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Manganese-tuned chemical etching of a platinum–copper nanocatalyst with platinum-rich surfaces

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HIGHLIGHTS

- PtCu particles with Pt-rich surfaces were used as precursors for etching.
- Manganese-tuned etching induced the formation of abundant Pt active sites.
- MOR activity of MnA-PtCu/C was ca. 4.0 times higher than that of Pt/C.
- Catalytic durability of MnA-PtCu/C towards MOR was improved significantly.

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ABSTRACT

This work presents a modified chemical etching strategy to fabricate binary metal nanocatalysts with large active areas. The strategy employs PtCu alloy particles with Pt-rich outer layers as the precursor and manganese species to manipulate the acid leaching processes. X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy techniques are used to analyze the catalyst structures and the tuning mechanism of manganese species during etching. It is found that the introduction of manganese species allows more Pt active sites to be formed onto the catalyst surface after etching, possibly due to reduction in the number of Pt atoms enclosed inside particles. The electrochemically active surface area of the synthetic MnA-PtCu/C catalyst increases by 90% relative to commercial Pt/C catalyst. As a result of the increase in active areas and the additional promotion effects by Cu, the MnA-PtCu/C catalyst reveals a methanol oxidation activity 1.7 and 4.0 times higher than that of the synthetic PtCu/C and commercial Pt/C catalysts, respectively.

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1. Introduction

Carbon-supported Pt nanoparticles are currently the most widely used nanocatalysts in proton exchange membrane fuel cells (PEMFCs) [1–5]. These catalysts, however, are not only expensive, but have limited applications due to low natural reservation of Pt. Alloying Pt with other low-cost transition metals, e.g. Ni, Fe, Cu, Sn and Pb, was demonstrated as an effective approach to simultaneously reduce Pt loading and enhance catalytic activity [6–9]. Among these transition metals, Cu stands out for its ability to combine with Pt toward enhanced oxygen reduction reaction (ORR) for the cathode of PEMFCs, and its ease of promoting catalytic activities of Pt anodes toward electro-oxidation of small organic molecules such as methanol, ethanol and formic acid [10–13]. Enhancement in catalytic properties of PtCu materials was generally attributed to modification in physical properties, e.g. electronic effects (ligand effect),

geometric effects (compressive strain), surface roughness (facets and steps) and particle size effect [14–16].

Various bottom-up approaches, such as impregnation reduction, electrodeposition and hydrothermal reduction, were used to fabricate binary Pt-based nanocatalysts [17–20]. However, these approaches usually involve an excessive use of organic solvents and surfactants. Additionally, catalyst composition is generally difficult to control, particularly for the preparation of alloy nanoparticles with a high content of non-noble metals (over 50 at.%). Numerous recent studies have used dealloying of Pt-based materials, through which one component is selectively etched from the binary/ternary alloy, for the preparation of binary metal nanoparticles. Dealloyed materials usually possess the desirable characteristic of Pt-rich shells and nanoporous structure which contains concave areas [21–23]. For example, PtCu core–shell nanoparticles were fabricated via electrochemically dealloying a bulk Pt–Cu binary alloy by Ge's group [24]. They found that the dealloyed nanoporous PtCu material exhibited enhanced electrocatalytic activities toward formic acid oxidation reaction (FAOR) and ORR via a mechanism of tailoring the compressive strain of metal particles. Qiu et al. prepared a

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nanoporous PtCu catalyst with high Cu content via a one-step chemical dealloying process of bulk $\text{Pt}_4\text{Cu}_{21}\text{Mn}_{75}$ precursor in an $(\text{NH}_4)_2\text{SO}_4$ aqueous solution [25]. They revealed that the dealloying processes to the formation of core-shell nanoparticles involved fast dissolution of Mn and slow dissolution of Cu. In comparison with electrochemical dealloying, chemical dealloying possesses the unique advantage of scalable production.

With that being said, however, it has been commonly reported that dealloyed PtCu materials showed similar or smaller electrochemically active surface areas in comparison with commercial Pt/C material. An investigation of the synthesis found that the Pt-containing precursors for dealloying were compositionally uniform materials. For these uniform precursors, platinum may partially remain inside the particles even after dealloying, leading to a loss of Pt active sites. Thus, one solution is to use the precursors with Pt-rich outer layers for etching. This proposal is also supported by the fact that the driving force from the redox potential difference is easily powerful enough to reduce Pt ions and deposit them onto Cu surfaces. In addition, the PtCu etching processes are easily further optimized by introducing a third species on the precursor surface. To the best of our knowledge, however, very little exploration on this aspect has been conducted so far.

In this work, Mn was selected to optimize the etching processes of PtCu precursor because it has a high redox potential at high valence, which makes it easy to deposit together with Pt on Cu surfaces through galvanic reactions. The deposited Mn oxides can be readily removed in an acid medium with reducing species. The PtCu composite can be prepared through this Mn-assisted etching approach, and the product is defined as MnA-PtCu/C. An initial Cu/Pt atomic ratio was set as 50:1 in order to facilitate fragmentation of the precursor [10], maximizing the effective electrochemically active surface area (ECSA). The surface analysis of the precursor during the etching processes was collected by X-ray photoelectron spectroscopy; a possible tuning mechanism of Mn toward Pt atom assembly on the particle surfaces was proposed. Methanol oxidation reaction (MOR) was used to test the catalytic performance of the PtCu nanoparticles.

