



Short communication

Overlapping structure of platinum-iridium oxide layers and its electrocatalytic behavior on bifunctional oxygen electrode

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ABSTRACT

Pt-Ir/IrO₂-PtO₂ composite with an overlapping structure as oxygen-electrode catalyst has been prepared by doping Ir into Pt, doping Pt into IrO₂, and then making the two layers combined with each other. This structure helps achieve positive interior modification on Pt and IrO₂ and active coupling effect between Pt^{Ir} ~ PtIrO₂ layers. Electrochemical analyses show that Pt-Ir/IrO₂-PtO₂ possesses 81.4% higher ORR activity and 45.5% higher OER activity than Pt/IrO₂ catalyst. Pt-Ir/IrO₂-PtO₂ especially exhibits remarkable ORR and OER durabilities in life tests, which are attributed to the stable overlapping structure.

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1. Introduction

Unitized regenerative fuel cell (URFC) provides a new insight into energy conversion and storage. This device collects discrete energy [1–3], like solar energy, wind energy, and water energy, and stores it in chemical energy by the conversion: H₂O → H₂ + O₂. Inversely, the stored chemical energy can be converted to electrical energy when needed by a reverse conversion: H₂ + O₂ → H₂O [4,5]. URFC can work as a self-governed system and serve in certain special conditions, such as space stations, solar aircraft, ships, vehicles, and the off-grid regions [3,6–10]. It can also be incorporated into the state grid [11].

The considerable worldwide research is being undertaken for applications of URFC technology. However, the bifunctional catalyst issue is the major barrier for its further development. There are kinetically sluggish reactions on the oxygen electrode, where oxygen evolution reaction (OER) occurs in electrolyzing mode and, inversely, oxygen reduction reaction (ORR) occurs in fuel cell mode [12,13]. Taking into account all the oxygen catalysts explored so far, the Pt/IrO₂ (Pt for ORR, and IrO₂ for OER) is considered the best candidate and has shown promising applications [14]. Currently, the conventional approaches utilized for Pt/IrO₂ preparation involve: (1) Pt precursors were reduced and deposited on IrO₂ NPs [13]. (2) Porous Pt/IrO₂ was fabricated for improving mass-transfer performance [15]. (3) Pt and IrO₂ were loaded on ATO, ITO, and magnéli-phase titanium oxide [16, 17]. Nevertheless, the overpotential on Pt/IrO₂ for ORR or OER still

remains a high level, resulting in lower energy efficiency. In order to reduce the overpotential and enhance the catalytic performance, further exploration on Pt/IrO₂ catalyst is required. Our group [18] previously conducted a surface modification of Pt/IrO₂ catalyst and achieved significant improvement in ORR and OER performance. However, nearly no report hitherto has appeared on the interior modification of Pt/IrO₂ catalyst. Evidently, it is necessary to perform an intrinsic modification on Pt/IrO₂ and obtain desired catalytic activity and stability.

We report here the interior modification of Pt/IrO₂ catalyst by doping Ir into Pt, and doping Pt into IrO₂ to form Pt-Ir/IrO₂-PtO₂ overlapping structure, in which the coupling effect between Pt-Ir ~ IrO₂-PtO₂ layers occurs (Fig. 1). We focus on examining the influence of this modification and such a structure on the catalytic activities and stabilities. The reasons for preparation of Pt-Ir/IrO₂-PtO₂ catalyst include three main respects. (1) Pt-Ir/IrO₂-PtO₂ as a bifunctional catalyst is used in special fields, e.g., space station, space ship etc., so the cost is not the first thing to be considered. (2) The non-precious catalysts are being developed widely, but the practical performance is far from the precious catalysts. (3) Reducing catalyst loading and enhancing catalyst efficiency by creating a novel structure, such as Pt-Ir/IrO₂-PtO₂ combination, may be the feasible approach.

