 2b. The Pt/C catalyst on 5.0nm remains about 84% specific activity at $I/C = 1.0$ compared with the activity at $I/C = 0$, while other catalysts only remained 73%~75% specific activity at the same condition. These results are come to similar tendency with other report¹⁶, indicated that 5.0nm micropores have better features to prevent the specific adsorption from ionomer and suffer less activity loss of Pt catalyst and reach an agreement with results from Figure 1.

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5.4 Conclusion

In this study, the influence of ionomer about the oxygen reduction reaction activity of Pt/C catalyst with various size micropores supporting carbon has been investigated. The specific activity decreased with increasing ionomer content but Pt/C catalysts on 5.0nm micropores supported carbon suffer less ORR activity loss compared with Pt/C catalysts on other supporting carbons. Oxygen coverage evaluation indicated that the oxide species adsorption have no obvious change at various I/C ratios and various

supporting carbons, which proved that the oxide species is not responsible to the decreased activity with increasing I/C ratios and also the different level of activity loss of Pt/C catalysts in various supported carbon. These results suggested that the Pt nanoparticles in 3.5nm micropores is hard to take part in the oxygen reduction reaction through narrow pathways in the micropores and only Pt on the surface of carbon could occur the reaction. Pt nanoparticles in 10.0nm micropores could take part in the reaction but also could suffer effect from ionomer at the same time. The Pt nanoparticles in 5.0nm micropores which considered as relatively appropriate diameter could take part in the reaction and prevent the ionomer adsorption at the same time.

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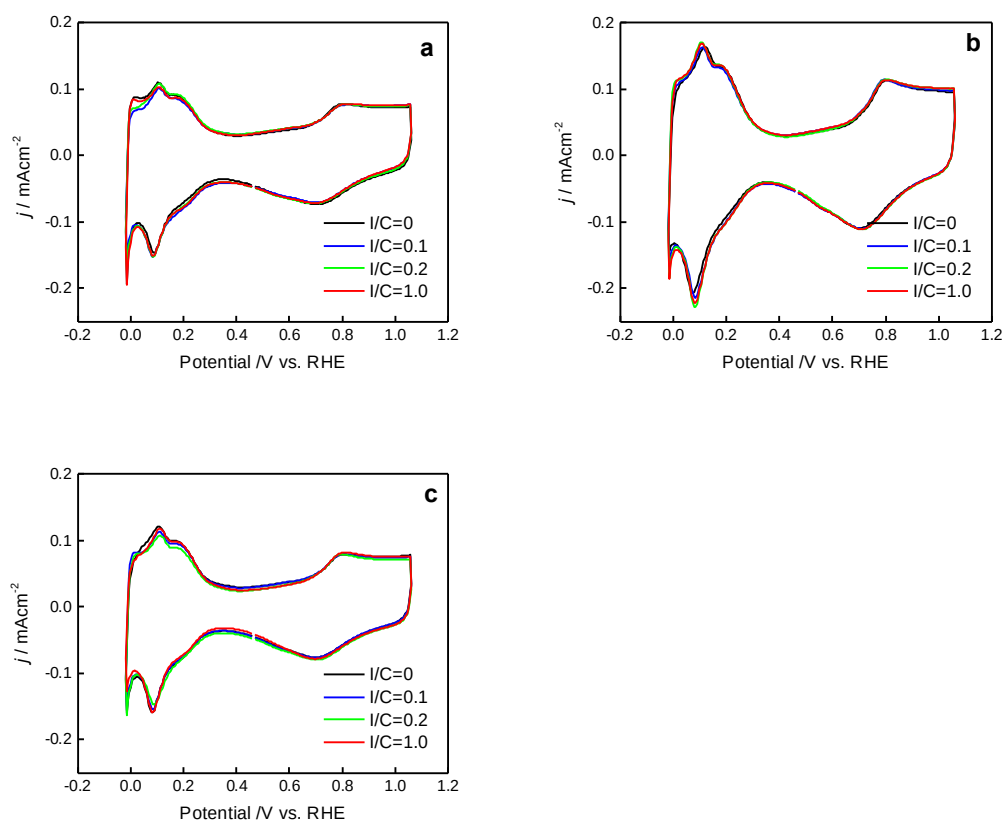


Figure 1. Cyclic voltammogram for Pt/C catalysts with varying I/C ratios on 3.5nm microporous (a), 5.0nm microporous (b) and 10.0 nm microporous (c) supporting carbon.

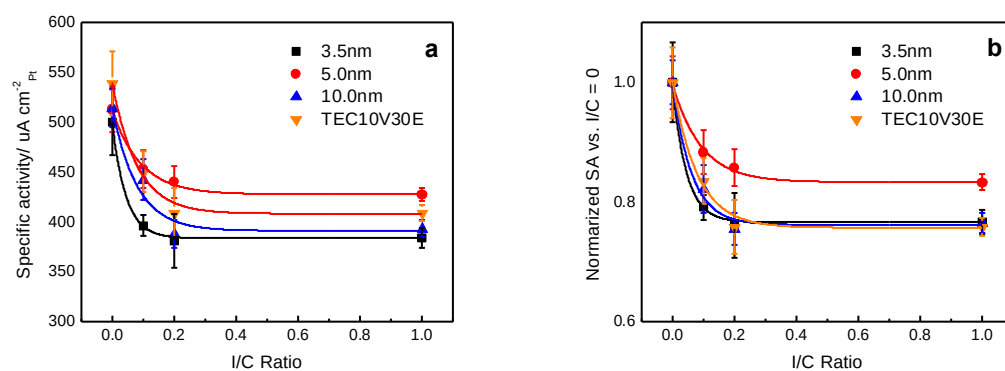


Figure 2. Influence of I/C ratio on the specific activity(a) and normalized specific activity (b) of Pt/C catalysts with various supporting carbon at 0.9 V vs RHE.

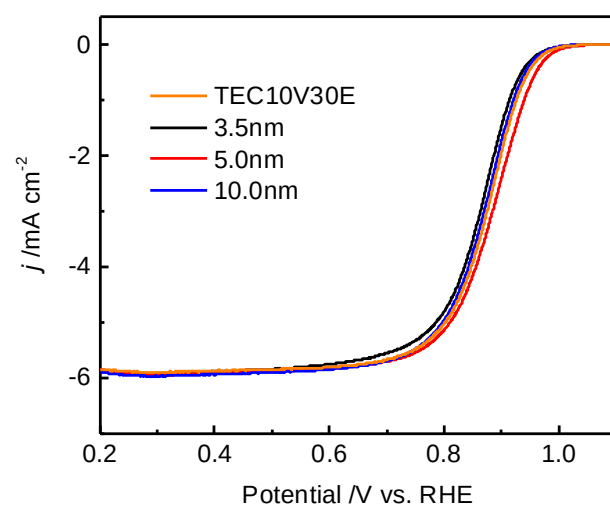


Figure 3. Linear sweep voltammogram for Pt/C catalysts with various supporting carbon at 1600rpm with 1.0 I/C ratios.

