

京都大学	博 士 (理 学)	氏名	Wu Tian
論文題目	Synthesis of Pt-Based Ordered Alloy Nanoparticles for Efficient Electrocatalytic Oxygen Reduction Reaction (Pt基規則合金ナノ粒子の合成と酸素還元電極触媒特性)		
(論文内容の要旨)			
For exploring sustainable and green substitutes of fossil fuels, polymer electrolyte fuel cells (PEFCs) are one of the most promising future energy candidates because they have significant advantages, such as zero emission, reproducible fuel resources, and high energy conversion efficiency. In PEFCs, hydrogen molecules are oxidized on the anode and electrons are transferred to the cathode for oxygen reduction, thus outputting electric energy as power sources for many applications. Because the main bottleneck to be overcome for large-scale application is the sluggish kinetics of oxygen reduction reaction (ORR) on the cathode, it is both scientifically and practically important to develop cost-effective, high-performance, and durable ORR catalysts. The synthesis of electrocatalysts has been extensively studied in recent years, although platinum (Pt) and Pt-based materials are still considered to be state-of-the-art catalysts for PEFCs. Alloying of Pt with transition metals has been basically proven to be an effective way to achieve high performance electrocatalysts, but most of them suffer from either complicated manufacturing process, insufficient intrinsic activity, or dealloying corrosion under acid conditions. Furthermore, owing to scarcity and huge cost of Pt, both maximization of the Pt efficiency and minimizing its usage are also required for large-scale commercialization. Herein, we synthesize a series of ordered Pt compounds nanoparticles (NPs) as electrocatalysts with superior activity and durability to satisfy the requirement of widespread application prospect of PEFCs. Chapter 2. PtP₂ nanoparticles on N, P Doped Carbon with Self-Converting Process to Core-Shell Pt/PtP₂ as Highly Active and Robust ORR Catalyst PEFCs are one of the promising alternative candidates for fossil fuel to generate electricity. It has been a challenge that limited ORR kinetics on the cathode remains the main bottleneck to increase the whole performance. The size-controllable monodisperse PtP₂ NPs on nitrogen- and phosphorus-doped carbon (NPC) were synthesized and showed initial ORR mass and specific activities of 0.466 A/mg_{Pt} and 0.438 mA/cm²_{Pt} at 0.9 V in 0.1 M HClO₄ solution, respectively. The mass and specific activities increased to 0.724 A/mg_{Pt} and 0.508 mA/cm²_{Pt}, respectively, after 3000 potential cycles and remain stable within further 20000 cycles, showing an obvious improvement over commercial Pt benchmark (0.098 A/mg_{Pt} and 0.142			

mA/cm²_{Pt} at 0.9 V, respectively). Enhanced ORR activity of PtP₂ NPs encapsuled in NPC after incipient circles of stability test was caused by the self-transformation from PtP₂ NPs to PtP₂@Pt core@shell NPs with a thin (≈ 1 nm) Pt-rich shell, leading to the significant strain effect of Pt-rich skin which contributes to both robustness and catalytic efficiency of the catalysts. In addition, computational analysis indicates that the PtP₂@Pt core@shell structure enhances the ORR activity by a more feasible rate-determining step by lowering *d*-band center value of Pt.

Chapter 3. Highly Ordered *L*₁₀-Type Pt(*M*,Zn) Electrocatalysts for Cathodic Oxygen Reduction Reaction in Fuel Cells

Recently it has been found that Pt-based intermetallic compound NPs show superior activity and durability even under a highly acidic conditions for the ORR in PEFCs. Although the Pt-based alloy NPs with the *L*₁₀ crystal structure have been well studied, further improvement of ordering degree has been required to drastically enhance the catalytic activity and durability for ORR. Synthesis of *L*₁₀-ordered Pt*M* (*M* : 3*d* transition metals) NPs is typically conducted by high-temperature annealing of disordered *A1*-type Pt*M* NPs to induce the disorder–order transformation, which leads to unfavorable NP aggregation. Considering that the *L*₁₀-PtZn phase requires much lower phase transformation temperature than other *L*₁₀-Pt*M*, we incorporated Zn as an ordering promoter to lower the phase transformation temperature of *L*₁₀-Pt(*M*,Zn) NPs as well as to suppress aggregation and increase average ordering degree of NPs. In this work, sub-6 nm *L*₁₀-Pt(*M*,Zn) NPs with high ordering degree were synthesized through a facile wet-chemical method, followed by low-temperature annealing. Lattice constant of *L*₁₀-Pt(*M*,Zn) NPs was controlled by precisely tuning the composition, demonstrating a positive correlation between the surface strain effect and the ORR activity, in which highly ordered *L*₁₀-Pt₅Co₄Zn₁ and *L*₁₀-Pt₅Ni₄Zn₁ NPs showed excellent specific activities of 1.71 and 1.40 mA/cm²_{Pt}, respectively, almost comparable to that of *L*₁₀-PtCo NPs.

(続紙 2)

(論文審査の結果の要旨)

固体高分子型燃料電池は、ゼロエミッション、再生可能な燃料資源、高いエネルギー変換効率などの利点があるため、最も有望な発電デバイス候補の一つである。大規模応用のために克服すべき主な欠点は、カソードでの酸素還元反応 (ORR) 速度の遅さであり、様々な Pt ベースの合金触媒が開発されてきた。Wu Tian 氏は、窒素およびリンをドーブした炭素上に担持した単分散 PtP₂ ナノ粒子を合成し、酸性条件下で非常に高い ORR 触媒活性を示すことを実証しました。また、反応サイクルが進に従い PtP₂@Pt コア@シェル構造に構造変態し、Pt コアに誘起される圧縮歪みが触媒活性をさらに向上させることを見出した。

Ptベースの規則合金ナノ粒子も、固体高分子型燃料電池の高酸性条件下で優れた ORR触媒活性と耐久性を示すことがわかっており、規則合金のさらなる規則度の向上が必要とされている。Wu Tian氏は、L1₀-PtZn相が他のL1₀-PtM相 (M: 遷移金属) よりもはるかに低いA1→L1₀相転移温度をもつことに着目し、L1₀-PtMナノ粒子にZnを添加することによりL1₀-Pt(M,Zn)ナノ粒子相転移温度を下げるとともに、規則化度を向上させることに成功した。高規則化L1₀-Pt₅Co₄Zn₁およびL1₀-Pt₅Ni₄Zn₁ナノ粒子は、非常に優れたORR比活性を示し、L1₀-PtCoナノ粒子とほぼ同等であった。この成果は、ORRの触媒設計に新たな観点を与え、極めて高活性かつ高耐久性を有するORR触媒開発への展開が期待される。

よって、本論文は博士 (理学) の学位論文として価値あるものと認める。また、令和 7 年 1 月 17 日、論文内容とそれに関連した事項について試問を行った結果、合格と認めた。

なお、本論文は、京都大学学位規程第 14 条第 2 項に該当するものと判断し、公表に際しては、当該論文の全文に代えてその内容を要約したものとすることを認める。

要旨公表可能日： 年 月 日以降