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One-pot synthesis of Ir@Pt nanodendrites as highly active bifunctional electrocatalysts for oxygen reduction and oxygen evolution in acidic medium

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A unitized regenerative fuel cell (URFC) is an electrochemical energy storage system combining a fuel cell and a water electrolyzer into one cell stack. Compared with conventional secondary batteries, URFCs have many advantages, such as long-term energy storage without self-discharge, high specific energy density and low environmental impacts [1]. URFCs can be applied not only in space field, but also in an on-site energy storage device used in photovoltaic and wind energy systems [2]. However, one of the most difficult challenges in the development of URFCs is the fabrication of active bifunctional electrocatalysts for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the oxygen electrode [3–11]. Although some transition metal oxide can be used as catalyst for both ORR and OER in alkaline medium [12], the practical bifunctional electrocatalyst applied in acidic medium is composed of two efficient electrocatalyst for ORR (e.g., Pt blacks) and OER (e.g., Ir/Ru oxides), respectively. The conventional bifunctional electrocatalysts are the physical mixture of Pt blacks and Ir blacks or Ir/Ru oxides [4,7]. Nevertheless, both of them are hardly well dispersed in the solvent, resulting in poor interdispersion of the two kinds of electrocatalysts and low bifunctional performance [8]. To resolve this problem, some researchers used Pt blacks or Ir/Ru oxides as support and deposited the other metal on the support [3,5,6,8,10]. However, both Pt blacks and Ir/Ru oxides are not ideal catalyst support due to their low specific surface areas. Moreover, the conventional preparation methods such as impregnation [10], adsorption/heat treatment [6] or deposition by chemical reduction [5] of one component on the other often lead to the formation of one catalyst component that is relatively large, irregular in morphology and non-uniform in size and composition. For this reason, other researchers [9,11] tried to develop supported Ir and Pt nanoparticles as bifunctional electrocatalysts. However, the exploring of supporting materials with high surface area, high electronic conductivity, appropriate porous structure and corrosion resistance at the same time is difficult.

Recently, the core-shell structured nanocatalysts have been used in proton exchange membrane fuel cells [13]. However, core-shell structured bifunctional electrocatalysts have not been reported. Hence we made use of successive reduction method to form dendritic Ir@Pt core-shell catalytic nanocatalysts with both Ir and Pt exposed. This Ir@Pt nanocatalyst is well dispersed and shows a uniform elemental distribution for every single catalyst particle, which leads to the better bifunctional performance of Ir@Pt than that of the mixture of Pt and Ir blacks.

2. Experimental

2.1. Materials synthesis

Ir nanodendrites were obtained from the reduction of H2IrCl6 by NaBH4 (NaBH4/H2IrCl6 molar ratio = 30:1) in the presence of cetyltrimethylammonium chloride (CTAC) at 333 K for 5 h in aqueous...
solutions. Subsequently, a given amount of H$_2$PtCl$_6$ and ascorbic acid (AA) were added and the mixture was stirred at 333 K for 6 h. During this time, the H$_2$PtCl$_6$ was reduced by AA and the metallic Pt was deposited on Ir nanodendrites, which gave rise to Ir@Pt core-shell structure. The obtained Ir@Pt bifunctional electrocatalysts was denoted as Ir$_{50}$@Pt$_{50}$ and Ir$_{67}$@Pt$_{33}$ for Ir/Pt molar ratios of 50:50 and 67:33, respectively. The EDX (Oxford Inca) analysis revealed that the actual Ir/Pt molar ratio for Ir$_{50}$@Pt$_{50}$ and Ir$_{67}$@Pt$_{33}$ was 44:56 and 62:38, respectively. For comparison, the mixture of commercial Pt and Ir blacks (JM) with Ir/Pt molar ratio of 57:43 measured by EDX was used as the reference catalyst, and it was denoted as Ir$_{57}$Pt$_{43}$. All catalysts were dispersed in water for further characterization and the content of Pt in the catalyst slurry was determined by inductively coupled plasma (ICP) analysis, while the content of Ir was calculated by the content of Pt and the Ir/Pt molar ratio. TEM images were taken using JEOL JEM-2000EX microscope. High-resolution TEM (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) were performed on FEI Tecnai G$^2$ Spirit F30 microscope. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Shimadzu Amicus instrument with Mg (Kα) X-ray radiation.

