Gold-iridium bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions ☆

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ABSTRACT

Carbon supported gold-iridium composite (AuIr/C) was synthesized by a facile one-step process and was investigated as the bifunctional catalyst for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The physical properties of the AuIr/C composite were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Although the Au and Ir in the AuIr/C did not form alloy, it is clear that the introduction of Ir decreases the average Au particle size to 4.2 nm compared to that in the Au/C (10.1 nm). By systematical analysis on chemical state of metal surface via XPS and the electrochemical results, it was found that the Au surface for the Au/C can be activated by potential cycling from 0.12 V to 1.72 V, resulting in the increased surface roughness of Au, thus improving the ORR activity. By the same potential cycling, the Ir surface of the Ir/C was irreversibly oxidized, leading to degraded ORR activity but uninfluenced OER activity. For the AuIr/C, Ir protects Au against being oxidized due to the lower electronegativity of Ir. Combining the advantages of Au and Ir in catalyzing ORR and OER, the AuIr/C catalyst displays an enhanced catalytic activity to the ORR and a comparable OER activity. In the 50-cycle accelerated aging test for the ORR and OER, the AuIr/C displayed a satisfied stability, suggesting that the AuIr/C catalyst is a potential bifunctional catalyst for the oxygen electrode.

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1. Introduction

A unitized regenerative fuel cell (URFC) combines a fuel cell and a water electrolyzer into one cell stack [1–3]. Compared with conventional secondary batteries, URFCs have many merits, such as long-term energy storage without self-discharge, high specific energy density and low environmental impacts [4]. However, one of the considerable challenges in the development of URFCs is to explore not only active but also stable bifunctional electrocatalysts for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the oxygen electrode [5–7]. The large overpotentials for ORR and OER require the bifunctional electrocatalysts work in a wide potential window, while most materials cannot meet this end due to the instability. Over the past decades,

many kinds of materials have been explored for using as bifunctional electrocatalysts for OER and ORR, including various combinations of noble metals [8–11], 3d-metal (hydro)-oxides [12–16], perovskites [17–20], and carbon-based materials [21,22]. Among them, the conventional bifunctional electrocatalysts are the physical mixture of Pt blacks and Ir/Ru blacks or Ir/Ru oxides [10,23]. Carbon-based materials, perovskite oxides and 3d-metals, taking into consideration of their low cost and rich abundance in earth, have attracted extensive attention. However, these materials presented either a larger overpotential compared with Ir [19] or a poor durability. As reported, only 53%–70% of the catalytic activity was left after the stability test [14]. In consideration of the high overpotential and the unsatisfied stability of these non-noble metal catalysts, there is still a long way to go before practical application [13,15,24–26].

Gold nanoparticles are reported to be a promising ORR catalyst in alkaline media and are much abundant in earth compared with Ir and Pt [27–29]. Recently, Lee et al. have reported that gold was stable as the ORR catalyst even after at potentials as positive as 1.0 V vs. SCE [30]. However, gold is nearly inactive to the OER. Enlightened by the idea of developing a bifunctional catalyst combining advantages of Ir, the best OER catalyst, and Au, the stable

ORR catalyst, we prepared a AuIr/C catalyst by a one-step method using NaBH$_4$ as the reducing agent and cetyltrimethylammonium bromide (CTAB) as protective agent. The electrochemical test results show that the AuIr/C catalyst presents an enhanced ORR and OER catalytic activity and a high catalytic stability.

2. Experimental

2.1. Synthesis of catalysts

The carbon support (Vulcan XC-72 carbon black, $S_{BET} = 250$ m^2/g) was purchased from Cabot Corporation. All the chemicals are analytical reagents and used as received without any further treatment. A typical synthesis of the AuIr/C composite was described as follows. Firstly, 150.0 mL deionized water was added into an ice-water bathed three-neck flask followed by adding 2.789 mL of aqueous HAuCl$_4$·4H$_2$O (10.0 mg/mL), 1.787 mL of aqueous H$_2$IrCl$_6$·6H$_2$O (10.0 mg/mL) and 25.0 mL of aqueous cetyltrimethylammonium bromide (CTAB) (18.6 mg/mL) under vigorous stirring. After the mixture was stirred for about 30 min under the protection of N$_2$ gas, 25.0 mL of ice-cold aqueous NaBH$_4$ (4.7 mg/mL) was added quickly under protection of nitrogen. After about 4 h in ice-water bath, 80.0 mg of Vulcan XC-72 carbon black dispersed in 20.0 mL deionized water was added and the mixture was continuously stirred for 12 h at room temperature to allow metal particles deposit on carbon surface. The resultant slurry was filtrated, washed by deionized water, and dried at 75 °C in vacuum. The obtained black powder is denoted as AuIr/C (the nominal metal loading is 20 wt% and the mass ratio of Au and Ir is 2).

Au/C and Ir/C with a nominal metal loading of 20 wt% were prepared by the similar procedure for comparison. The physical mixture of the Au/C and the Ir/C, denoted as Au/C+Ir/C, was also used for comparison. The mass ratio of Au/C and Ir/C in the physical mixture is 2 to keep the physical mixture having the same composition with AuIr/C.

