



Short communication

Nafion-stabilized Ir₈₅Se₁₅/C catalyst for oxygen reduction reaction in proton exchange membrane fuel cells

Ting Xu^{a,b}, Huamin Zhang^{a,*}, Yining Zhang^a, Hexiang Zhong^a, Hong Jin^{a,b}, Yongfu Tang^{a,b}^a PEMFC Key Materials and Technology Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

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ABSTRACT

Ir₈₅Se₁₅/C catalyst synthesized using Nafion as the stabilizer (Nafion-Ir₈₅Se₁₅/C) has been characterized by X-ray diffraction, transmission electron microscopy, electrochemical impedance spectra measurement, rotating disk electrode and single cell tests. In comparison with Ir₈₅Se₁₅/C catalyst prepared by a traditional polyol method, Nafion-Ir₈₅Se₁₅/C exhibits higher activity for oxygen reduction reaction and better single cell performance. The maximum power density of the single cell with the Nafion-Ir₈₅Se₁₅/C as cathode catalyst is 736 mW cm⁻², which is 1.8 times as much as that with the Ir₈₅Se₁₅/C catalyst. Therefore, Ir₈₅Se₁₅/C catalyst is expected to be used as an effective cathode electrocatalyst for proton exchange membrane fuel cells by employing Nafion as the stabilizer.

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1. Introduction

As a new kind of energy generator, proton exchange membrane fuel cells (PEMFCs) are expected to play a pivotal role in stationary and mobile applications due to their high power density and environmental benignancy. However, the commercialization of PEMFCs is facing many challenges, such as cost, durability and reliability. One of the major challenges is the fundamental limitation of Pt and its considerably high cost. Thus, it is a priority to find the less expensive metal alternatives of Pt that are stable and exhibit catalytic activity comparable to that of Pt/C catalysts for PEMFCs.

Tremendous efforts have been invested in developing non-platinum electrocatalysts [1–3]. As one of the most stable metals among Pt-group in acidic media [4], Ir has been investigated as the oxygen reduction reaction (ORR) catalyst, especially with the modification of Se, due to the relatively high ORR activity compared to other non-platinum catalysts [5–8]. Ir_xSe_y/C catalysts have been synthesized with a polyol method by our group [8], which present relatively high ORR activities. Additionally, Ir nanoparticles with good size control have been synthesized by our group using Nafion as the stabilizer, and Nafion is usually used to form the protonic conducting pathways for ORR in the catalyst layer of PEMFCs [9].

In this work, the synthesis method with Nafion as the stabilizer has been applied to prepare the non-platinum catalyst, Nafion-stabilized Ir₈₅Se₁₅/C (Nafion-Ir₈₅Se₁₅/C), aiming to control

the nanoparticle size. Furthermore, the Nafion added in the synthesis process is expected to absorb the Ir₈₅Se₁₅ particles in situ, in order to form the protonic conducting pathways for the reactions. The Nafion-Ir₈₅Se₁₅/C catalyst was characterized and explored as an alternative cathode catalyst for the PEMFCs. By employing Nafion as the stabilizer, the ORR activity of the Ir₈₅Se₁₅/C catalyst has been further improved.

2. Experimental

2.1. Catalysts synthesis

The 50 wt.% Nafion-Ir₈₅Se₁₅/C catalyst (atomic ratio of Ir:Se=85:15, which has been optimized in our previous work [8], and weight ratio of Ir and Se:carbon support=1:1) was synthesized as follows. 472.2 mg Nafion solution (DuPont Corp., 5 wt.%), 1 mL H₂IrCl₆ aqueous solution containing 100 mg Ir and 0.73 mL Na₂SeO₃ aqueous solution containing 7.3 mg Se were mixed with 10 mL deionized water and 15 mL ethanol. The mixed solution was homogenized with magnetic stirring for 30 min under N₂ atmosphere, followed by adding 2.7 mL 1 M NaOH aqueous solution. The mixture was transferred into a 40 mL autoclave tube, then the system was sealed and heated up to 135 °C, followed by further aging treatment at this temperature for 3 h. After cooling to room temperature, the obtained colloid solution was treated by dialysis process to remove impurity ions and organic byproducts. Then 107.3 mg Black Pearls 2000 carbon black powders (Cabot Corp., S_{BET} = 1500 m² g⁻¹) was added to adsorb the as-prepared Nafion-Ir₈₅Se₁₅ nanoparticles, and the resulting solid was fil-

* Corresponding author. Tel.: +86 411 84379072; fax: +86 411 84665057.
E-mail address: zhanghm@dicp.ac.cn (H. Zhang).

tered and dried in a vacuum oven at 60 °C for 8 h to obtain the Nafion-Ir₈₅Se₁₅/C catalysts.