2. Experimental

2.1. Synthesis of catalysts

Active carbon (Vulcan XC-72R) was pretreated with 5 M HNO_3 at 110 °C for 6 h. The mixture was subsequently neutralized with sodium hydroxide, filtered, rinsed with double distilled water and dried at 60 °C for 24 h. Acid treating was used to produce surface oxygen-containing groups such as carbonyl, carboxyl and hydroxyl groups, which provide anchoring sites for metal particle deposition [26]. The MnA-PtCu/C alloy catalyst was prepared via surface substitution and acid leaching. During synthesis, 30 ml of 93.4 mM CuCl_2 solution was diluted with 270 ml of double distilled water. 90 mg of the pretreated Vulcan XC-72R carbon was dispersed in 300 ml of double distilled water under ultrasonic stirring for 30 min; then 300 mg of NaBH_4 was magnetically stirred with the carbon suspension. The CuCl_2 solution was then dropped into the carbon/ NaBH_4 mixture and the reduction reaction was conducted for 1 h. The resultant suspension was filtered and rinsed to remove any residual NaBH_4 ; then the filter residue was rapidly dispersed in 200 ml of double distilled water again. 100 ml solution containing 3 ml of potassium permanganate (18.9 mM) and 3 ml of chloroplatinic acid (18.9 mM) was then added into this suspension. The galvanic substitution reactions between Mn (VII), Pt (IV) and Cu (0) were conducted for 2 h to obtain a PtMnCu/C precursor. Then, 2 ml of concentrated nitric acid (~65 wt.%) was slowly added into the mixture and the acid leaching reaction was conducted for 18 h to ensure complete dissolution of redundant metals.

Finally, the mixture was filtered, rinsed with double distilled water and dried overnight at 60 °C in air. Other two materials were prepared for comparison via the same method without the addition of potassium permanganate or chloroplatinic acid, and are defined as PtCu/C and (MnCu)/C, respectively.

2.2. Physical and electrochemical characterization

The contents of Pt, Mn and Cu in the catalytic materials were determined using an Ultima2 inductively coupled plasma optical emission spectroscopy (ICP-OES, Jobin Yvon). For the sample preparation, the carbon in the materials was removed at 700 °C in air. Any residue was dissolved by aqua regia at room temperature for 24 h; the solution was transferred to a centrifuge and diluted with double distilled water for analysis. X-ray power diffraction (XRD) was conducted with a Philip X'Pert Pro MPP diffractometer using a $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation source. The morphology, dispersed state and size distribution of the metal particles were characterized using a JEOL JEM-2010 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. The chemical valences of Pt, Mn and Cu in the materials during and after synthesis were analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250) with an Al $\text{K}\alpha$ X-ray source at 1487 eV. The chamber pressure was kept below 3×10^{-10} mbar during testing and specific correction was conducted the C 1s binding energy of 285 eV.

Electrochemical measurements were performed using a CHI604 electrochemical work station (CH Instrument Inc.). The reference electrode was the $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ M H}_2\text{SO}_4$ electrode (MMS) (0.62 V vs. SHE) and the counter electrode was the platinum net. A glassy carbon (0.1256 cm^2) electrode covered by the catalytic material was used as the working electrode. For Pt/C working electrode preparation, 5 mg of the Pt/C (JM) catalyst (10 wt.% Pt) was ultrasonically stirred in 1 ml solution containing 50 μl of 5 wt.% Nafion solution (DuPont, USA) and 950 μl of ethanol. 4 μl of the slurry was coated on the polished glassy carbon electrode surface and the electrode was dried at room temperature in air for 30 min. The MnA-PtCu/C and PtCu/C working electrodes were prepared in the same way. The amount of other catalysts for preparation of the slurry depended upon their practical Pt loading, determined by ICP-OES analysis. A total Pt loading for each catalytic material on the electrode was set at 2 μg . Prior to taking measurements, the 0.5 M H_2SO_4 and 0.5 M $\text{H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ electrolytes were first deaerated with high purity N_2 . The working electrodes were pretreated in the 0.5 M H_2SO_4 solution by cyclic voltammetry (CV) at a scan rate of 50 mV s^{-1} for several cycles in order to obtain a stable electrochemical response.

CO stripping experiments were conducted using the following procedure: an H_2SO_4 solution was first deaerated with high purity N_2 . Subsequently, CO was admitted into the solution in the electrolytic cell and the adsorption process on the catalysts was maintained for 15 min. Excess CO in the solution was eliminated with high purity N_2 before the stripping test. All electrochemical measurements were performed at room temperature.

3. Results and discussion

Table 1 lists the contents of Pt, Cu and Mn in the as-prepared catalysts. The practical Pt loading is 9.3 wt.% for MnA-PtCu/C with a Cu/Pt atomic ratio of 1.48:1 and 11.2 wt.% for PtCu/C with the Cu/Pt atomic ratio of 0.49:1, respectively. The Cu/Pt atomic ratio in the MnA-PtCu/C material is relatively high compared with that of numerous other dealloyed PtCu materials reported previously [10,11,21,24,25], suggesting that the Mn species-tuned etching processes using a precursor with Pt-rich outer layers, is an effective approach to the synthesis of Pt-based nanocatalysts with a high

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