Technical Communication

Preparation of Ir$_{0.4}$Ru$_{0.6}$Mo$_x$O$_y$ for oxygen evolution by modified Adams’ fusion method

Jinbin Cheng$^{a,b}$, Huamin Zhang$^a$*, Haipeng Ma$^a$, Hexiang Zhong$^a$, Yi Zou$^a$

$^a$Lab of PEMFC Key Materials and Technologies, Dalian Institute of Chemical Physics, Chinese Academy of Science, 457 Zhongshan Road, Dalian, Liaoning 116023, China

$^b$Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

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A B S T R A C T

A novel anodic electrocatalyst Ir$_{0.4}$Ru$_{0.6}$Mo$_x$O$_y$ for solid polymer electrolyte (SPE) water electrolysis is prepared by the modified Adams’ fusion method. The XRD, ICP, and BET are employed to determine the physical characteristics of Ir$_{0.4}$Ru$_{0.6}$Mo$_x$O$_y$ and Ir$_{0.4}$Ru$_{0.6}$O$_2$, and the electrochemical properties of the electrocatalysts are examined by cyclic voltammetry (CV) in 0.5 M H$_2$SO$_4$. The results show that Ir$_{0.4}$Ru$_{0.6}$Mo$_x$O$_y$ has much smaller particle size, larger specific surface areas and active surface area compared with Ir$_{0.4}$Ru$_{0.6}$O$_2$. The results of single cell performance and the electrochemical impedance spectroscopy (EIS) tests also prove that Ir$_{0.4}$Ru$_{0.6}$Mo$_x$O$_y$ has higher performance than Ir$_{0.4}$Ru$_{0.6}$O$_2$.

1. Introduction

The advanced water electrolyzers using solid polymer electrolyte (SPE), specifically proton exchange membrane (PEM), can be used to produce hydrogen, which is a recyclable and nonpolluting energy carrier. Water electrolysis is a process consuming a lot of energy, and the excessive energy loss of SPE water electrolyser is mostly attributed to the anodic overpotential. Since Henry B. Beer obtained the patent on the dimensionally stable anodes (DSA) in 1965 [1], the application of noble metal oxides as anodic electrocatalysts (particularly IrO$_2$ and RuO$_2$) of water electrolysis has been well established in many industrial electrochemical processes.

Ir$_x$Ru$_{1-x}$O$_2$ compound has been considered to possess considerable activity and stability in the acidic medium [2–5]. Wen and Hu [4] fabricated Ru–Ir binary oxides by thermal decomposition and found that the maximum electrocatalytic activity was demonstrated by the Ru$_{0.3}$Ir$_{0.7}$O$_2$ electrode. Matos-Costa et al. [5] prepared Ir$_x$Ru$_{1-x}$O$_2$ coatings on Ti plates via sol–gel method and observed the “best” performance for the Ru$_{0.7}$Ir$_{0.3}$O$_2$ coating. The Ir$_x$Ru$_{1-x}$O$_2$ catalysts studied above were prepared on Ti plates and used as DSA, which was distinguished from the SPE electrolysis cell.

The oxides used as anodic electrocatalysts in SPE water electrolyzers, such as IrO$_2$, Ir$_x$Sn$_{1-x}$O$_2$ and Ir$_x$Ru$_y$Ta$_{1-y}$O$_2$, had been investigated. Rasten et al. [6] prepared IrO$_2$ via Adams’
fusion method at various annealing temperatures, and the optimum temperature was found to be 490 °C. Marshall et al. [7,8] had studied Ir1–xSn1–x catalysts, and found that addition of tin oxide to iridium oxide particles showed no beneficial effect other than dilution of the more expensive iridium oxide at all the examined current densities. The IrRu1–xTa2O6 catalysts were also synthesized and examined by Marshall et al. [9], and high performance was obtained for anode materials containing 20–40 mol% Ru and 0–20 mol% Ta.

The Adams’ fusion method, first found by Adams and Shriner, was often used to prepare noble metal oxides [10,11] and was found to be fast and convenient for the screening of different catalysts [12]. To improve the active surface area of IrRu1–xO2, the preparation of IrRu1–xO2–MOy (M, dopant metal) is an effective way. Therefore, addition of some oxides during the process of Adams’ fusion method can be useful. Generally, a large amount of dopant should be added to the mixture. However, because the doped MOx often has weak catalytic activity and conductivity, high proportion of dopant has been proved to be unavailable [7–9,13,14]. Therefore, the doped content in IrRu1–xO2–MOy must be less. Molybdenum oxide was found to be contributory to the enlargement of RuO2–MoO3/Ti electrode [15]. Moreover, there was a reaction between MoO3 and NaNO3, and the formula can be written as follows:

\[ 2\text{MoO}_3 + 4\text{NaNO}_3 \rightarrow 2\text{Na}_2\text{MoO}_4 + 4\text{NO} \uparrow + 3\text{O}_2 \uparrow \]  

Because the product, Na2MoO4, was dissoluble in water, most molybdenum could be removed. As a result, a small quantity of molybdenum was doped in IrRu1–xO2 homogeneously.

