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# Designing Pt-Skin of Pt-Based Bimetallic Electrocatalysts for Oxygen Reduction Reaction

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**Abstract:** In the past decade, great advancement has been made in the development of nanocatalysts for energy conversion and storage. Platinum (Pt)-skin of Pt-based bimetallic nanocatalyst has shown a great potential in the tuning the electronic structures of electrocatalytically active materials toward oxygen reduction reaction. Here, we offer a brief overview of the recent research on the design and preparation of catalysts. Our focus is paid on the systematic studies of preparation and performance of Pt-skin catalysts towards oxygen reduction reaction.

**Key words:** Pt; bimetallic; electrocatalysts; oxygen reduction reaction

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Bimetallic catalysts (consisting of two metals) have been widely used in numerous reactions, including alcohol oxidation<sup>[1]</sup>, formic oxidation<sup>[2]</sup>, carbon dioxide reduction<sup>[3]</sup> and oxygen reduction reaction (ORR)[4], which have attracted increasing interest in the quest to develop advanced electrocatalysts. Unlike monometallic catalysts, bimetallic catalysts ordinarily present a better performance than the sum of its parts<sup>[5-6]</sup>. The addition of the second metal in catalysts may modify the electronic and geometric structures to achieve superior performance and durability than traditionally Pt/C. A great quantity of work have been done on Pt-based bimetallic electrocatalysts, such as alloying Pt with 3d-transition metals, including Fe<sup>[7]</sup>, Co<sup>[8-9]</sup>, Ni<sup>[9-11]</sup>, and Cu<sup>[5]</sup>. Other approaches have included monolayer coating of Pt on suitable metal nanoparticles[12-13] and preparation Pt-skin of Ptbased bimetallic electrocatalysts<sup>[14-15]</sup>.

The ORR is one of the key processes for the commercial viability of proton exchange membrane fuel cells<sup>[4,11,16-17]</sup>. It is widely accepted that ORR on the Pt-based bimetallic electrocatalysts follows the four-electron electrochemical reaction,  $O_2 + 4H^+ + 4e$ 

= 2H<sub>2</sub>O. However, the sluggish kinetics of the ORR requires a large amount of Pt metal in real electrochemical system (proton exchange membrane fuel cells), which limits the scale-up of corresponding renewable energy technologies. Enhancing the performance of electrocatalysts for ORR and reducing the amount of Pt needed are both required for the renewable and environment-compatible schemes in chemical-electrical energy conversion.

Bimetallic PtM (M = Fe, Co, Ni et al) catalysts have demonstrated good electrocatalytic activities toward ORR. Fundamental researches have shown that the enhanced catalytic activity originates from the modified electronic structures and geometric structures of Pt in these alloy catalysts<sup>[18-20]</sup>. The electrocatalytic reactions only take place on the surface of electrocatalysts<sup>[21]</sup>, and the surface composition determines the surface properties and the adsorption/desorption behaviors of the reactants and intermediates during catalysis. To understand the catalytic reaction kinetics and mechanisms, it is vital to investigate the surface composition of bimetallic catalysts. Here, we present a selective summary of recent advances on

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Pt-skin of PtM bimetallic catalysts (the outermost is Pt, the inside is PtM alloy), with focusing on catalysts preparations and their electrocatalytic performances. An in-depth appraisal of PtM bimetallic state-of-the art has allowed us to comment on the future directions in the developments and applications of commercially available PtM bimetallic catalysts.

### 1 Preparations for Pt-Skin of PtM Bimetallic Catalysts

Surface composition of PtM bimetallic is principally dependent on the surface free energy, size and temperature<sup>[21]</sup>. This section will discuss how to prepare Pt-skin of PtM bimetallic electrocatalysts.

#### 1.1 Electrochemical Method

Electrochemical method is a good choice to acquire the Pt outermost nanoparticles. It is difficult to eletro-eposit directly Pt monolayer (Pt ML) on the surface of electrocatalysts, because Pt is easy to form nano cluster<sup>[13]</sup>. Nevertheless, electrocatalysts are easy to be covered with Cu monolayer (Cu ML) by underpotential deposition (UPD). Pt ML could be deposited by galvanic displacement of a Cu monolayer at underpotentials, similarly, Pt/Au/Ni, Pt/Pd/Co, and Pt/Pt/Co could be acquired, as shown in Figure 1<sup>[13]</sup>.