2.2. Physical characterization

The morphology and dispersion of the catalysts were characterized by transmission electron microscopy (TEM) on a JEOL JEM-2011EM microscope operated at 120 kV. The X-ray diffraction (XRD) patterns of the AuIr/C, Au/C and Ir/C were recorded on a Rigaku X-2000 diffractometer using Cu $K\alpha$ radiation with a Ni filter. The tube voltage and the tube current were kept at 40 kV and 100 mA, respectively. The sample was scanned with the 2θ angle from 15° to 90° at a scan rate of 5°/min. X-ray photoelectron spectroscope (XPS, ESCALAB250Xi) with X-ray sources of Al $K\alpha$ was used to investigate the elemental valence of the catalysts. The binding energies were regulated according to C 1s peak at 284.6 eV from the samples.

2.3. Electrochemical measurements

Rotating disk electrode (RDE) measurements were performed on an electrochemical workstation (CHI 760D, Chenhua Company). The preparation of the thin-film electrode was described as follows: 5.0 mg of catalyst powder was dispersed in 2.0 mL of ethanol plus 30 μL of 5 wt% Nafion® solution (DuPont) to form a well-dispersed ink. Then 20 μL of the ink was pipetted on a cleaned glassy carbon electrode (5 mm in diameter) and the solvent was evaporated at room temperature. The electrochemical experiments were carried out in a conventional three-electrode cell. The cyclic voltammetry experiments were performed in O$_2$ or N$_2$ saturated 0.1 M NaOH solution at room temperature. A Pt wire was used as a counter electrode and an Hg/HgO electrode in 0.1 M NaOH
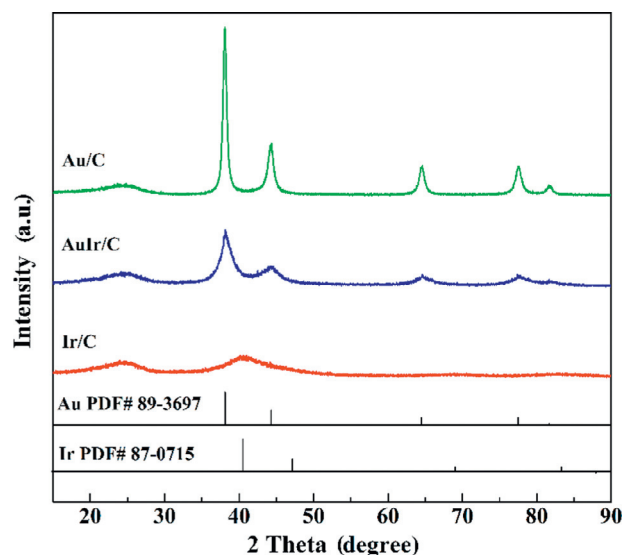

Fig. 1. X-ray diffraction (XRD) patterns of Au/C, Ir/C and AuIr/C.

solution (denoted as MMO) was acted as a reference electrode. All the potentials in this paper have been calibrated and converted to values vs. reversible hydrogen electrode (RHE). In order to evaluate the ORR and OER stability of the catalysts, an accelerated aging test was conducted in O$_2$ saturated 0.1 M NaOH electrolyte by holding the current at -3 mA/cm^2 and 10 mA/cm^2 for 50 s by turns. The stability test lasts for 5000 s, i.e. 50 cycles.

3. Results and discussion

3.1. Physical characterization of the catalysts

The crystal structures of the Au/C, Ir/C and AuIr/C composites were characterized by XRD as shown in Fig. 1. For comparison, the standard peak positions for Au (PDF 89-3697) and Ir (PDF 87-0715) are included in the bottom of Fig. 1. For all catalysts the peak locates at about 25° is attributed to the diffraction index of graphite (002) facet of carbon [31]. For the Au/C composite, the peaks located at about 38.2°, 44.4°, 64.6°, 77.5°, and 81.7° are attributed to the diffraction indices of (111), (200), (220), (311) and (222) crystal facets of Au, respectively. For the Ir/C catalyst, the peaks at 40.7°, 47.3°, 69.1° and 83.4° are attributed to Ir (111), (200), (220), (311) crystal facets, respectively. The diffraction peaks of Ir are broadened due to the small particle size. The average crystalline size of Ir for the Ir/C, calculated by Scherrer's formula [32], is 2.3 nm. As for the AuIr/C composite, the diffraction peak position accords well with that of Au, but no significant diffraction peak for Ir is observed, suggesting Au and Ir did not form alloy and Ir may exist in amorphous form. The average crystalline size of Au for the Au/C and AuIr/C composites, calculated by Scherrer's formula, is 10.1 nm and 4.2 nm, respectively.

We further analyze the morphology and the average particle sizes of the samples by TEM. As shown in Fig. 2(a), the dark aggregates in the Au/C are Au particles, which form a network-like structure. For the Ir/C in Fig. 2(c), the Ir nanoparticles are uniformly distributed on the carbon black and the statistic average Ir particle size is as small as 2.3 nm which is in accordance with the XRD result. For the AuIr/C (Fig. 2(b)), the dark dots aggregate slightly on the carbon supports. Combining with XRD and SEM mapping (Fig. 2(d)–(f)) analysis, the dark dots are determined to be Au and Ir nanoparticles and were distributed uniformly in the AuIr/C