Ir0.4Ru0.6O2 has been proved to have considerable activity and stability as an anodic electrocatalyst in acidic electrolyte water electrolysis [4,5,7–9]. In this work, Ir0.4Ru0.6O2 was prepared via Adams’ fusion method and Ir0.4Ru0.6MoO3 was prepared via modified Adams’ fusion method. Cyclic voltammetry, electrochemical impedance spectroscopy, and stationary current density-potential relations were used to investigate the properties of the two electrocatalysts. The crystal structure was characterized by XRD. The Mo content in Ir0.4Ru0.6MoO3 and the BET surface areas were investigated. The performance of single cells using the two electrocatalysts was also tested.

2. Experimental

2.1. Preparation of Ir0.4Ru0.6O2 and Ir0.4Ru0.6MoO3 oxides

The Adams’ fusion method was adopted to prepare Ir0.4Ru0.6O2. Metal precursors (H2Ir6Cl6–6H2O and RuCl3–3H2O (Sino-Platinum Metals Co) and NaNO3 (Tianjin Bodi Chemical Co) were added to distilled water and a homogeneous mixture was prepared. The Ir/Ru molar ratio in the precursor was 2:3. Water was evaporated from the mixture and the salt mixture was introduced into ceramic furnace. After heating to 350 °C at 10 °C/min (kept for 10 min), the mixture was heated to 490 °C at 5 °C/min and kept for 30 min. The salt mixture was cooled to room temperature and washed with distilled water. The oxides were obtained finally by drying the mixture at 60 °C in vacuum oven for 12 h.

The modified Adams’ fusion method was adopted to prepare Ir0.4Ru0.6MoO3. In the modified process, MoO3·H2O was added to the mixture, and the pH value of mixture was adjusted to about 7 with 1 M NaOH water solution. Mo was accounted for 40 mol% of the total metal content in the precursor. The remaining steps were the same as those for the preparation of Ir0.4Ru0.6O2.

2.2. Preparation of thin-film electrocatalyst layers (TFEL) and MEA

To prepare the TFEL, a homogeneous ink composed of catalyst, Nafion solution (5 wt%, DuPont; one-third of the mass of catalyst) and isopropanol was sprayed directly onto each side of a Nafion 1035 membrane [16]. The Nafion loading in the TFEL was 25 wt% for both sides, and the catalyst loading was 0.5 mg cm−2 Pt/C (28.4 wt%, T.K.K. Corp.) for cathode and 1.5 mg cm−2 Ir0.4Ru0.6O2 or Ir0.4Ru0.6MoO3 for anode. MEA (with 5 cm2 active area) was fabricated by placing the catalyst-coated membrane between two carbon papers (TGP-H-060, Toray) and hot pressed at 140 °C and 10 MPa.

2.3. Electrochemical analysis

The CV tests were conducted with a Potentiostat (EG&G PAR, Model 2273A). The catalyst layer deposited on the glassy carbon electrode (GCE) (4 mm in diameter) was prepared as follows [17]: a mixture containing 1 mL of ethanol, 5.00 mg of catalyst and 50 μL of Nafion solution (5 wt.%) was homogenized for 30 min in an ultrasonic bath. The mixture (25 μL) was cast on a clean GCE surface and dried in air. All the measurements were carried out in a standard three-electrode cell. A Pt foil served as counterelectrode and the saturated silver chloride (Ag/AgCl) electrode was used as reference electrode. A solution of 0.5 M H2SO4 was used as electrolyte. The scan range of CV was from 0.2 VAg/AgCl to 1.2 VAg/AgCl and the scan rate was 20 mV s−1. The electrolyte was deaerated with bubbling N2 prior and during all measurements.

Electrochemical impedance spectroscopy (EIS) of the water electrolysis with single SPE cell was conducted at 1.45 Vfcell with a Potentiostat (EG&G PAR, Model 2273A) for frequency measurements extending from 20 mHz to 100 kHz, and 10 mV amplitude of sinusoidal potential perturbation was employed. The impedance data were modeled via ZSimpWin software.