Stamenkovic et al. use under ultrahigh vacuum (UHV) methods to prepare well-characterized PtNi single-crystal electrode surfaces<sup>[14]</sup>. To determine the surface composition, the surface-sensitive techniques including low-energy electron diffraction (LEED), auger electron spectroscopy (AES), low-energy ion scattering (LEIS), and synchrotron-based high-resolution ultra-violet photoemission spectroscopy (UPS)

have been used (Figure 2). Single-crystal electrode is an ideal research model, because it is easy to control and determine the composition of the outermost atomic layer after annealing. And it is also easy to compare different crystal facets, namely, Pt<sub>3</sub>Ni(111), Pt<sub>3</sub>Ni(100), and Pt<sub>3</sub>Ni(110). This PtM bimetallic catalysts could be expanded to combine with other metals, like Fe, Co and Ti et al<sup>[15]</sup>. It is really convenient to research the role of Pt-skin on PtM electrocatalytic performance. The electocatalytic activity of those PtM bimetals is determined by Pt-skin surface, and by comparing their properties, their common features could be found. For example, by comparing Pt<sub>3</sub>M(111) single crystal surfaces using electrochemical characterization, Stamenkovic et al. found that the ratio between the integrated charges CO stripping  $(O_{CO})$  and electrochemical surface area (ECSA) for Hupd  $(Q_H)$ was directly related to Pt-skin and Pt-skeleton: i.e.,  $Q_{\rm CO}/2Q_{\rm H}$  =1.5 corresponded to to the Pt-skin surface, while  $Q_{\rm CO}/2Q_{\rm H}=1.0$  to the pure Pt<sup>[22]</sup>.

#### 1.2 Chemical Method

Electrochemical method could be employed to very precisely deposit Pt monolayer on other non-noble metals; however, it is difficult to be carried out in a large scale. Chemical method might have advantages from this point. Tuning  $H_2$  reduction temperature, the core-shell structured Pt-Co nanoparticles with  $2 \sim 3$  atomic-layer Pt shells (Pt<sub>3</sub>Co@Pt) could be prepared<sup>[16]</sup>. Controlled thermal treatment method (CTTM) is a simple and novel method to prepare Pt-skin nanoparticles<sup>[23]</sup>. Mixture, including Pt and Ni precursors, was ultrasonicated before the solvents were evaporated. Then following  $H_2$  reduction, the

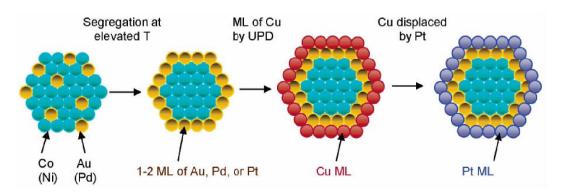


Fig. 1 Model for synthesis of Pt monolayer catalysts on non-noble metal-noble metal core-shell nanoparticles<sup>[13]</sup>

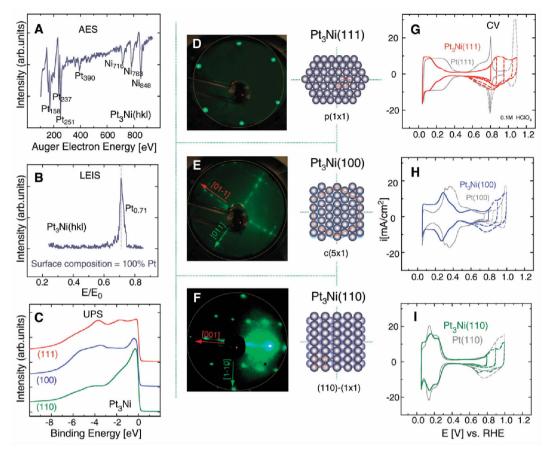


Fig. 2 Surface characterizations of the Pt<sub>3</sub>Ni single crystals in UHV and electrochemical environments<sup>[14]</sup>

A. AES spectrum; B. LEIS spectrum, where *E* is the energy of scattered electrons, and *E*<sub>0</sub> is the energy of the incident ion beam; C. UPS spectra; D to F. LEED patterns with the corresponding ball models; G to I. Cyclic voltammograms of Pt<sub>3</sub>Ni single crystals in 0.1 mol·L<sup>-1</sup> HClO<sub>4</sub> compared to those of the corresponding Pt single crystal (gray curves). RHE, reversible hydrogen electrode.

well-dispersed Pt-skin of Pt<sub>3</sub>Ni nanoparticles were obtained, as illustrated in Figure 3<sup>[10]</sup>. The outermost is made of Pt (white), and the subsurface is made of Pt (white) and Ni (red).

