RuSe catalysts modified by selenium have been introduced as alternative materials to Pt in Direct methanol fuel cells (DMFCs). RuSe nano-particles were synthesized on the Vulcan XC72R carbon supports via polyol method. The prepared catalysts were electrochemically and physically characterized by cyclic voltammetry (CV), linear sweep voltammetry, methanol tolerance test, X-ray diffraction (XRD), Transmission electron microscopy (TEM), Energy-dispersive Spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS). Increasing the Se concentration up to 20 at % increased the electro-catalytic activity for the oxygen reduction. By increasing Se amount, Ru metallic form on the surface was increased. The Ru80Se20/C catalysts showed the highest oxygen reduction reaction (ORR) activity and outstanding methanol tolerant property in half cell tests as well as single cell test.

Key Words: Ruthenium-chalcogenide, Fuel cell, Oxygen reduction reaction, Electro-catalysts, Methanol tolerant property

Introduction

DMFCs are becoming promising power sources to substitute fuel combustion energies as well as batteries in portable electronic devices. Significant and intensive investigations in this field have been progressed to commercialize this device. Until now, all low-temperature fuel cells including DMFCs have used platinum or platinum based materials as the electrode. PtRu alloy catalysts are widely used as the anode material. In the cathode, platinum shows an outstanding performance for oxygen reduction such as the highest catalytic activity and stability. Its high cost, however, is a serious problem. This problem has to be solved for successful commercialization. To solve the economic problem, Pt-transition metal alloy materials such as PtNi, PtCo, PtCr are developed as ORR catalysts to be solved for successful commercialization. To solve the economic problem, Pt-transition metal alloy materials such as PtNi, PtCo, PtCr are developed as ORR catalysts. Its high cost, however, is a serious problem. This problem has to be solved for successful commercialization. To solve the economic problem, Pt-transition metal alloy materials such as PtNi, PtCo, PtCr are developed as ORR catalysts. Furthermore, ternary or quaternary Pt based catalysts and Pt nano-particles with new support materials are introduced. These materials show the improved ORR activity because prevention of the particle sintering, surface roughening from the removal of some alloy metal, proper crystallographic geometry, and change of Pt-Pt inter-atomic distance causing change of Pt electro binding energy. Amounts of platinum, however, are still needed and it is not enough. Furthermore, platinum based catalysts show low methanol tolerance property. It is not suitable for the cathode material in DMFCs. Amount of methanol crossover generally occurs from the anode to cathode in DMFCs. Methanol crossover is the main reason for the drop in performance in the cathode. Development of economic catalysts with high ORR activity and methanol tolerant property is needed.

Recently, many researchers have interested in the development of Pt-free materials for oxygen electro-reduction. Efforts have been made to develop the non-platinum ORR catalysts such as Pd alloy materials, transition-metal macrocyclic compounds, Ru based materials, and N doped carbon materials. The approach of non-Pt catalysts not only makes fuel cells economical but also clears methanol crossover problem. Among various non-Pt catalysts, Ru based catalysts show good catalytic activity in ORR and high selectivity for four-electron reduction of oxygen to water in acidic media. The Ru based chalcogenides can be divided into Chevrel phases and amorphous ruthenium chalcogenides. The former shows good performance as a cathode material. They are generally prepared by solid-state reaction in high temperature and pressure which is very complicated and expensive. The latter shows efficient activity for ORR in acidic media at low temperatures.

In this study, the Ru-chalcogenide (RuSe) nano-particles were synthesized on the carbon support via polyol method and an optimum composition was found. Polyol reduction is a well known process for synthesizing metallic nanoparticles. For comparison, Ru/C was prepared with the same process. The prepared RuSe/C catalysts were tested for electro-chemical studies in half-cells as well as in single cells, and physical characteristics were carried out by XRD and XPS.

Experimental

RuSe nano particles were deposited on Vulcan XC72R using ethylene glycol as a reducing agent via polyol process. Ruthenium acetylacetonate and selenium tetrachloride were dissolved in ethylene glycol and then Vulcan XC72R was added to the solution. The suspension was sonicated and stirred for 1 h under N2 condition. The suspension was then refluxed at 160 °C under N2 condition with continuous stirring for 4 h. After the reflux, the suspension was filtered and washed with DI water and ethanol. Finally, the catalysts were dried at 80 °C, overnight. The prepared catalysts are notated as Ru/C, Ru90Se10/C, Ru90Se10/C, Ru90Se10/C, Ru50Se10/C, Ru50Se10/C, Ru50Se10/C, and Ru50Se10/C to their atomic composition ratios. The Ru50Se10/C notation means a prepared ratio. Loading of metals was 60 wt %. All chemicals were analytical grade or better and were purchased from Sigma-Aldrich.
XRD analysis was performed using a Cu Ka radiation with a D/Max-IIIC diffractometer for characterization of structural properties of the powder catalysts. XPS measurements were performed using Al Ka radiation and the constant pass energy of 25 eV. The XPS peak software version 4.1 was used, and spectral peaks were fitted using a mixed Gaussian-Lorentzian (80:20) line and Shirley baselines. TEM analysis was done on a field emission transmission electron microscope (Tecnai G2 F30 S-Twin). EDS analysis was carried out using a field emission SEM (Nova230) at an acceleration voltage of 20 kV.