For comparison, the 50 wt.% Ir₈₅Se₁₅/C catalyst was prepared with a polyol method as described in our previous work [8].

2.2. Physicochemical characterizations

The crystalline structures of the samples were analyzed using a Rigaku Rotaflex (RU-200B) with Ni filtered Cu-K_α radiation ($\lambda = 1.54056 \text{ \AA}$). The X-ray diffraction (XRD) patterns were recorded with the 2θ angular region from 30° to 90°. The scan rate is 5° min⁻¹ and the step size is 0.02°.

Transmission electron microscopy (TEM) characterization was performed using a TECNAI Spirit microscope operated at 120 kV. The samples were dispersed in ethanol by ultrasonic blending to form homogeneous slurry, which was applied onto a holey carbon-coated copper grid. Two hundreds of particles were calculated to obtain the particle size distribution diagram of each catalyst sample.

2.3. Electrochemical measurements

The activities of the samples toward ORR were evaluated by the rotating disk electrode (RDE) method with CHI 600 electrochemical station (CH Corp., USA) coupled with a RDE system (EG&G model 636). All the RDE measurements were carried out in a standard three-electrode cell and 0.5 M H₂SO₄ electrolyte at room temperature, with a saturated calomel electrode (SCE) and a Pt foil (3 cm²) as reference and counter electrodes. The working electrode with the catalyst layer deposited on the glassy carbon electrode (GCE, 0.1256 cm²) was prepared as follows: a measured amount of catalyst and Nafion solution (DuPont Corp., 5 wt.%) were mixed with 1 mL ethanol and ultrasonically blended into a homogenous slurry, 10 μL of which was deposited on the clean GCE surface and dried in air. The working electrodes with different catalysts were kept with the same metal loading (177 $\mu\text{g cm}^{-2}$) and Nafion loading. The RDE tests were obtained in O₂-saturated electrolyte by sweeping the working electrode from 0.95 to 0.1 V vs. reversible hydrogen electrode (RHE) at 5 mV s⁻¹ with a rotation speed of 1600 rpm.

2.4. Fabrication of membrane electrode assembly (MEA) and single cell tests

The cathode was prepared as described in our previous work [10]. For both Nafion-Ir₈₅Se₁₅/C and Ir₈₅Se₁₅/C cells, the Ir loading on the electrode was 0.5 mg cm⁻² and the total loading of dry Nafion was 0.5 mg cm⁻² (for Nafion-Ir₈₅Se₁₅/C catalyst, including the Nafion in situ absorption on Ir₈₅Se₁₅ particles in the synthesis process). The single cells were tested at 80 °C with over-saturated humidification. Pure hydrogen and oxygen were injected at 0.2 MPa (gauge pressure).

Electrochemical impedance spectra (EIS) of the cells were recorded using the KFM2030 impedance meter (Kikusui, Japan). The test was carried out at 100 mA cm⁻² between 10 kHz and 100 mHz.

3. Results and discussion

3.1. Physicochemical characterizations of the catalysts

Crystalline phase identifications of samples were carried out by XRD patterns presented in Fig. 1. Both the Nafion-Ir₈₅Se₁₅/C catalyst and Ir₈₅Se₁₅/C catalyst show the characteristic peaks of face-centered-cubic (fcc) crystalline iridium (JCPDS Powder Diffraction File No. 65-1686). The characteristic peaks at about 41°, 47°, 69° and 83° corresponds to the Ir(111), (200), (220) and (311) planes,

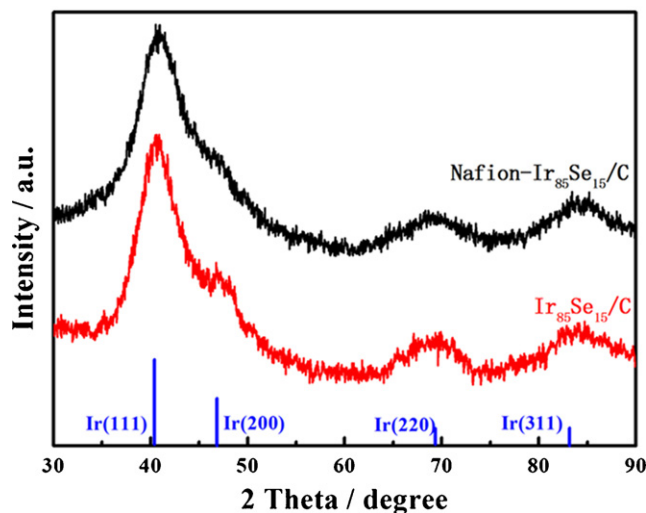


Fig. 1. XRD patterns of (a) Nafion-Ir₈₅Se₁₅/C and (b) Ir₈₅Se₁₅/C catalysts.

