Novel synthesis of a highly active carbon-supported Ru$_{85}$Se$_{15}$ chalcogenide catalyst for the oxygen reduction reaction

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Abstract

A carbon-supported Ru$_{85}$Se$_{15}$ chalcogenide catalyst was synthesized via a microwave-assisted polyol process using RuCl$_3$ and Na$_2$SeO$_3$ as the Ru and Se precursors. The Ru$_{85}$Se$_{15}$ chalcogenide catalyst was characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and inductively-coupled plasma-atomic emission spectroscopy (ICP-AES). The XRD pattern for Ru$_{85}$Se$_{15}$/C clearly exhibited the characteristic reflections of metallic ruthenium. The TEM image indicated that the Ru$_{85}$Se$_{15}$ chalcogenide catalyst was well dispersed on the surface of the carbon support with a narrow particle size distribution. Rotating disk electrode (RDE) and single-cell measurements were carried out to evaluate the electrocatalytic activity of the Ru$_{85}$Se$_{15}$ chalcogenide catalyst. The oxygen reduction reaction (ORR) activity of the Ru$_{85}$Se$_{15}$/C catalyst was compared with the commercial Pt/C catalyst with the absence/presence of methanol. In the absence of methanol, the Ru$_{85}$Se$_{15}$/C catalyst showed a comparable ORR activity with the Pt/C catalyst. However, in the presence of methanol, the Ru$_{85}$Se$_{15}$/C catalyst showed a better ORR activity than the Pt/C catalyst. The performance of the membrane electrode assembly (MEA) prepared with Ru$_{85}$Se$_{15}$/C as the cathode catalyst in a single proton exchange membrane fuel cell (PEMFC) showed the maximum power density of 400 mW cm$^{-2}$ at the current density of 1300 mA cm$^{-2}$.

Keywords: Ru-based chalcogenide catalyst; Microwave-assisted polyol process; Oxygen reduction reaction; Cathode; Fuel cell

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are particularly attractive for stationary and mobile applications [1]. In PEMFC, Pt supported on carbon is usually used as the catalyst for the electroreduction of oxygen. Due to the fact that Pt is an expensive metal with a limited relative abundance, the search for efficient and non-platinum catalysts for oxygen reduction reaction (ORR) becomes an important task in PEMFC catalyst research.

Ru-based cluster compounds containing Se (Ru$_x$Se$_y$, Mo$_x$Ru$_y$Se$_z$) were initially proposed as ORR catalysts by Alonso-Vante et al. [2,3]. These materials are conventionally synthesized from a solid-state reaction of high-purity Ru and Se at high temperatures between 1200 and 1700 °C in a vacuum [2,4]. As they require an environment of extremely high reaction temperature and long-time heat treatment in argon, this process for catalyst synthesis is therefore complicated and costly. Furthermore, the synthesized chalcogenides are strict with regard to the purity of Ru and Se reactants. Recently, low temperature methodologies have been developed to prepare amorphous chalcogenides by the thermolysis of Ru-carbonyls in organic solvents (xylene or 1,2-dichlorobenzene) in the presence of Se [5–8]. However, because this method involves some complex chemical reactions, several polynuclear compounds with amorphous structures could be produced. It is very difficult to separate the Ru$_x$Se$_y$ chalcogenide from...
the by-products, and the yield of the final product is always below 100% (normally ~40–60%) [9]. Moreover, the Ru-carbonyls precursors are relatively expensive and the solvents used in this method are toxic and environmentally damaging. Other synthesis methods, such as the traditional impregnation method [10] and the colloid method [11], are also proposed to prepare amorphous Ru₅Se₅ chalcogenides. However, the traditional impregnation method needs to sinter the catalyst particles at high temperature, thus reducing the active catalyst area. For the colloid method, the reproducibility is not sufficient. At the same time, the ORR activity of the synthesized catalysts using the two above-mentioned methods is only ~10–20% of Pt [12].