2. Experimental

2.1. Preparation of catalysts

Adams' method has successfully been used for preparation of platinum and iridium oxides [2,13]. For preparation of Pt doped IrO₂, 232 mg of H₂IrCl₆ and 11.5 mg of H₂PtCl₆ (Ir:Pt = 95:5 by weight)

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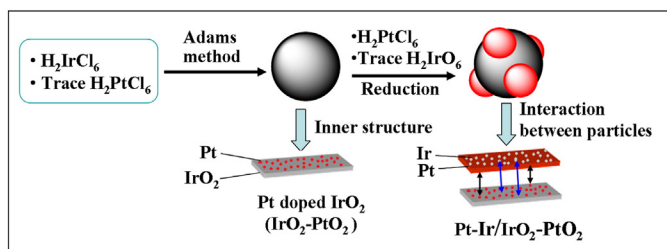


Fig. 1. Schematic diagram of Pt-Ir/IrO₂-PtO₂ preparation and structure.

were dissolved in 10 ml of distilled water. Then, the solution was poured into 50 g of ground NaNO₃ powder under stirring. After evaporating to dryness at 70 °C, the mixture was introduced into a ceramic furnace, pre-heated at 320 °C for 15 min, and further heated to 450 °C at 5 °C/min and maintained for 30 min. The mixture was treated with water, filtered, and dried in a vacuum oven at 80 °C.

For Pt-Ir/IrO₂-PtO₂ preparation, 50 mg of the obtained IrO₂-PtO₂ was ultrasonically dispersed in 40 ml of a mixed solution (glycol:isopropanol = 90:10 by volume). After stirring for 1 h, 127 mg of H₂PtCl₆ and 7.1 mg of H₂IrCl₆ in glycol (Pt:Ir = 47.5:2.5 by weight) was added to this solution, then adjusted the pH to 12, and further stirred for 3 h. Then the mixture was transferred to a microwave reactor and subjected to a rapid reaction at 135 °C for 60 s. Subsequently, it was filtered and dried in a vacuum oven at 80 °C [19].

2.2. Materials characterization

XRD pattern of Pt-Ir/IrO₂-PtO₂ catalyst was recorded on D/max-rB X-ray diffractometer (Japan) using Cu Kα as the radiation source. TEM images of Pt-Ir/IrO₂-PtO₂ catalyst were taken on TECNAI G2 F30 (USA). EDX spectra were collected on Hitachi-S-4700 analyzer (Japan).

2.3. Electrochemical measurements

The details of the electrochemical measurements were described elsewhere [18, 20, S1]. Briefly, LSVs for ORR were recorded within 0.4–1.1 V at 5 mV s⁻¹ in oxygen-saturated 0.5 M H₂SO₄. LSVs for OER were recorded within 1.3–1.6 V at 5 mV s⁻¹. EIS were recorded at 1.55 V (OER) and 0.85 V (ORR) from 10,000–0.01 Hz. Life tests were performed with accelerated potential cycling method (APCM, 2000 cycles) within 0.05–1.2 V (ORR) and 1.3–1.6 V (OER) at 50 mV s⁻¹ [21]. All the potentials are respect to the reversible hydrogen electrode (RHE). The catalyst loading on RDE is 0.024 mg. The mass activities were normalized with Pt weight [22].

3. Results and discussion

3.1. Physical analyses

The phase structure of the as-prepared Pt-Ir/IrO₂-PtO₂ catalyst is presented in Fig. 2. Fig. 2a and b show the reflections of single Pt nanoparticles (NPs) and single IrO₂ NPs (made by the same methods as Pt-Ir/IrO₂-PtO₂) respectively, in which the characteristic diffraction patterns for a face-centered cubic (fcc) structure of Pt, and a tetragonal structure of IrO₂ are observed. The broadened diffraction peaks indicate the formation of the ultrafine Pt and IrO₂ NPs, 2.9 nm for Pt NPs and 5.1 nm for IrO₂ NPs according to Scherrer's equation [20]. From Fig. 2c, we find all the corresponding peaks of Pt and IrO₂ appear in the Pt-Ir/IrO₂-PtO₂ curve, confirming coexistence of Pt and IrO₂ components in the sample. Noteworthy, it seems that the Ir doped in Pt, and the PtO₂ doped in IrO₂ do not appear in Fig. 2c. In fact, they substantially coexist in the form of overlapping combinations (Pt-Ir alloy, and IrO₂-PtO₂ solid solution), because either Ir and Pt, or IrO₂ and PtO₂ have extremely

