



Multi-component nanoporous platinum–ruthenium–copper–osmium–iridium alloy with enhanced electrocatalytic activity towards methanol oxidation and oxygen reduction



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HIGHLIGHTS

- Np-PtRuCuOsIr alloy can be fabricated by ball-milling and subsequent dealloying.
- Np-PtRuCuOsIr shows superior activity and CO tolerance towards methanol oxidation.
- Np-PtRuCuOsIr shows greatly enhanced catalytic activity and durability toward ORR.

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ABSTRACT

Multi-component nanoporous platinum–ruthenium–copper–osmium–iridium (np-PtRuCuOsIr) electrocatalyst has been facilely fabricated by chemical dealloying of mechanically alloyed AlCuPtRuOsIr precursor. The np-PtRuCuOsIr catalyst exhibits a typical three-dimensional bi-continuous interpenetrating ligament/channel structure with a length scale of ~2.5 nm. The np-PtRuCuOsIr catalyst reaches a higher level in the mass activity (857.5 mA mg_{Pt}⁻¹) and specific activity (3.0 mA cm⁻²) towards methanol oxidation compared to the commercial PtC catalyst (229.5 mA mg_{Pt}⁻¹ and 0.5 mA cm⁻² respectively). Moreover, the CO stripping peak of np-PtRuCuOsIr is 0.54 V (vs. SCE), 130 mV negative shift in comparison with the commercial PtC (0.67 V vs. SCE). The half-wave potential of np-PtRuCuOsIr is 0.900 V vs. RHE, 36 mV positive compared with that of the commercial PtC (0.864 V vs. RHE). The np-PtRuCuOsIr catalyst also shows 1.8 and 3.8 times enhancement in the mass and specific activity towards oxygen reduction than the commercial PtC. Moreover, the np-PtRuCuOsIr alloy exhibits superior oxygen reduction activities even after 15 K cycles, indicating its excellent long-term stability. The present np-PtRuCuOsIr can act as a promising candidate for the electrocatalyst in direct methanol fuel cells (DMFCs).

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising future energy devices alternative to conventional energy generating

counterparts, because of their low pollutant emission, availability of methanol fuel, easy distribution and high energy-conversion efficiency of the fuel [1–5]. As an important component, the state-of-the-art electrocatalysts must ensure the methanol oxidation reaction (MOR) at anode and oxygen reduction reaction (ORR) at cathode to generate electricity with water and carbon dioxide as the by-products [5,6]. As of now, Pt catalysts are still the well-known and commonly-adopted materials for DMFCs. However, major shortcomings hindering the successful application of DMFCs are low activity, serious CO poisoning, sluggish ORR kinetics and

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poor durability of Pt-based catalysts. To decrease the addition amount of Pt and enhance its utilization efficiency, one common strategy is to synthesize Pt-containing nanocatalysts through alloying Pt with other nonprecious metals. Over the past decade, incorporating other metals (e.g. Ru [7–9], Ni [10,11], Co [11,12], Fe [13], Cu [14] and Pd [15,16]) with platinum to generate alloyed nanostructures represents a robust approach toward improved catalytic performance. Among these, PtRu catalysts were believed to be the more suitable catalysts due to their completely rapid, two-step oxidation mechanism [17,18]. Moreover, it has been found that the compositional improvement of alloying elements substantially boosts the catalytic properties of electrocatalysts. Until recently, sufficient efforts have been devoted to the synthesis of PtRu-based catalysts [3,6,19–21] compared to other Pt catalysts. For example, Reddington et al. [6] brought a breakthrough in finding that multicomponent PtRuOsIr alloy catalyst exhibits significantly higher activity than PtRu. Whitacre et al. [22] also investigated a low Pt loaded catalyst ($\text{Ni}_{31}\text{Zr}_{13}\text{Pt}_{33}\text{Ru}_{23}$) with great activity towards MOR.

On the other side, the commercialization of DMFCs awaits not only efficient usage of platinum, but cost-effective preparation methods and techniques. Various synthetic strategies, such as microemulsions [9,21], microwave irradiation [23–25], electrodeposition [26] and chemical reduction [6,27] have been employed to prepare alloy electrocatalysts including multiple elements. However, all of these include meticulous chemical steps, use costly surfactant molecules, and require a substantial number of separation and washing steps [21,28]. This turns down the hope to have as many 3d metals as possible in the alloy catalyst for performance improvement and reduction of cost. Consequently these methods lead to the rather high threshold of large-scale production and application. Dealloying, during which an alloy is ‘parted’ by the selective dissolution of the most electrochemically active element(s) and the retaining noble one evolves to a bi-continuous structure of metal-and-void with an average ligament size at the nanoscale level [29]. This technique has recently been receiving considerable attention for tailoring nanoporous metallic materials with high specific surface areas aiming at acquiring improved properties in various fields such as sensing [30], actuation [31] and catalytic properties towards small organic molecules [32,33]. To date, nanoporous metals (e.g. Cu [34], Pd [35,36], Ag [37,38] etc.) and alloys (e.g. PdNi [32,33], PdCo [36], PtCu [39], PtAu [28,40] etc.) have been successfully synthesized through dealloying. In addition, morphological aspects and underlying physical mechanisms of dealloying process have also aroused considerable attention [29]. Our group has successfully fabricated a series of alloy nanostructures through this rapid and simple method [28,32,38,41].