In this paper, uniform Ru₅Se₅ nanoparticles with an average diameter of about 1 nm supported on carbon were prepared by a microwave-assisted polyol process using facile RuCl₃ and Na₂SeO₃ as the Ru and Se precursors. Not only was the preparation method simple and fast, the prepared Ru₅Se₅ clusters were also ultra-finely dispersed on a carbon support and were efficient for oxygen reduction.

2. Experiment

2.1. Electrocatalyst preparation

The synthesis was carried out with the aid of a LG WD700 microwave oven (700 W, 2450 MHz). Vulcan XC-72R carbon black (Carbot Corp., S_BET = 250 m² g⁻¹) was used as the support. The synthesis procedure for the 20% Ru₅Se₅/C (atomic ratio of Ru:Se = 85:15, the Ru and Se total loading is 20%) catalyst is as follows: first, we mixed 5.94 mL of 0.0366 M RuCl₃ in ethylene glycol (EG) and 1 mL of 0.0386 M Na₂SeO₃ in water with 50 mL EG. The mixed solution was homogenized for 20 min in an ultrasonic bath, followed by the addition of a 2 M EG solution of NaOH to increase the pH to >10. The mixed solution was performed in the above-mentioned microwave oven with total power for 90 s. The final temperature reached in the performed solution was about 190 °C. Then, 100 mg of Vulcan XC-72R carbon black was added to adsorb the as-prepared Ru₅Se₅ clusters. The resulting solid was filtered, washed with copious distilled water, and dried in a vacuum oven at 333 K for 8 h. The catalyst thus obtained was denoted as Ru₅Se₅/C. For comparison, the Ru/C and Se/C (Ru or Se loading is 20%) were also prepared by the same microwave-assisted polyol process.

2.2. Physicochemical characterization

XRD analyses of all samples were conducted on a PANalytical powder diffractometer (Philips X’Pert PRO) using Ni filtered Cu-Kα radiation (λ = 1.54056 Å) to characterize the structures of the Se/C, Ru/C and Ru₅Se₅/C catalysts. TEM images were recorded on a JEOL JEM-2000EX microscope operated at 120 kV. The Ru/C or Ru₅Se₅/C catalysts were placed in a vial containing ethanol and, then, were ultrasonically agitated to form homogeneous slurry. A drop of the slurry was dispersed on a holey, amorphous carbon film on a Cu grid for analysis. Two hundred particles were calculated to obtain the integrated information about the overall distribution of the catalyst.

Inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were conducted to determine the bulk contents of Ru and Se in the prepared Ru₅Se₅/C catalyst.

2.3. Electrochemical characterization

Electrochemical characterization was performed on CHI 660 electrochemical station (CH Corporation, USA) with an RDE system (EG&G model 636). A standard three-electrode electrochemical cell was used. A large-area Pt foil (3 cm²) and a saturated calomel electrode (SCE) were served as the counter and the reference electrode, respectively. The catalyst layer on the glassy carbon electrode (GCE) (4 mm in diameter) was prepared as follows. A mixture containing 5.0 mg Se/C or Ru/C or Ru₅Se₅/C or Pt/C (20%, Johnson Matthey), 1.0 mL ethanol and 50 µL Nafion solution (5 wt.%, Dupont corp.) was ultrasonically blended in a weighing bottle for 30 min to obtain a homogeneous ink. A 25 µL Se/C or Ru/C or Ru₅Se₅/C or Pt/C paint ink was spread on the surface of a glassy carbon electrode (area: 0.1256 cm²) and the electrode was dried in the air to obtain a thin active catalyst layer. The electrochemical measurements were carried out in 0.5 M H₂SO₄ solution with and without 0.5 M CH₃OH at room temperature. All electrode potentials in this paper were quoted to reversible hydrogen electrode (RHE). All RDE curves were obtained in the potential range of 0.2–0.95 V versus RHE with the applied scan rate of 5 mV s⁻¹ at room temperature. Prior to the RDE tests, the electrolyte was saturated with O₂ by bubbling O₂ for 30 min.