Using acid to treat PtM alloy also could be a strategy: acid could dissolve Co and Ni, and then following annealing, Pt-bimetallic catalysts with multilayered Pt-skin surfaces could be made. This method is easy to be operated, and the acid could use HClO<sub>4</sub> or HCl<sup>[24]</sup>. The dealloying methods include chemical dealloying and electrochemical dealloying. The electrochemical dealloying method may led to the formation of a thin Pt skin layer<sup>[5]</sup>.

Chen et al.<sup>[25]</sup> applied the crystalline PtNi<sub>3</sub> polyhedra as a starting material, synthesized in oleylamine with 20.1 nm. Then it transformed in solution

under ambient conditions for 2 weeks by interior erosion into Pt<sub>3</sub>Ni nanoframes with surfaces that offer three-dimensional molecular accessibility. Controlled thermal treatment of the resulting nanoframes could form the desired Pt-skin surface structure, as shown in Figure 4.

# 2 Electrocatalytic Preformance of Pt-Skin Catalysts

Advancement on the controlled synthesis of Pt-skin nanoparticles has enabled the systematic studies of these materials for catalytic applications. No matter using electrochemical method or chemical method, the obtained Pt-skin bimetallic catalysts hold a better electrocatalytic performance than pure Pt. In the following, we describe the performances of Pt-skin electrocatalysts prepred by different methods

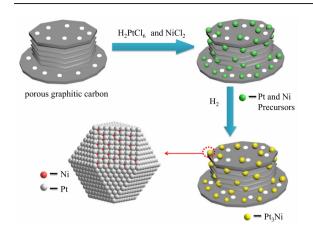


Fig. 3 A schematic illustration of Pt<sub>3</sub>Ni/PC (Pt-skin) catalyst preparation approach through combining impregnation and melt diffusion strategy of Pt and Ni precursors with the reductions of Pt and Ni precursors using the gas mixture (10vol.% H<sub>2</sub> in N<sub>2</sub>)<sup>[10]</sup>.

and then explain the relation between the Pt-skin nanostructures and their electrocatalytic performances.

The sizes, shapes, compositions, and supported materials of catalysts play important roles in electrochemical performances<sup>[26-27]</sup>. Oxygen reduction reaction (ORR) is a multi-electron process that may include a number of elementary steps intermediates. For pure Pt, the low effectiveness results from the higher

coverage by OH<sub>ad</sub> (where OH<sub>ad</sub> is the adsorbed hydroxyl layer), this is difficult to be further oxidized [14-15]. Pt-skin, Pt-skeleton, and pure polycrystalline Pt all have pure-Pt outermost layers, however, they are f ound to have different electronic structures, which originates from different arrangements of subsurface atoms of the alloying component. Their activity for ORR is following this order: Pt-skin > Pt-skeleton > Pt-polycrystalline<sup>[28]</sup>. For Pt/C, Pt particles were about  $3 \sim 4 \text{ nm}^{[29]}$ . To compare performance of Pt-skin catalysts, it is important to put Pt-skin catalysts on carbon supported materials, with the sizes of Pt-skin catalysts about  $3 \sim 4$  nm. Zhang et al. [10] used carbon as the supported material, and successfully prepared Pt<sub>3</sub>Ni with Pt-skin. This Pt<sub>3</sub>Ni with Pt-skin nanocatalysts showed over 300% increase in mass activity compared with Pt/C for ORR.