2.2. Electrochemical study

Electrochemical studies were performed at room temperature on CHI-730D electrochemical station with a rotating disk electrode (RDE) system in a conventional three electrode electrochemical system. Saturated calomel electrode (SCE), Pt foil and RDE with a glassy carbon disk were served as reference, counter and working electrode, respectively. All electrode potentials were given versus reversible hydrogen electrode (RHE). Based on the Ir and Pt concentration in the slurry, the Pt and Ir loading on RDE for Ir$_{57}$Pt$_{43}$, Ir$_{50}$@Pt$_{50}$ and Ir$_{67}$@Pt$_{33}$ was 30.9 and 40.4 μg cm$^{-2}$, 30.3 and 24.0 μg cm$^{-2}$, and 14.3 and 23.0 μg cm$^{-2}$, respectively. The ORR polarization curves were performed in O$_2$-saturated 0.5 M H$_2$SO$_4$ at 10 mV s$^{-1}$ with a rotation rate of 1600 rpm. The kinetic current of the catalysts was calculated by using the well-known mass-transport correction for rotating disk electrodes [14]. Prior to OER measurement, the electrocatalysts were swept three cycles between 0 and 1.54 V at 50 mV s$^{-1}$ in N$_2$-purged 0.5 M H$_2$SO$_4$ to oxidize the surface of Ir [15]. And then, the linear sweep voltammograms (LSVs) were recorded from 1.04 to 1.64 V at 5 mV s$^{-1}$ with a rotation rate of 1600 rpm. Subsequently, the cyclic voltammograms (CVs) were recorded between 0 and 1.44 V at 50 mV s$^{-1}$. The specific electrochemical surface area (ECSA) was estimated by measuring the integral charge of the hydrogen desorption area using 0.21 mC cm$^{-2}$Pt as the conversion factor [14].

3. Results and discussion

The Ir nanodendrites shown in Fig. 1 (a) are well dispersed and the size of every nanodendrite is evenly distributed around 15 nm which is remarkably smaller than that of Ir blacks (JM) (inset of Fig. 1 (d)). Accordingly, it is more suitable for Ir nanodendrites to serve as support for Pt. The TEM and HRTEM images of Ir$_{67}$@Pt$_{33}$ nanodendrites in Fig. 1 (b) illustrate the dendritic nanostructure of Ir$_{67}$@Pt$_{33}$ similar to Ir nanodendrites. The distinct lattice fringes shown in the HRTEM image indicate good crystallinity of the Ir$_{67}$@Pt$_{33}$. The elemental maps and line profiles detected in the HAADF-STEM-EDX analysis (Fig. 1 (c)) reveal that Pt is deposited on the surface of Ir. Moreover, the elemental maps of several randomly selected nanodendrites suggest that every nanodendrite is composed of Ir and Pt (not shown). In contrast, it is easy to find large

![Fig. 1. (a) TEM image of Ir nanodendrites. (b) TEM and (inset) HRTEM images of Ir$_{67}$@Pt$_{33}$ nanodendrites. (c) HAADF-STEM image and elemental maps and line profiles of Ir$_{67}$@Pt$_{33}$. (d) TEM images of Ir$_{57}$Pt$_{43}$ and (inset) Pt and Ir blacks. The scale bars unmarked are 50 nm.](image-url)
agglomerates of Pt or Ir in Ir57Pt43 (Fig. 1 (d)). The even elemental distribution of Pt and Ir will probably result in better bifunctional performance of the Ir@Pt electrocatalysts.

The surface Pt/Ir atomic ratio obtained from XPS measurements is 1.28 and 0.77 for Ir50@Pt50 and Ir67@Pt33 nanodendrites, respectively, confirming that Pt is enriched on the surface. Additionally, the above result reveals that more Ir surface is exposed on Ir67@Pt33 than that of Ir50@Pt50, which will be beneficial to the OER activity of Ir67@Pt33.