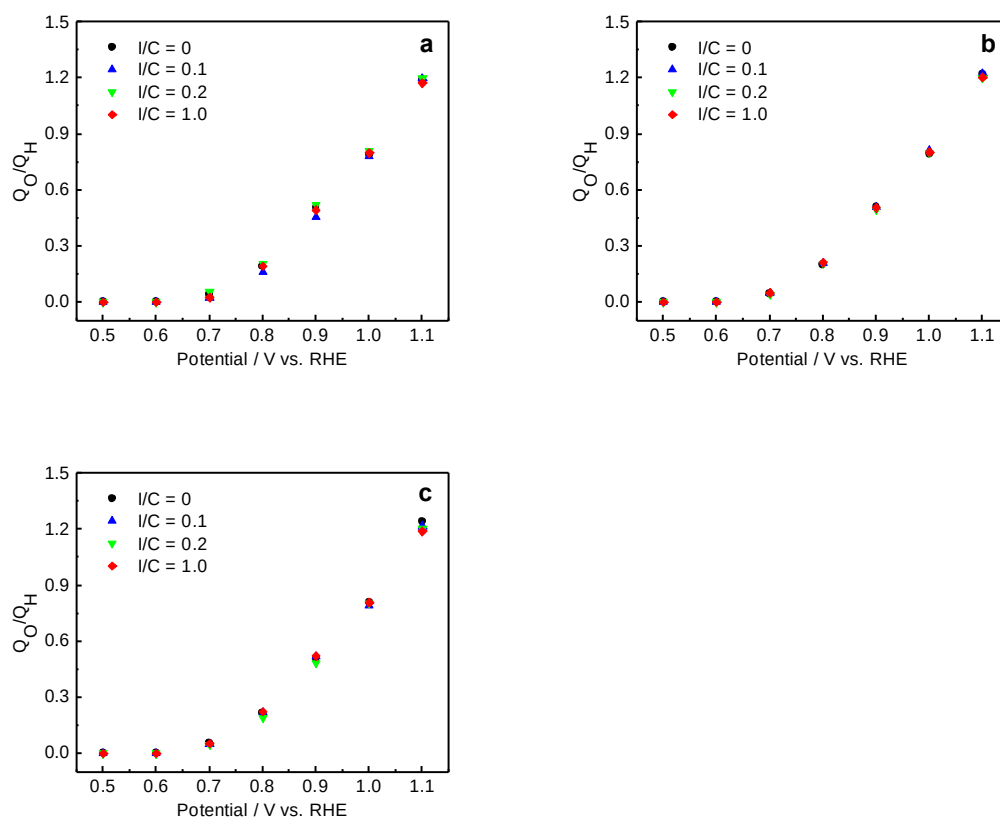


Figure 4. Dependence of I/C ratio on the oxygen coverage for Pt/C catalysts with 3.5nm microporous (a), 5.0nm microporous (b) and 10.0 nm microporous (c) supporting carbon.

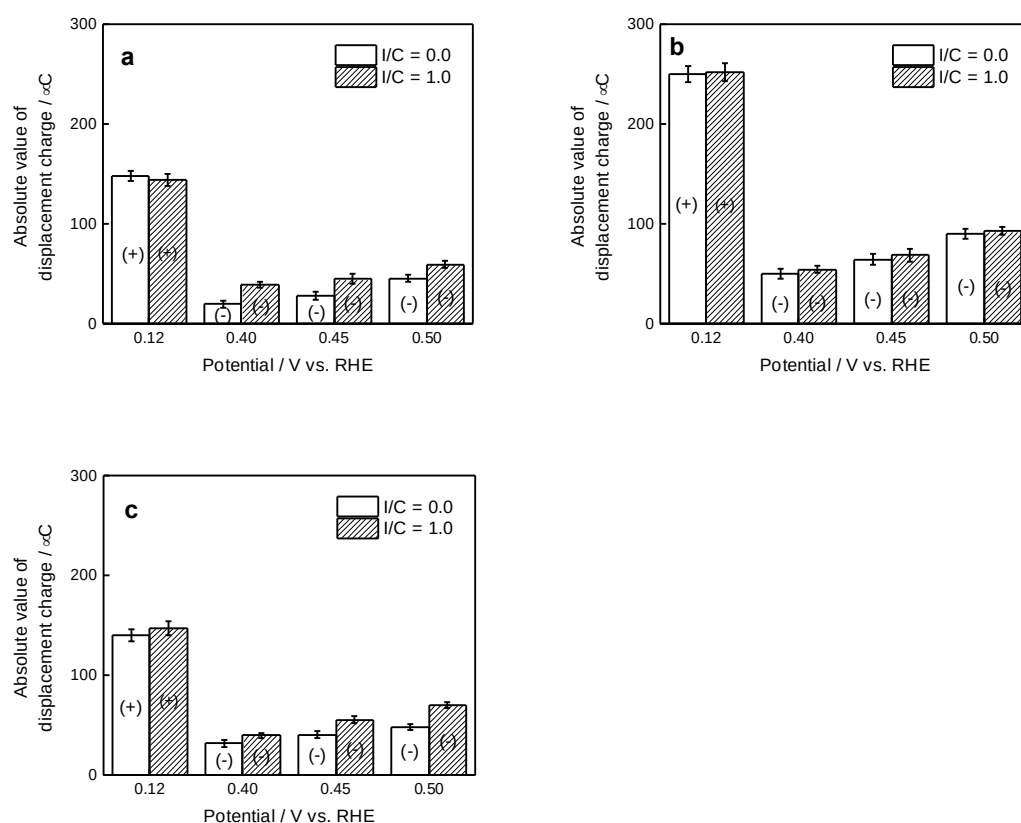


Figure 5. Absolute value of CO displacement charge as a function of measurement potential for Pt/C catalysts with I/C = 0.0 and 1.0. (+)/(-) indicates the polarity of the CO displacement charge on 3.5nm microporous (a), 5.0nm microporous (b) and 10.0 nm microporous (c) supporting carbon.

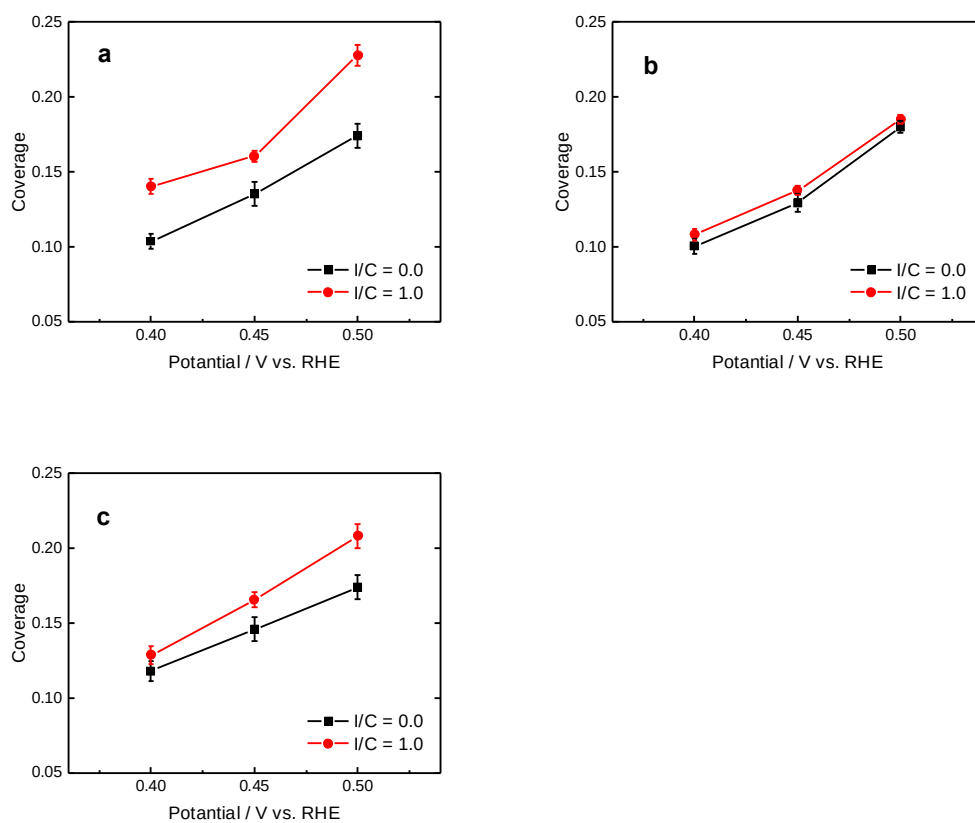


Figure 6. Effects of ionomer on anion coverage for Pt/C catalysts at various potentials on 3.5nm microporous (a), 5.0nm microporous (b) and 10.0 nm microporous (c) supporting carbon.