respectively. Compared to the characteristic peaks of Ir, the diffraction peaks of the two catalysts shift to the smaller angle due to the addition of Se. The peaks of the Nafion-Ir₈₅Se₁₅/C catalyst are broader than those of the Ir₈₅Se₁₅/C catalyst, denoting that the obtained Nafion-Ir₈₅Se₁₅/C catalyst has smaller particle size and lower crystallinity.

Fig. 2 shows typical TEM images of (a) Nafion-Ir₈₅Se₁₅ nanoparticles, (b) Nafion-Ir₈₅Se₁₅/C catalyst and (c) Ir₈₅Se₁₅/C catalyst. As shown in Fig. 2(a), the Ir₈₅Se₁₅ nanoparticles are aggregated, arranging in the network frame, which is possibly caused by the aggregation of in situ absorbed Nafion due to the volatilization of solvent in the sample preparation process of TEM characterization. In Fig. 2(b) and (c), nanoparticles of the two catalysts are all well dispersed on the support surfaces, and the histograms display the particle size distributions for the two catalysts. The particle size distribution of the Nafion-Ir₈₅Se₁₅/C catalyst is narrower than that of the Ir₈₅Se₁₅/C catalyst. The mean particle size of the Nafion-Ir₈₅Se₁₅/C catalyst is about 1.3 nm, which is much smaller than that of the Ir₈₅Se₁₅/C catalyst (2.0 nm). It indicates that the particle size of Ir₈₅Se₁₅ nanoparticles can be efficiently controlled by introducing Nafion as the stabilizer.

3.2. Electrochemical measurements

The polarization curves obtained from RDE test were used to evaluate the ORR activities of Nafion-Ir₈₅Se₁₅/C, Ir₈₅Se₁₅/C and Pt/C (TKK, 47.6 wt.%) catalysts. The current–potential plots in Fig. 3(a) indicate that the ORR activity of Nafion-Ir₈₅Se₁₅/C is much higher than that of Ir₈₅Se₁₅/C. The potential value of Nafion-Ir₈₅Se₁₅/C is 771 mV vs. RHE at 2 mA cm⁻², which is 41 mV positive in comparison with that of the Ir₈₅Se₁₅/C catalyst. The higher ORR activity of Nafion-Ir₈₅Se₁₅/C is mainly proffered by the higher electrochemically active surface area attributed to the smaller particle size. Though Nafion-Ir₈₅Se₁₅/C catalyst showed exciting ORR activity, the ORR activity of Nafion-Ir₈₅Se₁₅/C catalyst is still lower than that of the Pt/C catalyst.

According to the rotating disk electrode theory, the current density (i) at each electrode potential, shown in Fig. 3(b), should contain two contributions: the kinetic current density (i_k) and the diffusion-limited current density (i_d), which can be expressed as the following equation [11]:

$$i_k = \frac{i \cdot i_d}{i_d - i}$$

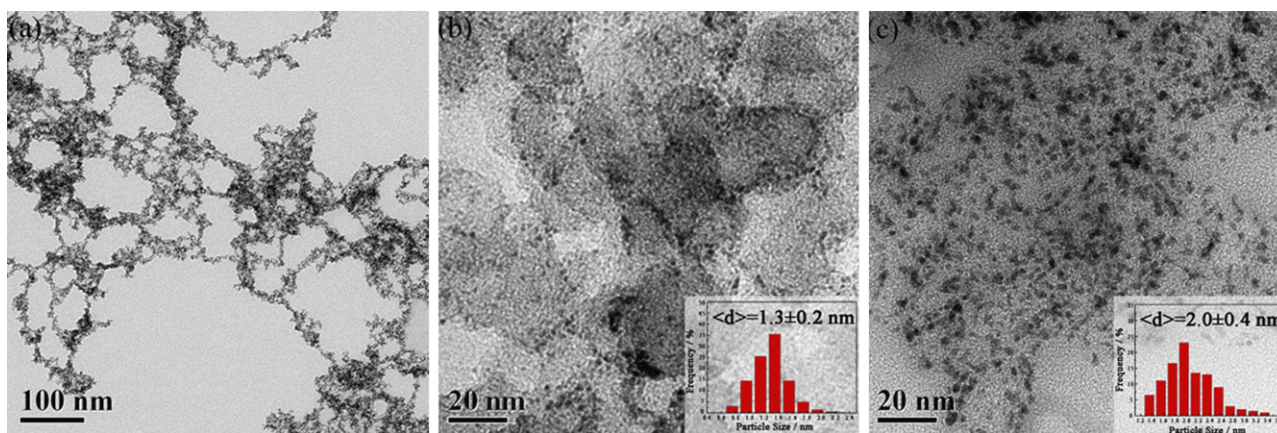


Fig. 2. TEM images of (a) Nafion-Ir₈₅Se₁₅ nanoparticles, (b) Nafion-Ir₈₅Se₁₅/C and (c) Ir₈₅Se₁₅/C catalysts. The particle size distributions of Nafion-Ir₈₅Se₁₅/C and Ir₈₅Se₁₅/C catalysts are also shown.

The values of i and i_d are taken from the corresponding polarization shown in Fig. 3(a). The kinetic current density at 0.8 V (vs. RHE) is 1.46 mA cm⁻² on Nafion-Ir₈₅Se₁₅/C catalyst, which is more than 2 times of that on Ir₈₅Se₁₅/C catalyst (0.71 mA cm⁻²) but still far from that on Pt/C catalyst (11.96 mA cm⁻²). The Tafel slopes are 87, 107 and 132 mV decade⁻¹ for Pt/C, Nafion-Ir₈₅Se₁₅/C and Ir₈₅Se₁₅/C, respectively, indicating much better activity for the catalyst synthesized from the synthesis method with Nafion as the stabilizer.

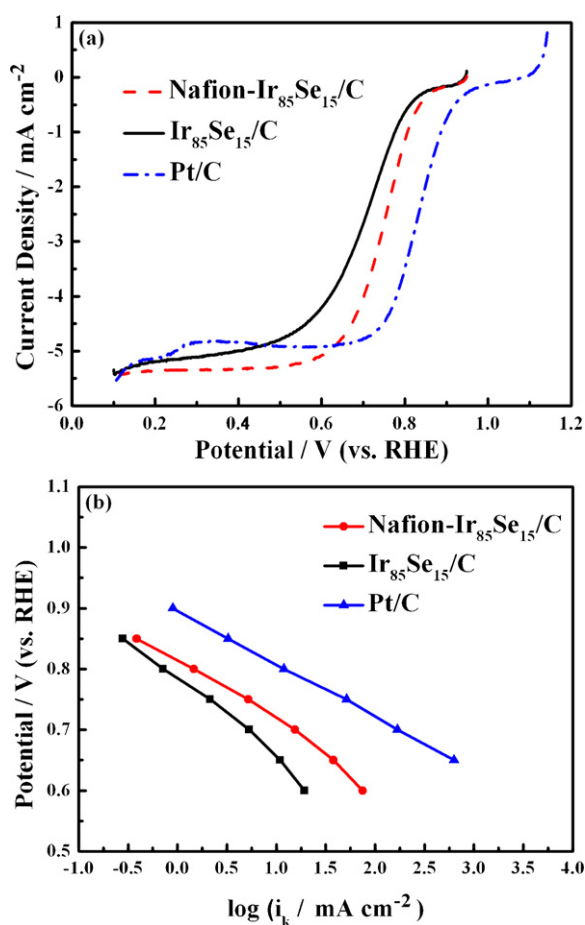


Fig. 3. (a) ORR polarization curves of Nafion-Ir₈₅Se₁₅/C, Ir₈₅Se₁₅/C and Pt/C catalysts. (b) Tafel plots for the ORR on Nafion-Ir₈₅Se₁₅/C, Ir₈₅Se₁₅/C and Pt/C catalysts. Data were extracted from (a).