Fig. 2 (b) shows the CV curves of Ir50@Pt50, Ir67@Pt33 and Ir57Pt43 after electrochemical oxidation. The surface of Ir was oxidized, thus no peaks were observed for Ir in the Hupd region (Fig. 2 (a)) and the contribution of Ir to ECSA can be neglected. The specific-ECSA of Ir50@Pt50 and Ir67@Pt33 is 54.1 and 72.0 m² gPt⁻¹, which is 2.7 and 3.6 times that of Ir57Pt43 (19.6 m² gPt⁻¹), respectively, indicating the better dispersion of Pt on Ir@Pt than that of Pt blacks. In addition, the peak around 0.9 V on the CV curve attributed to the Ir(III)/Ir(IV) redox couple become more obvious with the increase of Ir/Pt molar ratio, suggesting more Ir active sites are exposed on Ir67@Pt33 [10], which is consistent with the result of XPS.

The polarization curves for ORR on Ir50@Pt50, Ir67@Pt33 and Ir57Pt43 are presented in Fig. 2 (c). The Pt mass activity of ORR at 0.85 V for Ir50@Pt50 and Ir67@Pt33 is ca. 1.6 and 2.4 times that of Ir57Pt43, respectively (Fig. 2 (c)). The higher ORR activity of Ir@Pt than Ir57Pt43 may probably come from two reasons. The first is the much higher specific-ECSA of Ir@Pt nanodendrites than Pt blacks [16]. Moreover, the exposed Ir surface and the effect of Ir core on the Pt shell may be another reason. It is reported that the lateral repulsion between the OH or O adsorbed on Ir and the OH adsorbed on a neighboring Pt atom (a block to ORR on Pt) will lower the coverage of OH on Pt [17]. And the electronic modifications of Pt shell induced by strain, ligand or segregation effects from Ir core may also enhance the ORR activity of Ir@Pt [18]. The greater Pt mass activity of ORR for Ir67@Pt33 than Ir50@Pt50 is owing to its higher specific-ECSA.

For the OER activity, Ir57Pt43 has the highest Ir mass activity followed by Ir50@Pt50 and Ir67@Pt33 (Fig. 2 (d)). On the basis of total metal mass, Ir57Pt43 still possesses the highest mass activity (289.6 mA mgmetal⁻¹), which is 1.5 times that of Ir50@Pt50 (187.4 mA mgmetal⁻¹). This enhanced OER activity of Ir@Pt nanodendrites than Ir57Pt43 is probably attributed to the dendritic structure [15] and the interaction between Ir core and Pt shell. Additionally, the exposed surface of Ir core for OER on Ir67@Pt33 is higher than that of Ir57Pt43 (Fig. 2 (b) and XPS results), which causes the greater Ir mass activity of Ir67@Pt33 than that of Ir50@Pt50. Furthermore, in order to maintain the conduction path of electrons, the mass fraction of Pt in the bifunctional electrocatalysts should not be too low, because Ir will eventually be oxidized to low electronic conductive Ir oxides [6]. In addition, the total metal mass activity of ORR for Ir67@Pt33 is lower than that of Ir50@Pt50 (Fig. 2 (c)), and if the fraction of Pt in Ir@Pt further declines, the total metal mass activity of OER will be even lower. Therefore, we considered that the Ir67@Pt33 should approach the optimum Ir/Pt molar ratio.

4. Conclusions

Nanodendritic Ir@Pt bifunctional electrocatalysts were synthesized by a one-pot synthesis method. In addition to good dispersion and uniform composition distribution, the Ir@Pt bifunctional electrocatalysts have shown a remarkable enhancement in the catalytic activity of ORR and OER in comparison with the mixture of commercial Ir and Pt blacks. The improvement of the ORR and OER activities is probably attributed to the better dispersion of Pt, interaction between Pt and Ir, and special morphology of Ir@Pt nanodendrites. This novel core-shell structure allows for the development of highly
active bifunctional electrocatalysts, with potential for the application in URFCs.

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