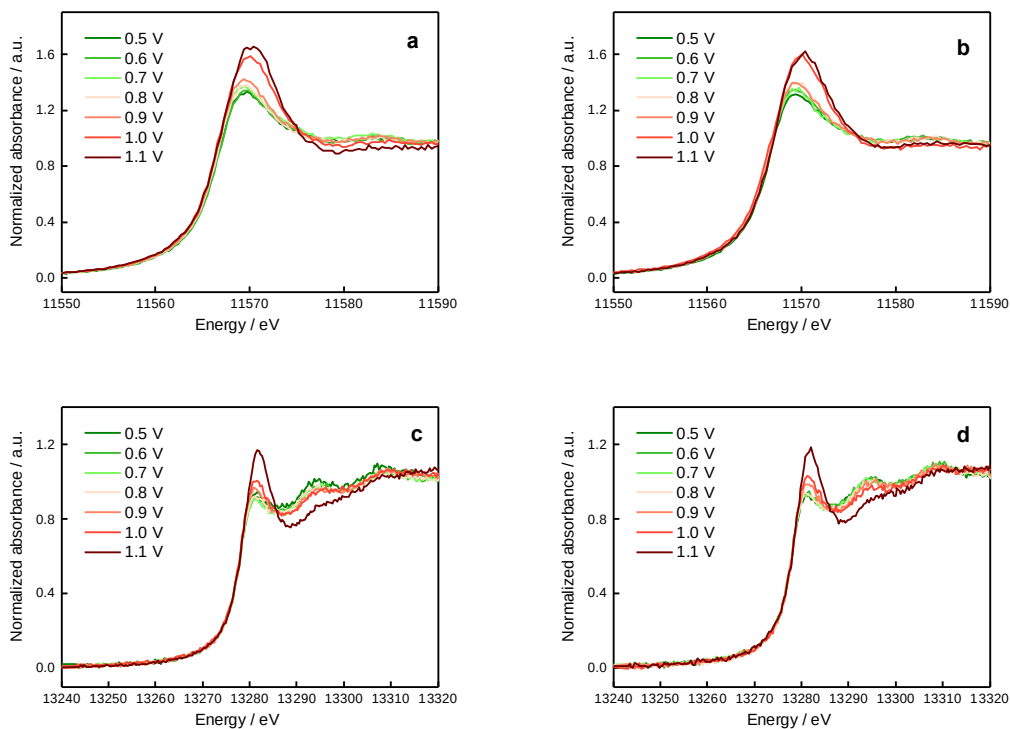


Figure 7. XANES spectra for (a) Pt L_{III}-edge and (c) Pt L_{II}-edge of I/C = 1.0 and (b) Pt L_{III}-edge and (d) Pt L_{II}-edge of I/C = 0.0 for Pt catalyst with 3.5nm microporous supporting carbon.

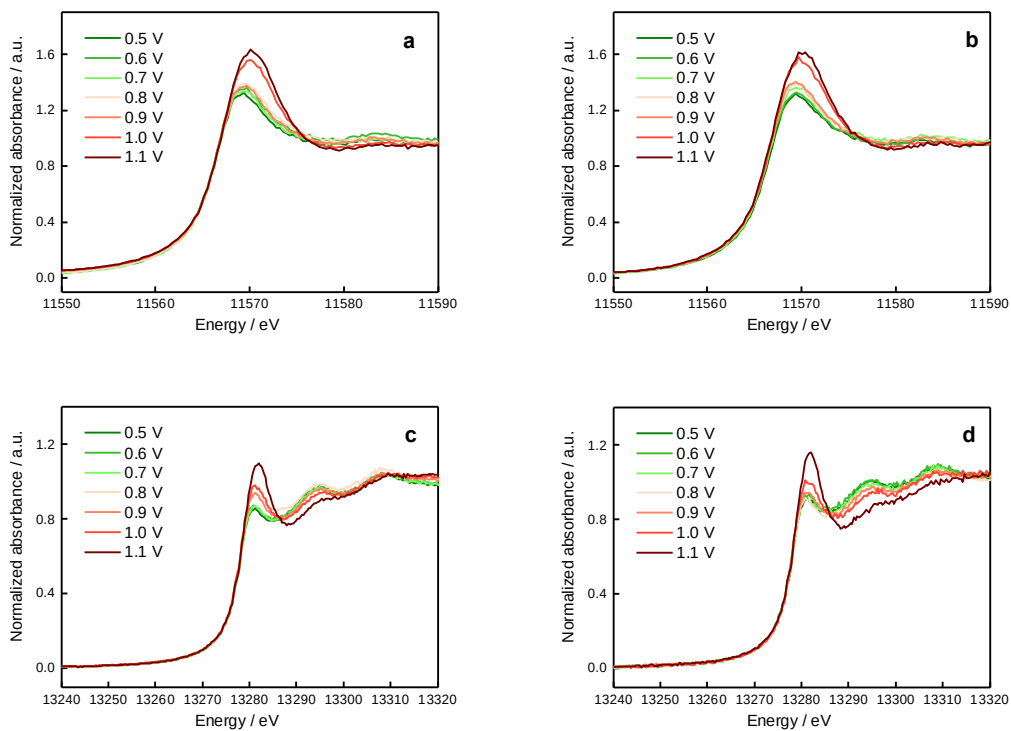


Figure 8. XANES spectra for (a) Pt L_{III}-edge and (c) Pt L_{II}-edge of I/C = 1.0 and (b) Pt L_{III}-edge and (d) Pt L_{II}-edge of I/C = 0.0 for Pt catalyst with 5.0 nm microporous supporting carbon.

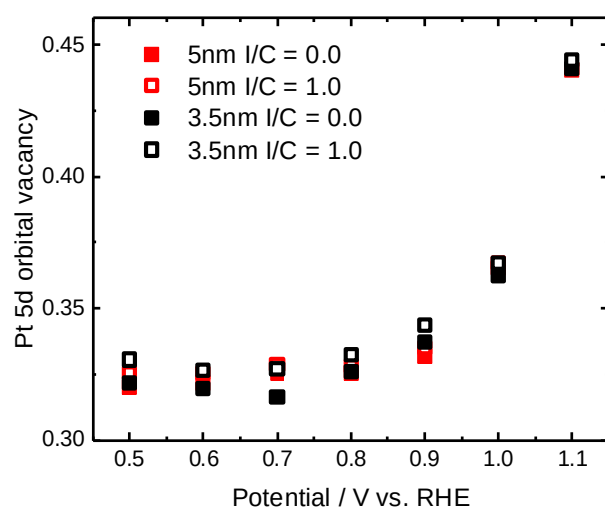


Figure 9. 5d orbital vacancy of Pt catalysts with I/C = 0.0 (solid) and 1.0 (orbital) from 0.5 to 1.1 V on 3.5nm microporous (black), and 5.0nm microporous (red) supporting carbon.

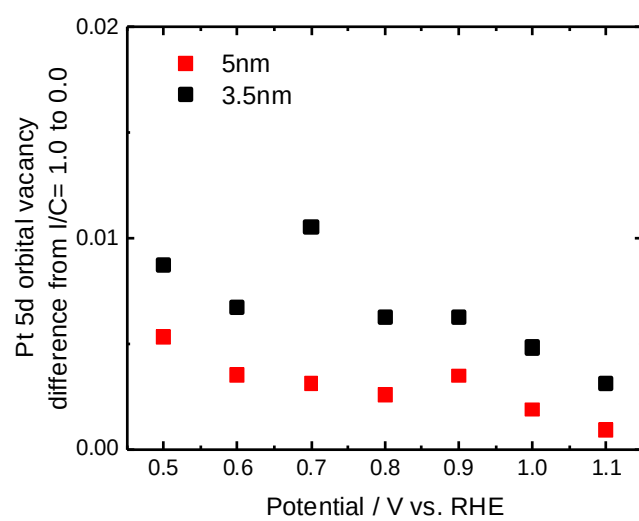


Figure 10. 5d orbital vacancy increased of Pt catalysts from I/C = 0.0 to 1.0 on 3.5nm microporous (black), and 5.0nm microporous (red) supporting carbon.

Chapter 6. *Operando* X-ray Absorption Spectroscopic Study on the Effect of Ionic Liquid Coverage upon the Oxygen Reduction Reaction Activity of Pd-core Pt-shell Catalysts

6.1 Introduction

Polymer electrolyte membrane fuel cells (PEFCs) are considered a key technology for zero-emission power sources in transportation and stationary applications because of their low operating temperature and high power density¹⁻³. Platinum (Pt) is the most promising electrocatalyst for the cathode. However, high Pt loadings are required to accelerate the sluggish kinetics for the oxygen reduction reaction (ORR), and the consequent high cost of the stacks greatly impedes widespread application of PEFCs⁴⁻⁷. In the past decade, many researchers have been devoted to minimizing the use of expensive Pt for ORR by engineering the active site in terms of composition, morphology, and local structure⁷⁻¹⁰. For example, nano-segregated multi-metallic nanoframes¹¹ and nanowires¹² constitute one of the notable recent innovations in ORR catalysts. Intense research efforts have also been focused on developing core-shell structured catalysts with Pt shells on transition metal cores¹³⁻¹⁵ because Pt-based core-shell catalysts possess lower Pt loading. Core-shell catalysts also have other features that make this structure attractive, principally because of their potential to control ORR activity by changing the core materials¹⁶⁻²⁰. The activity of the Pt catalyst is related to the substrate-induced strain, whether tensile or compressive, in combination with the ligand effect^{16,17}. The status of the *d*-band on the Pt surface layer, which is modified by ligand and strain effects, can influence the binding strength and adsorption properties of the oxide species¹⁶⁻¹⁸. Therefore, the moderate compressive strain on the Pt surface layer enhances its activity for the ORR.