2.4. Preparation of membrane electrode assembly (MEA) and single-cell test

The electrode was prepared as follows: mixing Ru₅Se₅/C catalyst, 5% Nafion (Du Pont Corp.) and ethanol to form a homogeneous mixture, spraying the mixture onto the wet-proofed carbon paper (SGL, 39% PTFE). The Ru loading in the electrode was about 0.4 mg cm⁻² and the dry Nafion loading was about 0.5 mg cm⁻². This electrode was used for the cathode. The Pt/C (20%, Johnson Matthey) cathode was prepared by the same procedure. The Pt loading in the Pt/C cathode was about 0.3 mg cm⁻² and the dry Nafion loading was about 0.4 mg cm⁻². The anode adopted the commercial 28.4% Pt/C catalyst (TKK Corp.) with Pt loading of 0.3 mg cm⁻². The dry Nafion loading in the anode was about 0.4 mg cm⁻². The MEA was fabricated by hot-pressing the anode and the cathode to the Nafion 212 membrane (50 µm, Du Pont) at 140 °C and 1 MPa for 1 min. The MEA active area
was 5 cm². The single-cell performances were tested at 80, 60 and 40 °C with saturated humidification, respectively. The single-cell was fed with pure hydrogen and oxygen and operated at 0.2 MPa.

3. Results and discussion

ICP-AES analyses were conducted to determine the bulk contents of Ru and Se in the prepared Ru₈₅Se₁₅/C catalyst. The bulk composition of Ru and Se in Ru₈₅Se₁₅/C were 17.5 wt.% and 2.3 wt.%, respectively. The composition of Ru and Se in the Ru₈₅Se₁₅/C catalyst was very close to the nominal values.

Fig. 1a shows the XRD pattern of 20% Se/C. The Se/C showed characteristic reflections of hexagonal selenium (JCPDS Powder Diffraction File no. 65-1876). This proved that the Se was easily reduced from Na₂SeO₃ under the experimental conditions and gave a base for the synthesis of the RuₓSeᵧ chalcogenide. Fig. 1b shows the XRD patterns of 20% Ru/C and 20% Ru₈₅Se₁₅/C. Both the Ru/C and Ru₈₅Se₁₅/C samples showed the crystalline structures of metallic ruthenium (JCPDS Powder Diffraction File no. 06-0663). The peaks located at the diffraction angle of 2θ = 38–45° is attributed to the Ru metal, whereas no Ru oxide diffraction peaks were presented in the whole range, indicating the complete reduction of RuCl₃. The average size of Ru particles in 20% Ru/C was calculated using Scherrer’s equation from a full width at half-maximum (fwhm) of the Ru(101) diffraction line. The Scherrer’s equation is as follows [13].

\[
L = \frac{0.9 \lambda_{\text{X-ray}}}{B_{\text{fwhm}} \cos \theta_{\text{max}}} 
\]

where \(L\) is the average size of metal crystallites, \(\lambda_{\text{X-ray}}\) is the X-ray wave-length (Cu-Kα, \(\lambda_{\text{X-ray}} = 1.54,056 \text{Å}\)), \(\theta_{\text{max}}\) is the angle value of Ru(101) peak, and \(B_{\text{fwhm}}\) is the fwhm of the Ru(101) diffraction line. The calculated average particle size of Ru particles in 20% Ru/C was 1.7 nm. The addition of Se to Ru/C resulted in the following remarkable and systematic changes in the XRD patterns. (i) The Ru(101) diffraction peak shifted to a smaller angles for 1.2° (compared with Ru(101) in Ru/C, see inset in Fig. 1b), which was in agreement with the research of Zaikovskii et al. [14]. Zaikovskii et al. also found that the Ru(101) diffraction peak of Se modified carbon-supported Ru was shifted to a smaller angles for about 1° when compared with the Ru(101) diffraction peak of carbon-supported Ru. This change indicated the presence of another new compound; and (ii) The intensity and broadening of the Ru(101) diffraction peak increased compared with the changeless peak of C(002). This change was opposite to the experimental results obtained by Zaikovskii et al. The different synthesis procedure may be responsible for the difference. After the addition of Se, the mean particle size of RuₓSeᵧ particles decreased to 1.2 nm.