Meanwhile, the different low-index surfaces hold markedly different activities toward ORR: Pt<sub>3</sub>Ni (100)-skin < Pt<sub>3</sub>Ni(110)-skin <<< Pt<sub>3</sub>Ni(111)-skin, as seen in Figure 5<sup>[14]</sup>. Notably, the Pt<sub>3</sub>Ni(111)-skin (prepared by electrochemical method) is 10-fold more active than the corresponding Pt(111) and 90-fold more active than the current state-of-the-art Pt catalysts for ORR. The Pt<sub>3</sub>Ni nanoframe (Pt-skin) catalysts (prepared by chemical method) achieved a factor of 36

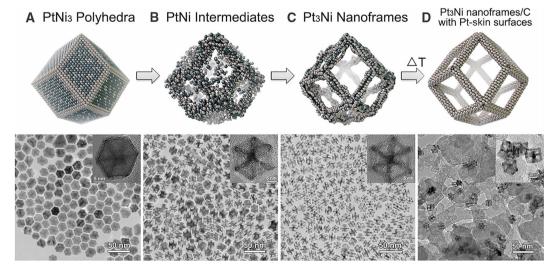


Fig. 4 Schematic illustrations and the corresponding TEM images of the samples obtained at four representative stages during the evolution process from polyhedra to nanoframes<sup>[25]</sup>

A. Initial solid  $PtNi_3$  polyhedra; B. PtNi intermediates; C. Final hollow  $Pt_3Ni$  nanoframes; D. Annealed  $Pt_3Ni$  nanoframes with Pt(111)-skin like surfaces dispersed on high surface area carbon

enhancement in mass activity and a factor of 22 enhancement in specific activity for ORR, relative to state-of-the-art Pt/C<sup>[25]</sup>. It is interesting that this Pt<sub>3</sub>Ni nanoframe (Pt-skin) also showed better activity than Pt/C toward hydrogen evolution reaction (HER). When doped other transition metals on Pt<sub>3</sub>Ni (Pt-skin), the obtained materials will achieve surprise outcomes. Huang et al. [11] surface-doped Pt<sub>3</sub>Ni octahedral supported on carbon with transition metals, termed M-Pt<sub>3</sub>Ni/C, where M is V, Cr, Mn, Fe, Co, Mo, W and Re. The Mo-Pt<sub>3</sub>Ni/C, which were prepared by chemical method, revealed the best ORR activity, with 10.3 mA·cm<sup>-2</sup> (specific activity) and 6.98  $A \cdot mg_{P}^{-1}$  (mass activity), which are 81- and 73-fold enhancements, respectively, compared with the specific activity and mass activity of commercial Pt/C  $(0.127 \text{ mA} \cdot \text{cm}^{-2} \text{ and } 0.096 \text{ A} \cdot \text{mg}_{P^{-1}}).$ 

ORR is a multielectron reaction that may include a number of elementary steps involving different reaction intermediates<sup>[30]</sup>. From DFT calculations, the ideal ORR catalyst should bind oxygen around 0.2 eV weaker than Pt<sup>[31]</sup>. For Pt-skin catalysts

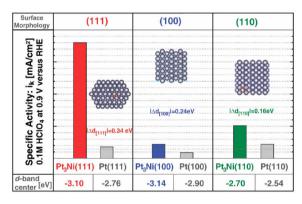


Fig. 5 Influences of the surface morphology and electronic surface property on the kinetics of ORR. RRDE measurements for ORR in HClO₄ (0.1 mol·L¹) at 333 K with 1600 r·min¹ on Pt₃Ni(hkl) surfaces as compared to the corresponding Pt(hkl) surfaces (a horizontal dashed gray line marks specific activity of polycrystalline Pt) are shown. Specific activity is given as a kinetic current density *i*<sub>k</sub>, measured at 0.9 V versus RHE. Values of d-band center position obtained from UPS spectra are listed for each surface morphology and compared between corresponding Pt₃Ni(hkl) and Pt(hkl) surfaces<sup>[14]</sup>.

(Pt-skin of PtM), the contraction of Pt surface atoms is induced by the adsorption of oxygenated species, which is determined by the M-induced modification of the Pt-skin electronic structure. For different low-index surfaces, the synergy between surface geometry and surface electronic structure for ORR is illustrated in Figure 5. For metals that bind oxygen too strongly, the rate is limited by the removal of adsorbed O and OH species: Pt-skin surface, which the electronic structure is modified by the M-induced, could cause a lower surface coverage of spectator oxygenated species and hence superior catalytic properties<sup>[14]</sup>. Pt alloyed by the 3d metals, which is dependent on the nature of the alloying component, show different rates of the ORR. Activity versus the experimentally measured d-band center relative to platinum is shown in Figure 7. The activity predicted from DFT simulations is shown in black, and the measured activity is shown in red. The Ni, Co, and Fe alloys exhibited a large improvement in activity compared to pure Pt[32].