Apart from tuning the active sites, the Pt-electrolyte interface has an important role in ORR^{21,22}. A hydrophobic ionic liquid (IL) modification of Pt surface has recently emerged as another method to enhance the activity of Pt-based catalysts for ORR²³⁻²⁵. Many groups have investigated the ability of IL modifications to enhance ORR activity with a variety of IL²⁶⁻²⁸. Snyder et al. firstly reported the development of a new architecture in which high surface area and nanoporous Ni-Pt alloy nanoparticles

encapsulated with a hydrophobic [7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD)][bis(pentafluoroethylsulfonyl)imide(BETI)] IL²³. The ORR activity of this porous PtNi was improved 2–3 times after IL modification; the resultant activity was nearly an order of magnitude higher than that of commercial Pt/C²³. In addition, Li et al. demonstrated that [MTBD][BETI] IL present at the catalyst interface can prevent the specific adsorption of sulfonate groups of Nafion on the Pt(111) single crystal surface for ORR²⁹. Recently, the conventional imidazolium-based ILs have also shown to be capable of improving Pt/C catalyst in both activity and stability³⁰. By systematically changing the side chain length of the imidazolium cations, ([C_nC₁ im][bis (trifluoromethylsulfonyl)imide(NTf₂)], *n* = 2, 4, 6, and 10), a clear dependence of Pt catalytic activity on ORR for side chain length was observed, with the highest activity obtained using medium chain length IL (*n* = 4)²⁷. While the mechanism of the observed activity enhancement of IL remains elusive, the increased oxygen solubility^{24,31}, inhibition of Pt oxidation^{27,30,32}, and lower adsorption of nonreactive species^{25,27,30} are considered among the factors that enhance ORR activity. A recent study by Zhang et al. concluded that the presence of IL improved the electrochemical stability of Pt/C catalysts by suppressing the formation of oxygenated species and / or the initial oxidation of low-coordinating Pt sites at edges, corners, and / or defect Pt sites²⁷. Although the addition of IL may improve the ORR activity, as described above, there are several theories regarding the cause.

operando XAS is a valuable tool for analyzing the effects of changes in electronic states and local structure of the Pt alloy and core–shell catalyst, as reported in our previous papers^{33,34}. Currently, to the best of our knowledge, the electronic states and local structural changes of the catalyst covered with IL have not been investigated. Improvements in ORR activity with the addition of ionic liquids have been reported in various ionic liquid systems for example; [MTBD][BETI]^{23, 24}, [C_nC₁ im][NTf₂]²⁷, and [MTBD][NTf₂]³⁰. We choose [MTBD][NTf₂] as one of the typical ionic liquids. In this study, to comprehensively understand the behavior of IL-modified catalytic systems, the electronic and local structures were analyzed using *operando* XAS. A Pd-core Pt-shell catalyst and [MTBD][NTf₂] was used as the model electrode and IL, respectively, to investigate the interaction between Pt and IL. The catalytic promotion effect of IL is discussed by combining the results of the electrochemical techniques and XAS.

6.2 Experiment

6.2.1 Reagents

30 wt% Pd/C catalyst was provided from Ishifuku Kinzoku Kogyo Co. Ltd., Japan and a 30 wt% Pt/C catalyst (TEC10V30E) was purchased from Tanaka Kikinzoku Kogyo Co. Ltd., Japan. 7-Methyl-1,5,7-triazabicyclo [4.4.0]dec-5-ene ([MTBD]) (98%) and lithium bis (trifluoromethylsulfonyl)imide ([NTf₂]) (99%) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification.

6.2.2 Synthesis of [MTBD][NTf₂] IL

[MTBD][NTf₂] IL was synthesized following a procedure from the literature³⁰. Equal quantities of [MTBD] (33.9 mmol) and Li [NTf₂] (33.9 mmol) were individually dissolved in water at 0 °C. Then, 10.6 M HNO₃ was slowly added dropwise to the [MTBD] solution to form [MTBD][NO₃] until a neutral pH was obtained. Next, the Li[NTf₂] solution was slowly added to the [MTBD][NO₃] solution and [MTBD][NTf₂] IL was precipitated. The detailed scheme was illustrated in Figure 1. The IL was washed several times with ultrapure water and then placed in a rotary evaporator at 60 °C for one day to remove residual water. The IL was further dried under high vacuum.

6.2.3 Preparation of the Pd-core Pt-shell catalyst by underpotential deposition of Cu (Cu-UPD)

Our previously reported method was used for producing the Pd-core Pt-shell catalyst³³. The Pd/C catalyst ink consisted of water:2-propanal (99.99%, Wako) in 2:3 ratio, and the loading of Pd/C was adjusted to 5 µg Pd cm⁻² by dropping 5 µL of the ink on a glassy carbon rotating disk electrode (GC RDE) (HOKUTO DENKO, area = 0.196 cm²). The RDE was dried at 700 rpm at 25 °C. Then, 5 wt% Nafion® solution (Sigma-Aldrich) was casted at a thickness of 200 nm. A Pd-core Pt-shell catalyst (denoted as Pt/Pd/C) was prepared by depositing Pt through the galvanic displacement of the Cu monolayer. Under-potential deposition (UPD) measurements were carried out in a three-electrode cell. A Pt mesh and reversible hydrogen electrode (RHE) were used as the counter electrode and reference electrode, respectively. Next, the deposition of Cu was conducted under 10 mM CuSO₄ in a 0.1 M HClO₄ solution, and RDE was rinsed with N₂-saturated water and soaked with a N₂ saturated 5.0 mM K₂PtCl₄. Figure 2 shows that the cyclic voltammogram (CV) during underpotential deposition was typical for the underpotential deposition of Cu on Pd³⁵. After completely replacing Cu with Pt in 8 min, the RDE was rinsed again with N₂-saturated water. A commercially available Pt/C catalyst (TEC10V30E, Tanaka Kikinzoku Kogyo) was used as a reference. Finally, the synthesized

[MTBD][NTf₂] IL (1 μ L) was drop-casted onto the electrode. For Pt/C and IL-modified Pt/C, the electrochemical surface area was calculated from hydrogen underpotential deposition region from 0.05 to 0.40 V (vs. RHE). For Pt/Pd/C and IL-modified Pt/Pd/C, the hydrogen deposition potential from 0.1 to 0.4 V (vs. RHE) was used for estimation of the electrochemical surface area because the hydrogen storage occurs under 0.1 V (vs. RHE).

6.2.4 Transmission Electron Microscopy (TEM) observations

Transmission electron microscope (TEM), scanning transmission electron microscope and elemental mapping images was obtained by using JEM-F200 and SDD (Silicon drift detector, JEOL Ltd.) at 200 kV.

6.2.5 Electrochemical measurement

ORR activity measurements were carried out in a three-electrode cell at 25 °C. The counter electrode was a Pt mesh, and the reference electrode was RHE. Prior to the catalyst activity measurements, the potential was cycled 50 times between 0.02 and 1.0 V (vs. RHE) at 200 mVs⁻¹ to obtain a stable cyclic voltammogram (CV) in N₂-saturated 0.1 M HClO₄. The final CV was obtained at 50 mVs⁻¹. After the CV measurements, the electrolyte was saturated in O₂. Then, hydrodynamic voltammograms were recorded between 0.2 and 1.2 V vs. RHE at 10 mVs⁻¹ at rotation speeds ranging from 100 rpm to 2500 rpm. The data regarding oxygen reduction for all materials were analyzed using the Koutechy-Levich (K-L) equation at 0.9 V (vs. RHE).

6.2.6 *operando* XAS (X-ray absorption spectra) measurement

operando XAS measurements for Pt L_{III}-edge of Pt/C and Pd-core Pt-shell catalysts were performed using a home-made *operando* cell at BL37XU and BL14B2 of SPring-8, Hyogo, Japan. A Si 111 monochromator and a Pt or Rh mirror were used to obtain collimated and monochromatic X-rays. Prior to the experiments, the samples were electrochemically cleaned by CV in the range from 0.0 to 1.1 V (vs. RHE). Data processing was analyzed using ATHENA and ARTEMIS, a suite of IFEFFIT software programs³⁶.