2.4. Physical characteristics of Ir0.4Ru1–xMo2O3 oxides

XRD analyses were performed with a Shimadzu diffractometer (XRD-6000) with a Cu Kα radiation source (λ = 1.54056 Å) to characterize catalysts’ crystalline structure. The TEM microscope was used to investigate the morphology of both electrocatalysts with a JEOL JEM-2011 electron microscope operated at 120 kV. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis with a model Plasma-Spec-II (LEEMAN USA) was conducted to determine the content of Mo in Ir0.4Ru0.6MoO3. BET surface areas of the different
catalysts were determined by an ASAP-2010 (Micromeritics) physisorption system with N2 as the adsorbate at 77 K.

3. Results and discussion

3.1. Physical characterization measurements

Fig. 1 shows XRD patterns of Ir0.4Ru0.6O2 and Ir0.4Ru0.6Mo0.4Oy powders. As can be seen in Fig. 1, all peaks match a rutile structure, and there are no reflections corresponding to molybdenum oxides. The lattice parameters of Ir0.4Ru0.6O2 and Ir0.4Ru0.6Mo0.4Oy calculated by Jade software are as follows: Ir0.4Ru0.6O2, a = 4.50 and c = 3.11 Å; Ir0.4Ru0.6Mo0.4Oy, a = 4.49 and c = 3.09 Å. Mo doping appears to have little effect on the structure of the rutile phase, which suggests that little molybdenum has been doped inside the Ir0.4Ru0.6O2 crystallites. The relative intensities of the (1 1 0), (1 0 1), (2 1 1) and (3 0 1) rutile lines found to be slightly decreased in the composite phase indicate that Ir0.4Ru0.6Mo0.4Oy has smaller average size of crystallites than Ir0.4Ru0.6O2. Calculated with the Scherrer formula according to peak (1 0 1), the average sizes of crystallites in Ir0.4Ru0.6O2 and Ir0.4Ru0.6Mo0.4Oy are estimated to be 4.2 nm and 2.1 nm, respectively.

Fig. 2a and b show typical TEM images for Ir0.4Ru0.6O2 and Ir0.4Ru0.6Mo0.4Oy, respectively. Because of the conglomeration of oxide particles, there is no considerable uniformity of particles observed. However, it is easy to distinguish that Ir0.4Ru0.6Mo0.4Oy consists of smaller particles. The particle size for Ir0.4Ru0.6O2 catalyst ranges between 5 and 8 nm, and the mean particle diameter for Ir0.4Ru0.6Mo0.4Oy is from 2 to 4 nm, which accords with the results of XRD.

The result of ICP test shows that the content of molybdenum doped in the Ir0.4Ru0.6Mo0.4Oy is 2.73 wt%. Therefore, the possible reason for the “absence” of the typical diffraction peaks for molybdenum oxides can be the extremely low content of molybdenum in the catalyst. The other possible reason is that the molybdenum oxides are well dispersed in Ir0.4Ru0.6O2 particles and exist in an amorphous form. It is suggested that iridium and ruthenium ions at the interface can connect with molybdenum by the Ir(Ru)–O–Mo bonds around the rutile crystallite, which causes the distortion stress of the rutile matrices and inhibits the growth of crystallite grains. As a result, more defects of lattice may appear and particle size may be reduced.

The BET surface areas of Ir0.4Ru0.6O2 and Ir0.4Ru0.6Mo0.4Oy are 138.4 m² g⁻¹ and 214.8 m² g⁻¹, respectively. It can be found that Ir0.4Ru0.6Mo0.4Oy prepared by modified Adams’ fusion method is associated with a considerable increase in the specific surface area, which can be ascribed to the smaller particles.

3.2. Cyclic voltammetry

The voltammetric curves of Ir0.4Ru0.6O2 and Ir0.4Ru0.6Mo0.4Oy at 20 mV s⁻¹ scan rate in 0.5 M aqueous H2SO4 at room temperature are shown in Fig. 3. For the curve of Ir0.4Ru0.6O2, the peaks of redox transition are not clear due to the superposition of the redox processes. The apparent peak in the curve for

Fig. 1 – XRD patterns of Ir0.4Ru0.6O2 and Ir0.4Ru0.6Mo0.4Oy.