Fig. 2a shows the TEM image of 20% Ru/C. As can be seen, Ru nanoparticles were well dispersed on the carbon surface. Based on the measurements of 200 particles in random regions, the average particle size was estimated to be 1.8 nm. The corresponding histogram (the inset in Fig. 2a) revealed that the particle size distribution was rather narrow and exhibited the log–normal distribution feature. The TEM image of 20% Ru₈₅Se₁₅/C is shown in Fig. 2b. After the incorporation of Se, the morphology of Ru₈₅Se₁₅/C changed from that of Ru/C. The Ru nanoparticles were ultrafine with an amorphous layer of Se or RuₓSeᵧ covered on them. Under the microwave-assisted polyol process, the Ru and Se precursors were reduced simultaneously. The modification of Ru with Se prevented the Ru particles from aggregation, which contributed to the small particle size. Because of the Ru particle cover and the poor contrast of the image we were not able to build particle size distributions and calculate the average particle size for Ru₈₅Se₁₅/C.

Fig. 3 displays the ORR polarization curves for Se/C, Ru/C, and Ru₈₅Se₁₅/C catalysts including the conventional Pt/C catalyst (20% Pt, Johnson Matthey) in O₂-saturated
0.5 M H₂SO₄ solution at room temperature. The potential sweep rate is 5 mV s⁻¹ and the disk electrode rotation rate is 1600 rpm. As shown in Fig. 3, the Se/C showed no obvious activity for the ORR. On the Ru/C catalyst, the cathodic current produced by the ORR commenced at 0.88 V and increased as the potential was scanned negatively from 0.88 to 0.2 V. On the Ru₆₅Se₁₅/C catalyst, during the whole cathodic scan, it showed a superior ORR activity to the Ru/C catalyst, and the well-defined limiting current was reached below 0.5 V. During the synthesis of Ru/C and Se/C, the color of RuCl₃ solution was changed from orange to black brown and the color of Na₂SeO₃ solution was changed from colorless to pink after the microwave irradiation for 90 s. These phenomena suggested that the reduction reactions of Ru³⁺ and SeO₃²⁻ to Ru and Se were very quick in the microwave-assisted polyl process. Therefore, it was possible that the microwave-assisted polyl process can effectively control particles size and distribution, which may contribute to the high ORR activity of the Ru₆₅Se₁₅/C catalyst. Meanwhile, microwave irradiation promoted the further reaction between Ru and Se, which then led to the generation of a new compound, Ru₆₅Se₃₇, that can be traced from the XRD pattern of Ru₆₅Se₁₅/C. The incorporation of Se to Ru nanoparticles not only stabilized the nanostructural nature (geometric effect) of the chalcogenide, but also provided the electronic effect for electrocatalysis [14–16]. Recent studies have also shown that the ORR enhancement can be reached by modifying Ru nanoparticles with Se [17–20]. The half-wave potential E½ (the potential corresponding to one-half of the diffusion current) of Ru₆₅Se₁₅/C and Pt/C were 712 mV and 836 mV versus RHE, respectively. It meant that the catalytic activity of Ru₆₅Se₁₅/C for oxygen reduction approached to that of Pt with an increase of about 120 mV in overpotential.