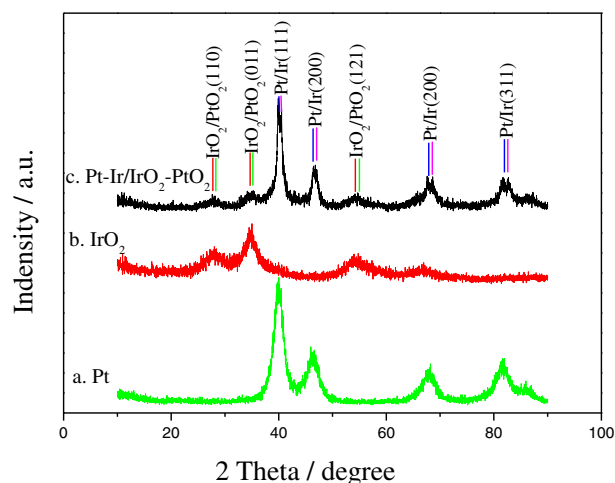


Fig. 2. XRD patterns of Pt (a), IrO₂ (b) and Pt-Ir/IrO₂-PtO₂ (c) catalysts.

similar property. The overlapping combinations of Ir with Pt, and IrO₂ with PtO₂ help to tune the electron structure of composite catalyst, and facilitate the enhancements of the ORR and OER activities (as shown in Fig. 5).

As is observed in Fig. 3a, the Pt-Ir/IrO₂-PtO₂ NPs are well dispersed with a narrow particle size distribution. The mean particle size of Pt-Ir/IrO₂-PtO₂ NPs is 5.3 nm, ranging from 4.7–6.2 nm (Fig. 3a inset). The high-resolution TEM image (Fig. 3b) demonstrates two different kinds of lattice fringes, one lattice fringe with a d-spacing value of 0.2265 nm corresponds to Pt-Ir (111) plane (JCPDS 65–2868), and another with a d-spacing value of 0.3181 nm corresponds to IrO₂-PtO₂ (110) plane (JCPDS 65–2822) [23]. This is an indication of coupling effect taking place between Pt-Ir and IrO₂-PtO₂ layers, although such spots are seldomly found due to the extremely low probability for both kinds of fringes coexisting at the same focal plane under TEM scene.

EDX spectrum of Pt-Ir/IrO₂-PtO₂ is displayed in Fig. 4, which is taken on a randomly selected region in SEM scene (Fig. S1) and allows achieving globe elemental analyses. We can readily find out the O, Pt, and Ir signals originated by electrons from different electron shells, confirming the presence of oxygen, platinum and iridium elements in the sample. The atomic Pt/Ir ratio detected in Pt-Ir/IrO₂-PtO₂ sample is ca. 1:1, which agrees with the designed value. The distributions of Pt and Ir elements in the testing region are presented in Fig. S1, and both of the elemental mappings intuitively display high degree of dispersivity of Pt (green dots) and Ir (red dots).

3.2. Electrochemical analyses

Fig. 5a illustrates the ORR measurements of Pt/IrO₂ and Pt-Ir/IrO₂-PtO₂ catalysts. It is clearly defined that ORR on the two catalysts is diffusion-controlled when the potential is less than 0.7 V, and mixing-controlled when the potential is more than 0.7 V. The onset potential of Pt-Ir/IrO₂-PtO₂ is higher than that of Pt/IrO₂ catalyst, verifying the higher ORR activity of Pt-Ir/IrO₂-PtO₂ catalyst preliminarily. Also, the kinetic current density (j_k , 0.85 V) of Pt/IrO₂, calculated by Koutecky-Levich equation, is 15.1 mA mg⁻¹, while that of Pt-Ir/IrO₂-PtO₂ is 27.4 mA mg⁻¹ (81.4% higher). It is further confirmed by EIS analyses (Fig. 5a insert), in which the polarization resistances (R_{ct}) of Pt/IrO₂ and Pt-Ir/IrO₂-PtO₂ are 68.8 and 39.1 Ω cm², respectively, suggesting an excellent activity on Pt-Ir/IrO₂-PtO₂ catalyst. Fig. 5b depicts the OER polarization on Pt/IrO₂ and Pt-Ir/IrO₂-PtO₂ catalysts. We can find that Pt-Ir/IrO₂-PtO₂ has a lower onset potential than Pt/IrO₂ catalyst, and that the current densities of Pt/IrO₂ and Pt-Ir/IrO₂-PtO₂ catalysts at 1.6 V are 142.5 and 207.3 mA mg⁻¹ (45.5% higher), respectively. The

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