6.3 Results and discussion

6.3.1 TEM observations

The high-resolution TEM images of the prepared catalysts are shown in Figure 3. Energy-dispersive X-ray (EDX) mapping of Pd and Pt (Figure 3a) confirmed the successful formation of the Pd-core Pt-shell structure through Cu-UPD. According to Figure 3b, the Pt nanoparticles were highly dispersed on the carbon support. The black arrow in Figure 3c shows the IL

covering the surface of the catalyst. The thickness of IL covering the catalyst was about 3 nm. Figure 4a indicates the scanning transmission electron microscope image. The particle size distribution (Figure 4b) was made by counting 200 particles from the Figure 4a and the average particle size of Pt/Pd/C was estimated to 2.7 nm.

6.3.2 Electrochemical measurements

The electrochemical properties of the Pt/C and Pt/Pd/C catalyst [MTBD][NTf₂] IL-modified systems were studied and compared with those without IL. Figure 5a and b show CV curves for Pt/C and Pt/Pd/C at 25 °C in a 0.1 M N₂-saturated HClO₄ solution. Both catalysts showed the characteristic features of H adsorption on Pt in the potential region from 0.05 to 0.4 V (vs. RHE) and the formation of Pt oxide species over 0.6 V (vs. RHE). Comparing the CVs of Pt/C and Pt/Pd/C with/without IL, the H adsorption peaks for the IL-modified system were slightly suppressed, and the peaks shifted to a lower potential range, which agreed with previous reports^{25,37}. These results suggest that the presence of IL suppresses the access of H on the Pt surface by reducing the bonding strength of Pt and H through a ligand effect^{37,38,39} and/or the occupation of certain Pt sites by IL molecules³⁸. Figure 5a and b also show the smaller coverage of the oxide species on Pt when modified with [MTBD][NTf₂] IL, confirming that the IL-modified system suppressed the oxidation of Pt. It is well known that an excessively strong Pt-O bonding strength leads to slow ORR kinetics^{40,41}. Therefore, the weakened Pt-O interaction is expected to improve the ORR kinetics when modified with IL. The influence of IL modification on the ORR specific activity is compared in Figure 6 and Table 1 shows the electrochemical surface area and the specific activity for each catalyst. For Pt/C, the estimated electrochemical surface area was decreased 21% while the specific activity was increased 207%. For Pt/Pd/C, the estimated electrochemical surface area was decreased about 6% while the specific activity was increased 131%. Therefore, the increase in ORR activity is not due to the underestimation of the electrochemical surface area but due to the IL addition effect, which indicates that the intrinsic ORR activity is actually improved. Linear sweep voltammograms (LSVs) at 1600 rpm for Pt/C and Pt/Pd/C are also illustrated in Figure 7a and b of the Supporting Information, and their voltammograms clearly indicate the positive shifts upon modification with the IL. As the IL-modified Pt/Pd/C catalyst have a better oxygen reduction reaction activity, the onset potential showed the more positive shift than Pt/Pd/C. This result was also supported by the cyclic voltammogram in Figure 5 since the oxidation peak at 0.8 V (vs. RHE) was suppressed by IL modification. The reason of this activity improvement is discussed on *operando* X-ray absorption spectroscopy section. The Tafel plots and slopes of Pt/C and Pt/Pd/C were shown in Figure 8. They showed about 60 mV/dec and 120 mV/dec respectively for low and high current density region, which was characteristic to Pt-based

catalysts²⁴. As there were no obvious differences in Tafel slope between Pt/C and Pt/Pd/C regardless of IL, the reaction mechanism was not changed by IL modification, which was also identical to the previous report²⁴. The impact of IL on ORR activity was different between Pt/C and Pt/Pd/C. The cause was not determined; however, these results may be partially due to the greater quantity of free active sites on the IL-modified system and the resulting accelerated ORR kinetics.

6.3.3 *operando* XAS measurement

To understand the behavior of IL-modified catalytic systems, the electronic state of Pt was analyzed by *operando* XAS. Pt L_{III}-edge X-ray absorption near-edge spectra (XANES) for Pt/Pd/C and IL-modified Pt/Pd/C at 0.50, 0.85, and 1.15 V (vs. RHE) are shown in Figure 9a and c. This provides a different insight into the reaction mechanism through electronic structural changes induced by Pt oxidation. In addition, the difference spectra from 0.5 V (vs. RHE) are shown in Figure 9b and d. The clear increase in the white line of Pt/Pd/C (Figure 9a) suggested an increase in unoccupied Pt 5d states due to charge transfer from Pt to the adsorbed oxygen species³⁴. In contrast, the IL-modified Pt/Pd/C (Figure 9c) shows suppression of oxidation when compared with Pt/Pd/C. These results are in agreement with those of the electrochemical measurement described above. The oxygen species adsorbed on the Pt were analyzed based on the difference spectra ($\Delta\mu$ XANES)⁴², as shown in Figure 9b and d. There was not much difference in peak position between Pt/Pd/C and IL-modified Pt/Pd/C probably because the adsorbed species were nearly the same regardless of the presence of IL. Figure 9e shows 5d orbital vacancies evaluated by using Mansour's method⁴³, which is a quantitative technique for determining the number of unoccupied 5d electron states in Pt. In Pt/Pd/C, the 5d orbital increased with potential and reached a value of 0.42 and 0.33, respectively, for without and with IL. Density functional theory studies have predicted that the quantity of charge transfer from Pt to oxygen species was 0.37 when atomic oxygen was adsorbed at face-centered cubic (fcc) hollow sites with full coverage⁴⁴. The 5d orbital vacancy of Pt/Pd/C was slightly larger than DFT calculation, which might be because of the further oxidation of Pt such as formation of Pt oxides^[34]. On the other hand, IL-modified Pt/Pd/C showed a lower value than Pt/Pd/C because of the lower coverage of oxide species.

The local structure around Pt in Pt/Pd/C was investigated through extended X-ray absorption spectra (EXAFS). The non-phase-shift-corrected Fourier-transformed EXAFS at 0.50, 0.85, and 1.15 V (vs. RHE) are shown in Figure 10a and b. The features at 0.50 V indicated the typical Pd core Pt-shell structure reported elsewhere³³ regardless of the IL. At 0.85 V, the peak at 1.44 Å, corresponding to the Pt-O bond, was observed for Pt/Pd/C without IL, and the peak intensity of the Pt-O bond was further increased at 1.15 V, indicating that the coverage of

the oxygen species increased (Figure 10a). In contrast, the Pt-O bond could not be observed until 1.15 V for the IL-modified system (Figure 10b). These results also suggested that the adsorption of oxygen species in Pt/Pd/C was suppressed by the coverage of the IL, as expected from the XANES and electrochemical measurements. In addition, the estimated Pt-Pt distance (Figure 10c) of IL-modified Pt/Pd/C was relatively smaller than that of naked Pt/Pd/C at any potential. This shrinkage might be caused by adsorption of IL on the Pt surface and charge transfer from IL to Pt, the so-called ligand effect^{38,39}, and this compressive Pt-Pt bond-induced structure had an advantage for the ORR kinetics. In other words, our results provide clear evidence that IL suppresses the adsorption of oxygen species on the Pt surface and improves the ORR activity.

6.4 Conclusion

This study provides evidence that the activity of Pt/C and Pt/Pd/C catalysts for ORR can be greatly enhanced by [MTBD][NTf₂] IL modification. Electrochemical analysis revealed lower coverage of the oxide species on the Pt surface when modified with [MTBD][NTf₂] IL. This suggests that the IL-modified system suppressed the oxidation of Pt. According to *operando* XAS of Pt/Pd/C, the increase in unoccupied Pt 5d states at higher potentials due to charge transfer from Pt to adsorbed oxygen species and the IL-modified Pt/Pd/C showed suppression of oxidation. These results provide clear evidence that IL suppresses the oxidation of Pt and improves the ORR activity. Thus, we anticipate that IL-modified systems are highly promising for future fuel cell applications.