According to the rotating disk electrode theory, the current density (i) at each electrode potential (E), shown in Fig. 3, should contain two contributions: the kinetic current density (iₖ) and the diffusion-limited current density (i₉). The relationship among these current densities can be expressed as Eq. (2) [21].

\[ i_k = \frac{i - i_d}{i_d - i} \]  

Fig. 4 shows the mass transfer corrected Tafel plots for the ORR on Ru/C, Ru₆₅Se₁₅/C and Pt/C catalysts in O₂-saturated 0.5 M H₂SO₄ solution at room temperature. As shown in Fig. 4, the Ru₆₅Se₁₅/C catalyst exhibited much better activity than the Ru/C catalyst. As shown in Table 1, the Tafel slopes were 156, 92, and 58 mV dec⁻¹ for the Ru/C, Ru₆₅Se₁₅/C, and Pt/C catalysts, respectively. Table 1 also shows other kinetic parameters for the ORR on Ru/C, Ru₆₅Se₁₅/C, and Pt/C catalysts. The kinetic current
densities were obtained based on the data in Fig. 3. In terms of kinetic current density, after the incorporation of Se, the Ru85Se15/C catalyst showed a kinetic current density 3 times than that of the Ru/C catalyst at 0.8 V versus RHE. However, it was still far lower than that of the Pt/C catalyst. At a defined current density of 1 mA cm\(^{-2}\), the overpotential of the Ru85Se15/C catalyst is 286 mV, which is 109 mV lower than that of the Ru/C catalyst and 121 mV higher than that of the Pt/C catalyst.

To compare the methanol tolerance ability between Ru85Se15/C and Pt/C, the ORR polarization curves for Ru85Se15/C and Pt/C catalysts in O\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) solution with and without 0.5 M CH\(_3\)OH are shown in Fig. 5. For the Pt/C catalyst, a large anodic current was presented above 0.6 V due to the CH\(_3\)OH oxidation. The onset potential for ORR by Pt/C in the methanol-containing solution began at a potential not higher than 0.6 V, which was over 400 mV lower than that when CH\(_3\)OH was absent. The mixed potential caused by the simultaneous reactions of oxygen reduction and CH\(_3\)OH oxidation attributed to the large drop of ORR onset potential. Nevertheless, the Pt/C showed no oxygen reduction current at 0.8 V versus RHE due to the mixed potential caused by the simultaneous reactions of oxygen reduction and CH\(_3\)OH oxidation.

The performances of MEA achieved at 40, 60 and 80 °C with Ru85Se15/C as cathode catalyst are shown in Fig. 7. For comparison, the performance of MEA made using
Pt/C as cathode catalyst at 80 °C is also shown in the same figure. The open circuit potentials of the Ru85Se15/C MEA were found to be approximately 0.9 V. At 80 °C, the polarization curve shows the current density of ca. 1900 mA cm⁻² at 0.2 V and the maximum power density of ca. 400 mW cm⁻² at 1300 mA cm⁻², which are superior to the single-cell performance with the Ru-based cathode catalysts reported in the literature [22]. Although a maximum power density of about 400 mW cm⁻² was achieved in our work, the performance of Ru85Se15/C MEA was still lower than that of Pt/C MEA. However, as shown in Fig. 7, the cell performance of Ru85Se15/C MEA operated at 80 °C gave a better performance than that operated at 60 and 40 °C. At the current density of 300 mA cm⁻², the cell voltage is 0.58 V, which is about 20 mV and 40 mV higher than that at 60 and 40 °C, respectively. These initial results indicated that the Ru85Se15/C catalyst cell performance could be improved when operated at a higher temperature. Moreover, better performance can be obtained by optimization in the catalyst preparation process and MEA manufacture.

4. Conclusion

In this study, a carbon-supported Ru85Se15 chalcogenide catalyst was synthesized via a microwave-assisted polyol process by the use of the cheapest and the most readily available starting materials of RuCl₃ and Na₂SeO₃. The results obtained showed that the microwave-assisted polyol process effectively controlled the particles’ size and distribution, which contributed to the high ORR activity of the Ru85Se15/C catalyst. Microwave irradiation promoted the further reaction between Ru and Se, which led to the generation of a new compound, Ru₅Se₄. The Ru₅Se₄/C catalyst showed high catalytic activity for the ORR with a strong methanol tolerance. Furthermore, the synthetic process was simple, fast, and relatively environmentally friendly.

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References