3.3. Single cell tests

The single cell performance with Nafion-Ir₈₅Se₁₅/C as cathode catalyst was evaluated and shown in Fig. 4. The cell voltage and power density are 0.664 V and 332 mW cm⁻² at 500 mA cm⁻², which are obviously higher than those of Ir₈₅Se₁₅/C (0.583 V and 291 mW cm⁻²). The maximum power density of Nafion-Ir₈₅Se₁₅/C single cell is 736 mW cm⁻², which is 1.8 times as much as that of the Ir₈₅Se₁₅/C catalyst. The improvement of the single cell performance may be attributed to the beneficial effect by introducing Nafion as the stabilizer, which is further proved by the results from EIS as shown in Fig. 5. The high frequency interception on the real impedance axis represents the total ohmic resistance of the cell, and the diameter of the kinetic loop corresponds to the charge transfer resistance for the ORR [12,13]. It is obvious from Fig. 5 that the charge transfer resistance of Nafion-Ir₈₅Se₁₅/C single cell is smaller than that of Ir₈₅Se₁₅/C single cell, which could be attributed to the profits from two aspects by introducing Nafion as the stabilizer. Firstly, the Nafion can act as a stabilizer during Ir₈₅Se₁₅ preparation process, which can help to control the particle size and prevent the agglomeration of Ir₈₅Se₁₅ nanoparticles, benefiting the higher effective electrochemically active surface area of the catalyst. Secondly, to improve the utilization of the supported active components, it is general to increase contact area between the ionic conducting polymers and active particles [14–16]. For the Nafion-Ir₈₅Se₁₅/C catalyst, Nafion absorbs the Ir₈₅Se₁₅ particles in situ, which is proved by the TEM characterization. Therefore, with

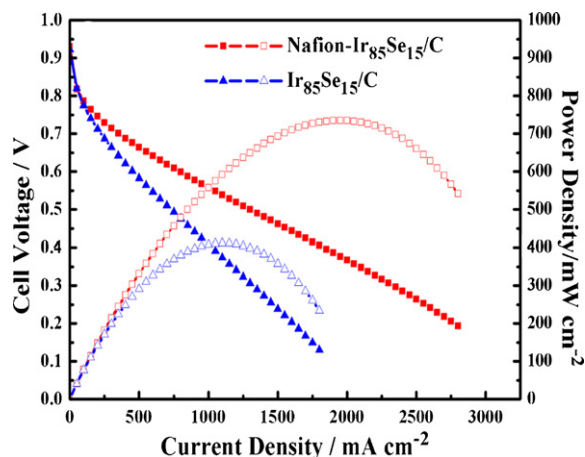


Fig. 4. Cell performances of Nafion-Ir₈₅Se₁₅/C and Ir₈₅Se₁₅/C catalysts.

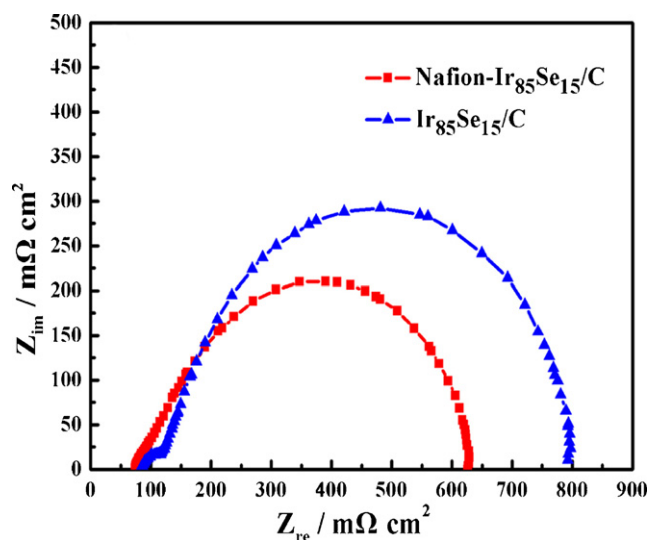


Fig. 5. EIS of single cells with Nafion-Ir₈₅Se₁₅/C or Ir₈₅Se₁₅/C as the cathode catalyst.

the same loading of Nafion in the catalyst layer, the distribution of Nafion for Nafion-Ir₈₅Se₁₅/C single cell is more homogeneous, which contributes to the larger interface of three-phase reaction [9]. Moreover, the total ohmic resistance of Nafion-Ir₈₅Se₁₅/C single cell is also smaller than that of Ir₈₅Se₁₅/C single cell with the same reasons.

4. Conclusions

The Nafion-Ir₈₅Se₁₅/C catalyst prepared using Nafion as the stabilizer exhibits higher ORR activity and better single cell performance than the catalyst synthesized with the traditional method.

The introduction of Nafion in the synthesis process is probably beneficial to obtaining higher effective electrochemically active surface area through better catalyst particle size control and catalyst utilization from the in situ absorption of Nafion on the Ir₈₅Se₁₅ particles. The Nafion-Ir₈₅Se₁₅/C catalyst, whose activity could be enhanced by optimizing the synthesis process, is expected to be a good alternative of the platinum catalyst.

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