In the present investigation, the peculiar nanoporous structures of np-PtRuCuOsIr can be directly fabricated by mild chemical dealloying of multicomponent AlCu-based precursor alloy which was obtained through a simple mechanical alloying process. The facile and green technique shows great advantages in the design of nanostructured alloy electrocatalysts: (i) the combination of mechanical alloying with dealloying could reduce the complexity and limitation to design various multiple-component nanoporous alloys, (ii) the nanoporous alloy catalysts can be produced in mass (dozens of grams) to meet the requirement of commercialization of electrocatalysts, (iii) the obtained unique three-dimensional bi-continuous interpenetrating ligament/channel structure proves to be ideal to the electro-catalytic reaction including MOR and ORR. This new catalyst was characterized with electrochemical measurements at the anode as well as the cathode for DMFCs. Our testing results show that the np-PtRuCuOsIr catalyst performs far better than the commercial PtC catalyst. Considering the advantages of design technology as well as the enhanced electrocatalytic

activities, this novel np-PtRuCuOsIr alloy is expected to act as a promising electrocatalyst in the DMFCs.

2. Experimental section

To achieve easy dealloying and good control for the resulting alloy composition, a multi-component $\text{Al}_{66}\text{Cu}_{30}(\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5)_4$ alloy (nominal composition, at.%) was chosen as the precursor. The starting $\text{Al}_{66}\text{Cu}_{30}(\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5)_4$ alloy powders was prepared from pure Al, Cu, Pt, Ru, Os and Ir (99.9 wt.%) powders using a planetary ball milling machine. Then dealloying of the $\text{Al}_{66}\text{Cu}_{30}(\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5)_4$ alloy powders was performed in a 1 M HNO_3 solution at room temperature until no obvious bubbles emerged. After the facile dealloying, the as-dealloyed samples were rinsed in distilled water and dehydrated alcohol to gain the final np-PtRuCuOsIr.

X-ray diffractograms of the mechanically alloyed $\text{Al}_{66}\text{Cu}_{30}(\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5)_4$ precursor and as-dealloyed samples were obtained by an X-ray diffractometer (XRD, Rigaku D/max-rB) with Cu $K\alpha$ radiation. The chemical compositions of the as-dealloyed samples were determined by an energy-dispersive X-ray (EDX) analyzer in an area-analysis mode (a typical area of $50\ \mu\text{m} \times 50\ \mu\text{m}$), in order to accurately obtain the compositions of the samples. At least three areas were analyzed and the average values were given in the results. The microstructure of the as-dealloyed catalyst was characterized using a transmission electron microscope (TEM, FEI Tecnai G2), and high-resolution TEM (HRTEM, FEI Tecnai G2). In addition, selected-area electron diffraction (SAED) patterns were also obtained. The fast Fourier transform (FFT) patterns were obtained from the corresponding HRTEM images using a software named Gatan Digital Micrograph.

All electrochemical measurements were carried out in a standard three-electrode cell with a CHI 760E Potentiostat. A saturated calomel electrode (SCE) was used as the reference electrode and a bright Pt plate was used as the counter electrode for the electrochemical measurements of methanol electro-oxidation. We benchmarked the electrochemical properties of the np-PtRuCuOsIr against the commercial (Johnson's Matthey) PtC (40 wt.%) catalyst under the identical experimental conditions. The catalyst ink was prepared as follows: 2.0 mg of the synthesized alloy, 3.0 mg XC-72 carbon powder, 1.5 mL isopropanol and 0.5 mL Nafion solution (0.5 wt.%) were ultrasonically mixed for 30 min. Afterward, 4 μL homogeneously mixed catalyst suspension was dropped on a freshly polished glassy carbon (GC) electrode with a diameter of 4 mm (apparent surface area, $0.126\ \text{cm}^2$). The loading of Pt for the commercial PtC catalyst was $31.7\ \mu\text{g}_{\text{Pt}}^{-1}\ \text{cm}^{-2}$ and that for the np-PtRuCuOsIr was $18.0\ \mu\text{g}_{\text{Pt}}^{-1}\ \text{cm}^{-2}$ (with total metal loading of $31.7\ \mu\text{g}^{-1}\ \text{cm}^{-2}$), which were consistent with some examined electrocatalysts in the literature [42,43]. The coated GC electrode was used as the working electrode after drying in a vacuum tank at room temperature for at least 3 h. The cyclic voltammetry (CV) behavior of the catalyst was determined in a 0.5 M H_2SO_4 solution deaerated with N_2 . Several scans were performed until reproducible voltammograms were obtained. The electrocatalytic activity of the as-prepared catalyst for the methanol oxidation was characterized in a N_2 -purged 0.5 M $\text{H}_2\text{SO}_4 + 0.5\ \text{M}\ \text{CH}_3\text{OH}$ solution at $30\ ^\circ\text{C}$. The CO tolerance was characterized by CO stripping firstly maintaining the working electrode in the 0.5 M H_2SO_4 solution saturated with bubbling CO gas for the period of 500 s. After CO adsorption, the electrode was transferred into a CO-free 0.5 M H_2SO_4 solution followed by potential scanning between -0.21 and $1.06\ \text{V}$ (vs. SCE).

In the cathode scanning, a rotating disk electrode (RDE) technique was employed to electrochemically evaluate the ORR process of the catalyst. A reversible hydrogen electrode (RHE) and a rotating

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