#### 3 Conclusions

Recent advancement in the syntheses and electrocatalytic properties of Pt-skin catalysts for the ORR has been reviewed. The development in the electrochemical method and chemical method has been enabled systematic studies of these Pt-skin materials for possible applications. These systematic studies could eventually lead to advanced electrocatalysts and electrochemical systems suitable for a large-scale application. Although significant progress has been made, there is still a lack of complete fundamental understanding of materials properties at a nanoscale. Taking this into consideration, ex-situ and in-situ techniques could provide a new insight into properties of nanocatalysts that determine their catalytic performance. Electrochemical in-situ TEM has been given a lot of expectations, which could follow processes that may be responsible for dissolution of the particles. Therefore, this technique will be crucial for addressing issues related to the stability of the catalysts. In addition to advanced microscopy tools, surface-specific (spectroelectrochemical infrared mea-

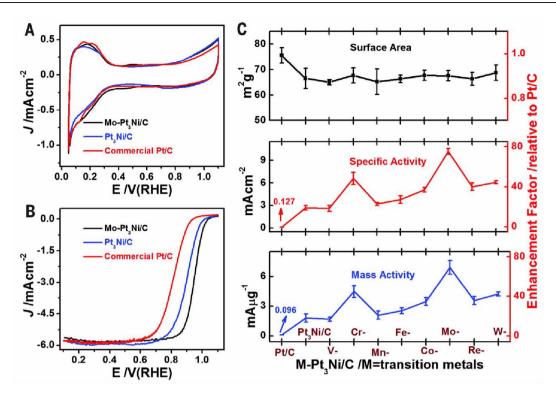


Fig. 6 Electrocatalytic properties of high-performance transition metal-doped octahedral Pt<sub>3</sub>Ni/C catalysts and a commercial Pt/C catalyst<sup>[11]</sup>

A. Cyclic voltammograms of octahedral Mo-Pt<sub>3</sub>Ni/C, octahedral Pt<sub>3</sub>Ni/C, and commercial Pt/C catalysts recorded at room temperature in N<sub>2</sub>-purged 0.1 mol·L<sup>-1</sup> HClO<sub>4</sub> solution with a sweep rate of 100 mV·s<sup>-1</sup>; B. ORR polarization curves of octahedral Mo-Pt<sub>3</sub>Ni/C, octahedral Pt<sub>3</sub>Ni/C, and commercial Pt/C catalysts recorded at room temperature in an O<sub>2</sub>-saturated 0.1 mol·L<sup>-1</sup> HClO<sub>4</sub> aqueous solution with a sweep rate of 10 mV·s<sup>-1</sup> and a rotation rate of 1600 r·min<sup>-1</sup>. C. The electrochemically active surface area (ECSA, top), specific activity (middle), and mass activity (bottom) at 0.9 V versus RHE for these transition metal-doped Pt<sub>3</sub>Ni/C catalysts, which are given as kinetic current densities normalized to the ECSA and the loading amount of Pt, respectively. In (A) and (B), current densities were normalized in reference to the geometric area of the RDE (0.196 cm<sup>2</sup>).

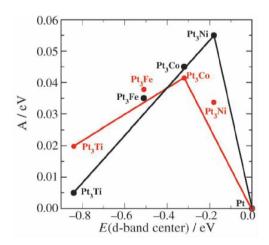


Fig. 7 Activity versus the experimentally measured d-band center relative to platinum. The activity predicted from DFT simulations is shown in black, and the measured activity is shown in red<sup>[32]</sup>.

surements) investigations could provide a reflective mode during electrochemical reaction to reveal bond-making and -breaking processes. All of these represent a great challenge, and the electrocatalytic mechanism will be made a great progress in the near future, which would assist to design ideal electrocatalysts for electrochemical reaction.

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## Pt 皮肤的 Pt 基双金属电催化的氧还原设计

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摘要:过去几十年,能源储存转化领域取得重大的进展,而 Pt 皮肤的 Pt 基双金属电催化剂在调控电催化剂的电子结构具有巨大的前景,特别是对于氧还原反应而言.本工作主要综述了最近几年关于 Pt皮肤的 Pt 基双金属电催化剂的设计制备以及其性能.本文的主要重点在于系统地综述了Pt皮肤的 Pt 基双金属电催化剂的合成方法,以及其对于氧还原反应的机理研究.

关键词: Pt;双金属; 电催化剂; 氧还原