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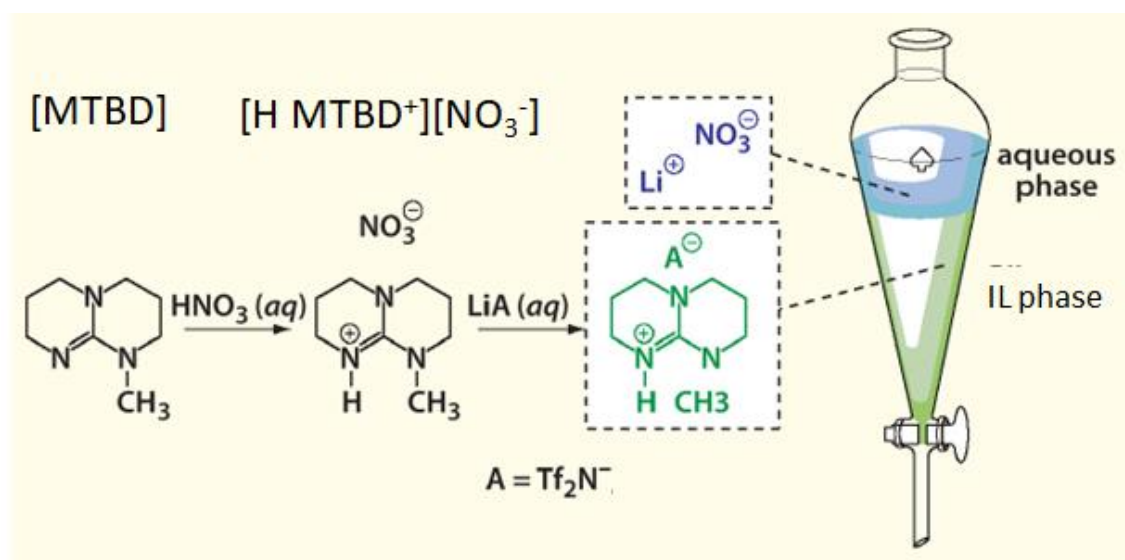


Figure 1. Scheme of synthesis of $[MTBD][NTf_2]$

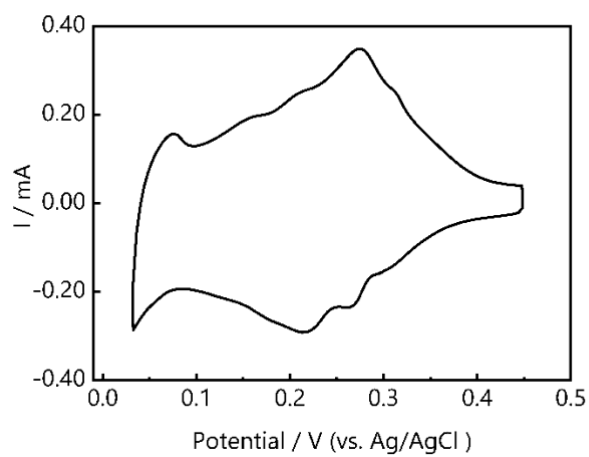


Figure 2. Cyclic voltammograms for the underpotential deposition of Cu on Pd/C in 0.1 M HClO₄ with 10 mM CuSO₄.

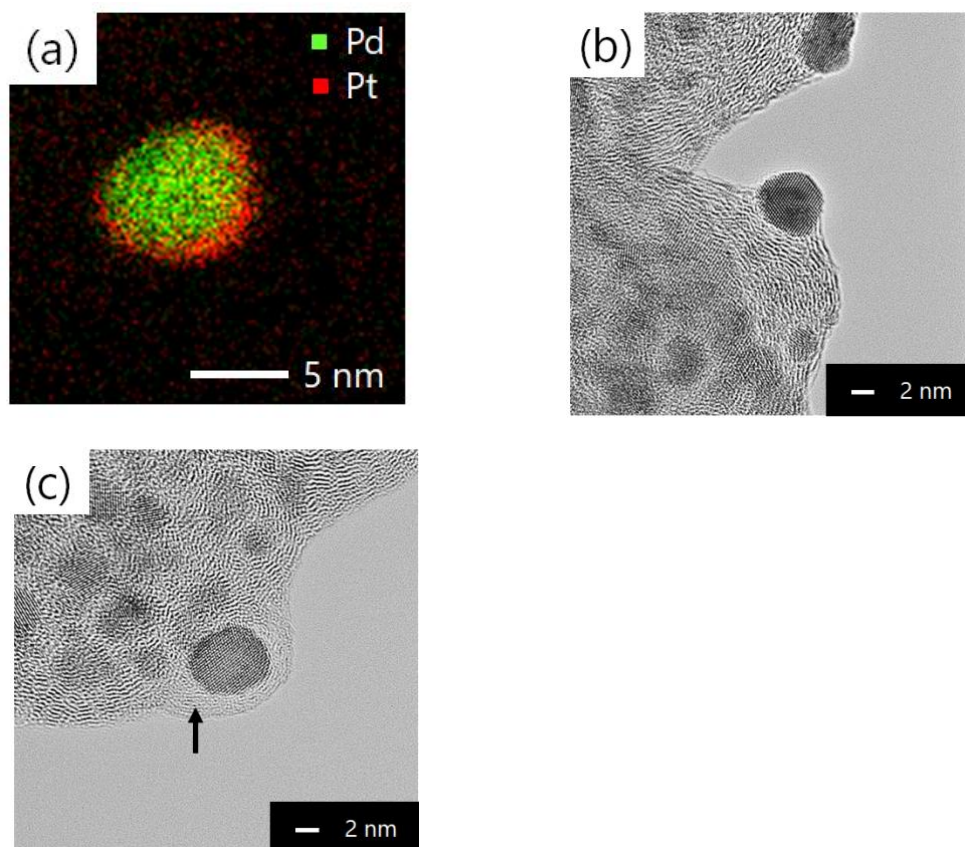


Figure 3. TEM images and EDX mapping for (a, b) Pd-core Pt-shell catalyst and (c) IL-modified Pd-core Pt-shell catalyst; The black arrow indicates the IL covering the surface of the catalyst.

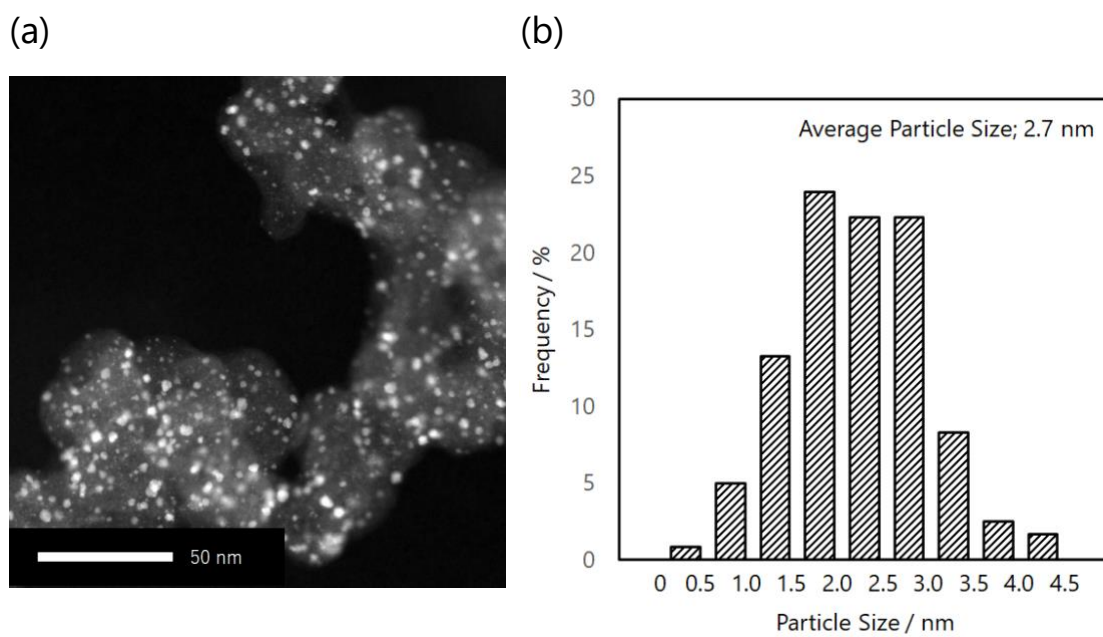


Figure 4. (a) Scanning transmission electron microscope image and (b) Particle size distribution of Pt/Pd/C.