Fig. 2 – TEM images of (a) Ir0.4Ru0.6O2 and (b) Ir0.4Ru0.6Mo0.4Oy catalysts.
Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ observed at about 1.05 V$_{Ag/AgCl}$ is attributed to the redox transitions of surface oxyruthenium groups: Ru(IV)/Ru(VI). The peaks corresponding to the molybdenum oxide are hard to find, and the possible reason is the very low content of the molybdenum oxide.

Fig. 3 shows larger voltammetric charge from Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ than from Ir$_{0.4}$Ru$_{0.6}$O$_2$, which indicates that the active surface area increases through modified Adams’ fusion method. As a technique to determine the in situ surface area [18], the $q^*$ is the sum of the anodic and the cathodic charge densities measured from voltammograms, and higher $q^*$ value means larger activity area. The $q^*$ values are 100 and 174 mC cm$^{-2}$ for Ir$_{0.4}$Ru$_{0.6}$O$_2$ and Ir$_{0.4}$Ru$_{0.6}$MoO$_y$, respectively, and the result indicates that the activity area increases through modified Adams’ fusion method. This result can be ascribed to the reduction of particle size, enlargement of active surface area and perhaps increasing defects of the lattice. The anodic/cathodic voltammetric charge ratios, $Q_a/Q_c$, are 1.05 for Ir$_{0.4}$Ru$_{0.6}$O$_2$ and 1.04 for Ir$_{0.4}$Ru$_{0.6}$MoO$_y$. The values are close to 1, supporting the reversible behaviour of the solid state surface redox transition for both electrocatalysts.

3.3. Electrochemical impedance spectroscopy

The typical Nyquist plots of the electrochemical impedance behaviour for single cell in Fig. 4 are determined at a potential of 1.45 V$_{RHE}$ corresponding to the oxygen evolution region. The equivalent circuit matching closely the observed impedance diagrams can be represented by $R_u$ $R_1$ $Q_1$($R_{ct}$ $Q_{dl}$, where $R_u$, $R_1$, $R_{ct}$, $Q_1$ and $Q_{dl}$ represent ohmic resistance, resistance of mass of the catalytic film, charge transfer resistance, constant phase element (CPE) and double layer capacitance of the oxide film/solution interface ($C_{dl}$), respectively. The $R_u$ values for cells with Ir$_{0.4}$Ru$_{0.6}$O$_2$ and Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ as anodic electrocatalysts are 0.128 and 0.117 $\Omega$ cm$^2$, respectively, which indicates that the conductivity of catalyst does not change a lot. The $R_{ct}$ values for cells with Ir$_{0.4}$Ru$_{0.6}$O$_2$ and Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ are 0.74 and 0.52 $\Omega$ cm$^2$, respectively. This result indicates that the Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ has higher activity than Ir$_{0.4}$Ru$_{0.6}$O$_2$, which is ascribed to the larger active area.

3.4. Single cell test

Fig. 5 shows the single cell performance with Ir$_{0.4}$Ru$_{0.6}$O$_2$ and Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ as anodic electrocatalysts. The typical polarization is carried out at 80 °C, which is under normal water electrolysis conditions. The cell with Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ shows higher performance than the cell with Ir$_{0.4}$Ru$_{0.6}$O$_2$. The cell voltages at 1000 mA cm$^{-2}$ are 1.606 and 1.646 V for Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ and Ir$_{0.4}$Ru$_{0.6}$O$_2$, respectively. The IR-free curves of the cell voltage are also shown in Fig. 5, and it reveals the cell performance excluding the loss due to increased ohmic resistance at high current. The result also shows that Ir$_{0.4}$Ru$_{0.6}$MoO$_y$ prepared by modified Adams’ fusion method has higher activity than Ir$_{0.4}$Ru$_{0.6}$O$_2$.
4. Conclusions

In this work, Ir$_0.4$Ru$_0.6$Mo$_x$O$_y$ was prepared by modified Adams’ fusion method. As a result, a minute quantity of Mo was doped and the amorphous form was depicted. The modified Adams’ fusion method could decrease the particle size and improve the BET surface area without deteriorating the conductivity. The possible reason for the reduced particle size is that iridium and ruthenium ions at the interface can connect with molybdenum by the Ir(Ru)–O–Mo bonds around the rutile crystallite, which inhibits the growth of crystallite grains during the fusion process. Considering the less electrocatalytic activity of MoO$_x$, the decrease of particle size and the increase of active area can be the primary reasons for the increase of performance. Moreover, it is hoped that the modified Adams’ fusion method will be a convenient technique to obtain other noble metal oxides (PtO$_2$, AuO$_2$, etc) with smaller particle size and larger active area. Further research is ongoing in our lab.

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REFERENCES