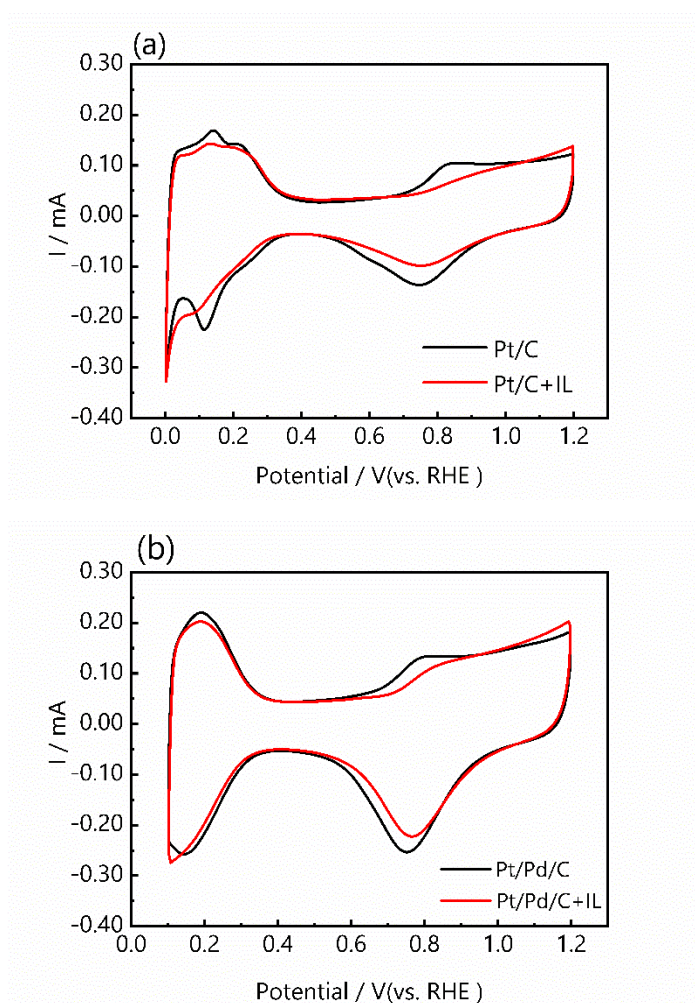


Figure 5. Cyclic Voltammograms (CVs) for (a) Pt/C and (b) Pt/Pd/C (black line) covered with [MTBD][NTf₂] IL (red line) in N₂-saturated 0.1 M HClO₄ at 25°C.

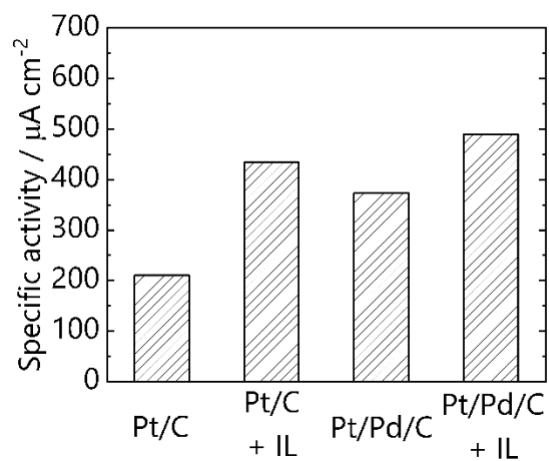


Figure 6. Specific activities of Pt/C and Pt/Pd/C with/without [MTBD][NTf₂] IL in O₂-saturated 0.1M HClO₄ at 10 mVs⁻¹. Specific activities were estimated using the Koutechy-Levich (K-L) equation at 0.9 V (vs. RHE).

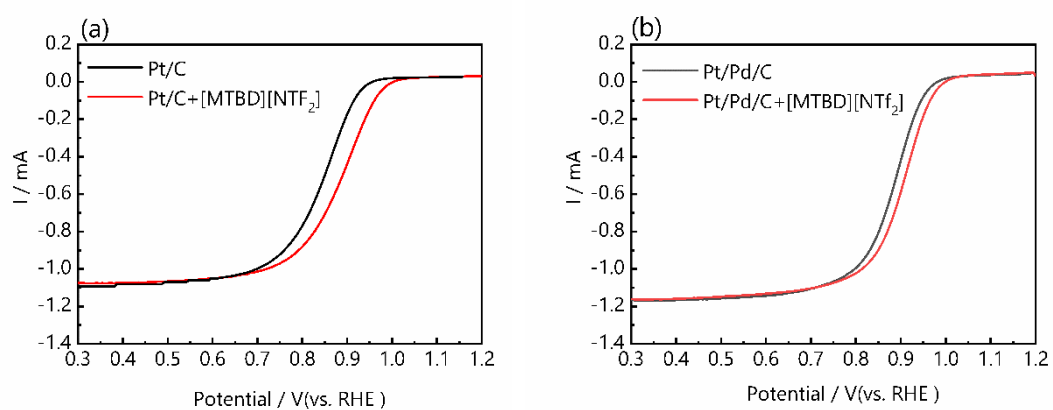


Figure 7. Linear Sweep Voltammograms for (a) Pt/C and (b) Pt/Pd/C (black line) covered with [MTBD][NTf₂] (red line) in O₂-saturated 0.1 M HClO₄ at 25°C at 1600 rpm.

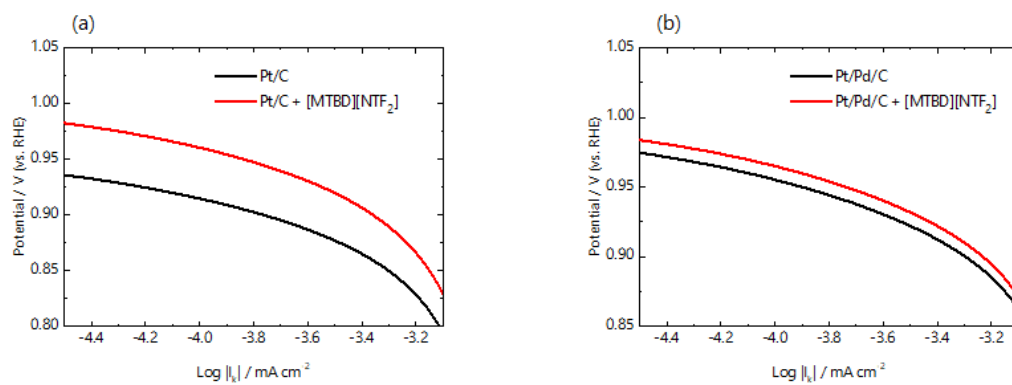


Figure 8. Tafel plots of (a) Pt/C and (b) Pt/Pd/C with/without IL

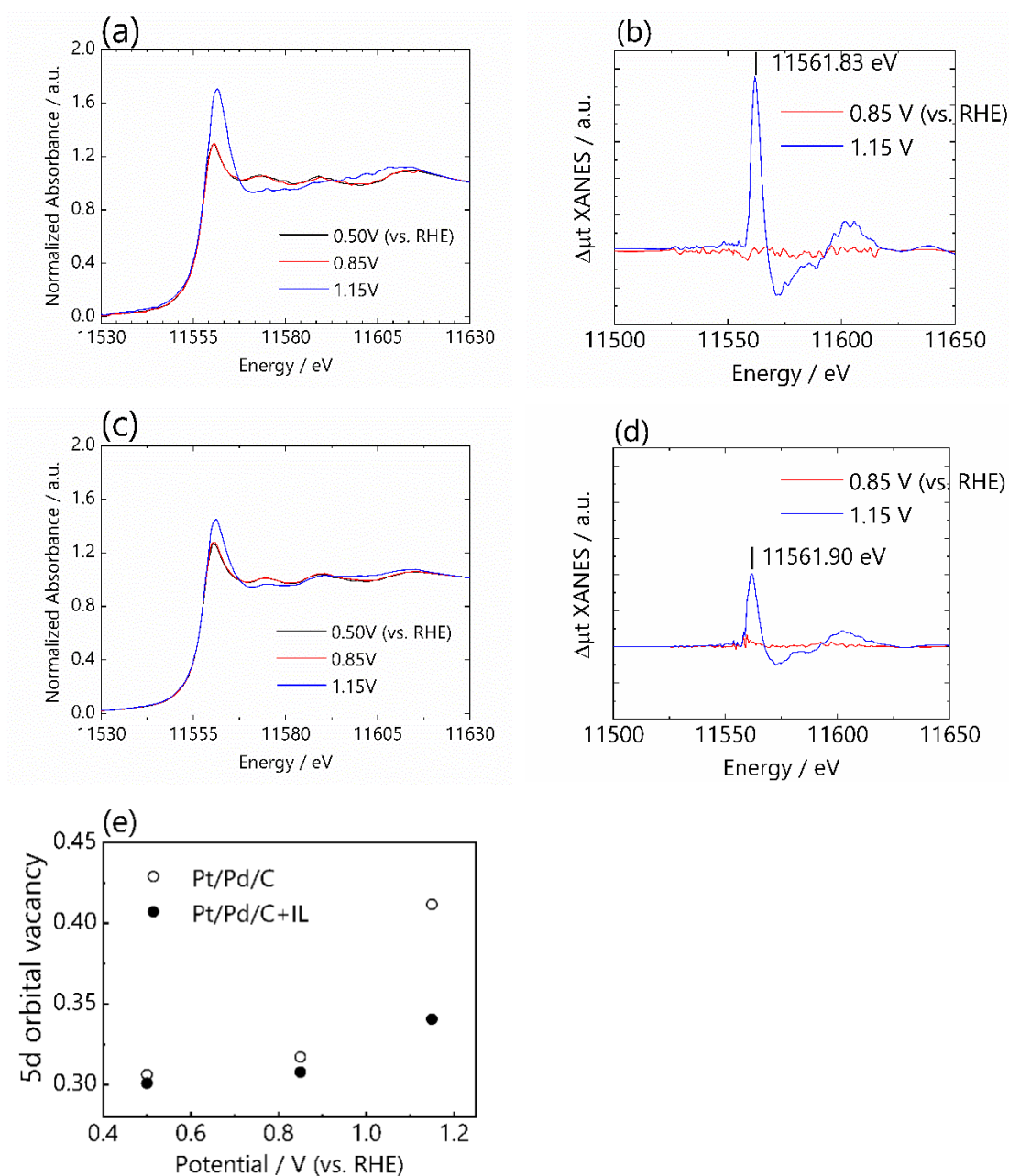


Figure 9. Pt L_{III}-edge XANES of Pt/Pd/C at 0.50, 0.85 and 1.15 V (vs. RHE) in O₂-saturated 0.1 M HClO₄ (a) without and (c) with IL. Panels (b) and (d) indicate the difference spectra from 0.5 V (vs. RHE) respectively for without and with IL. (e) The potential dependence of 5d orbital vacancy of Pt/Pd/C without (○) and with (●) IL.

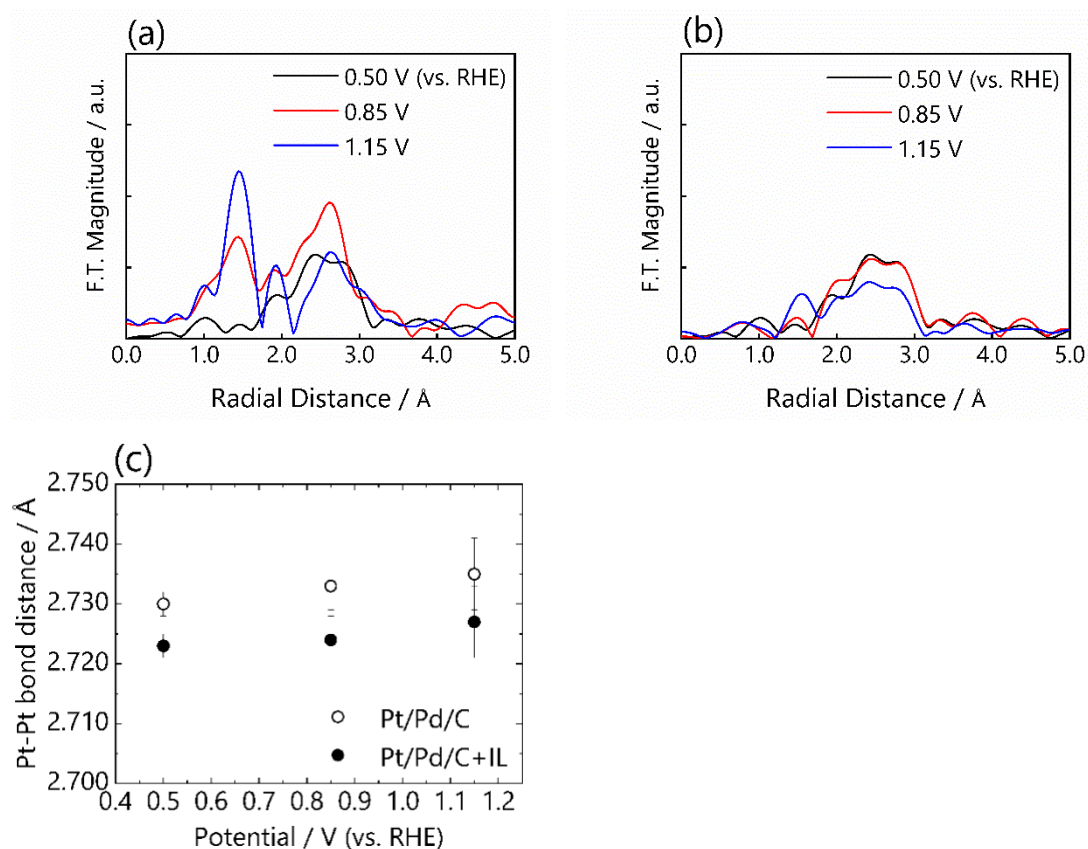


Figure 10. The potential dependence of Pt L_{III}-edge Fourier-transformed EXAFS (Δk range: 3.0–12.5 Å⁻¹) for Pt/Pd/C (a) without and (b) with IL and (c) Pt-Pt bond distance of Pt/Pd/C without (○) and with (●) IL.

Chapter 7. General conclusion

Environment and global warming issue is one of the main global issues around the world. The polymer electrolyte fuel cells (PEFCs) supposed to be one of the main devices used in the global renewable energy system and pure hydrogen energy society in the future. Polymer electrolyte fuel cells have been developed for the electric device applications such as residential fuel cell cogeneration system and fuel cell vehicles . PEFC cathode catalyst requires an excess amount of platinum due to the degradation of oxygen reduction reaction (ORR) activity. High performance, high durability and low-cost cathode catalyst is expected for the wide use of PEFC devices. Therefore, it is important to reduce the use of platinum in the catalyst and improve its catalytic activity as well as durability. In this study, electrochemical measurement, characterization measurement, operando XAS method used on several proposal about improve the performance and ORR activity of PEFC cathode catalyst, analysis the mechanism detail of enhanced activity on local structure level.

In chapter 1, general introduction of the research about fuel cell, the type and the factors influenced oxygen reduction reaction (ORR) activity about the electrode catalysts.

In chapter 2, the temperature effect toward the ORR activity of various particle size Pd core-Pt shell catalyst has been discussed. Through the characterization, electrochemical measurement and operando XAS analysis, the decreasing activity of Pd core-Pt shell catalyst has been observed in high temperature as PEFC working temperature (60 °C). Due to higher thermal expansion coefficient of Pd than Pt, thermal expansion of Pd core at high temperature lead the extreme Pt-Pt bond extension and the decrease of compressive strain effect and ORR activity. Catalyst with smaller size Pd core suffer less thermal expansion effect from Pd core and remain higher ORR activity.

In chapter 3, the specific absorption effect of ionomer towards Pt/C catalyst has been quantitatively evaluated through electrochemical measurement and operando XAS analysis. The increasing ionomer/carbon ratio lead decreasing ORR activity of Pt/C catalyst. Through operando XAS analysis, the specific absorption of ionomer at the active potential has been quantitatively evaluated on various ionomer/carbon ratio, illustrated the relationship between the ORR activity and the 5d orbital vacancy.

In chapter 4, the specific absorption effect of ionomer towards Pd core-Pt shell catalyst has been quantitatively evaluated through electrochemical measurement and operando XAS analysis. The increasing ionomer/carbon ratio lead decreasing ORR activity of Pd core-Pt shell catalyst. Operando XAS analysis of Pd core-Pt shell catalyst could avoid receive signal from Pt bulk and focus on the information of ionomer specific absorption effect on the surface of the catalyst, quantitatively evaluated the specific absorption of ionomer from 5d orbital vacancy.

In chapter 5, the inhibition effect of ionomer specific absorption from micropore carbon supported Pt/C catalyst has been evaluated through electrochemical measurement and operando XAS analysis. Pt/C catalyst with appropriate diameter micropore carbon support could protect the Pt nanoparticles buried in micropore from the ionomer specific absorption but can occur ORR at the same time.

In chapter 6, enhancement of the ORR activity of Pt/C and Pd-core Pt-shell catalysts upon ionic liquid modification has been evaluated. Electrochemical analysis revealed lower coverage of the oxide species on the Pt surface when modified with [MTBD][NTf₂] IL. This suggests that the IL-modified systemsuppressed the oxidation of Pt. According to operando XAS of Pt/Pd/C, the increase in unoccupied Pt 5d states at higher potentials due to charge transfer from Pt to adsorbed oxygen species and the IL-modified Pt/Pd/C showed suppression of oxidation.

In Chapter 7, the results of the thesis were summarized.

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