Electrochemical analysis was carried out in a three electrode cell with a platinum counter electrode, an Ag/AgCl reference electrode (BAS Co., Ltd., MF-2052 RESB), and a glassy carbon working electrode (3 mm dia, BAS Co., Ltd., MF-2012). The working electrodes were prepared by the thin-film electrode method and had a loading of 80 μg catalyst. The prepared electrodes were tested for CV and linear sweep voltammetry tests. The CV test was performed between 0.0 and 0.8 V (vs. reference hydrogen electrode (RHE)) at a scan rate of 15 mV s⁻¹. Nitrogen purged 1 M HClO₄ solution was used as an electrolyte. The linear sweep voltammetry was performed by rotating the working electrodes at a scan rate of 5 mV s⁻¹ in oxygen saturated 1 M HClO₄ and in oxygen saturated 1 M HClO₄ + 0.1 M methanol solution, respectively. All electrochemical experiments were carried out at room temperature and at ambient pressure. All potentials in this study were converted to RHE scale.

The membrane electrode assemblies (MEAs) were fabricated by spraying the catalyst onto Nafion 112. The anode catalyst was Pt/Ru/C (E-tek, 60 wt %, Pt:Ru = 1:1 atomic ratio) and the cathode catalyst was Pt/C (E-tek, 60 wt %) and Ru₁₀₀₋ₓSₓ/C. The catalyst loading was 2.5 mg cm⁻². The catalyst-coated membranes were hot-pressed at 120 °C for 3 min. Polarization curves were obtained using a homemade single cell with an active area of 4 cm². 1 M methanol and oxygen were fed into the anode and cathode at the flow rate of 1 mL min⁻¹ and 100 cc min⁻¹, respectively. The single cells were operated at 70 °C.

Results and Discussions

Fig. 1(a) shows a TEM image of the Ru₈₀Sₑ₂₀/C catalyst. There are nano sized metal particles on the carbon support. However, a non-homogeneous particle distribution is observed due to the high RuSe loading. Reliable analysis of the particle size is difficult from TEM image. The particle size of each catalyst was calculated from XRD analysis. The average particle sizes were calculated using the Debye-Scherrer equation. The average particle sizes were 4.9, 5.1, 3.9, 3.6, 4.1, and 4.6 nm for the Ru/C, Ru₉₅Sₑ₁₀/C, Ru₈₅Sₑ₁₅/C, Ru₈₀Sₑ₂₀/C, and Ru₇₅Sₑ₂₅/C catalysts (b). The calculated average particle size was 2.5 µm. The catalyst loading was 2.5 mg cm⁻². The catalyst-coated membranes were hot-pressed at 120 °C for 3 min. Polarization curves were obtained using a homemade single cell with an active area of 4 cm². 1 M methanol and oxygen were fed into the anode and cathode at the flow rate of 1 mL min⁻¹ and 100 cc min⁻¹, respectively. The single cells were operated at 70 °C.

Electrochemical analysis of the synthesized catalysts is shown in Fig. 2. Fig. 2(a) shows CV results of the Ru/C, Ru₉₀Sₑ/C, Ru₈₀Sₑ₁₀/C, Ru₈₅Sₑ₁₅/C, Ru₈₀Sₑ₂₀/C, and Ru₇₅Sₑ₂₅/C catalysts. With Ru/C catalyst in the range 0 - 0.2 V, an anodic peak was attributed to hydrogen desorption from Ru surface. In the region 0.2 - 0.8 V, an increasing anodic current was detected due to the ruthenium surface oxidation and adsorption of water related species, such as the hydroxyl group. The cathodic peak around 0.2 V was caused by reduction of oxidized Ru surface and adsorption of hydrogen on Ru surface. Increasing Se amount in the catalysts, however, the hydrogen adsorption peak is significantly suppressed, indicating that Ru surface was modified by Se. Furthermore, increasing Se amount, Ru oxidation peaks were significantly suppressed. It was reported that Se stabilized Ru surface against oxidation.

Following the CV studies, we conducted ORR measurements (Fig. 2(b)). For a comparison, Pt/C (E-tek, 60 wt %) is also measured. Current densities at 0.7 V were −1.26, −1.47, −1.55, −1.74, −1.87, −0.95 and −2.23 mA cm⁻² for the Ru/C, Ru₉₀Sₑ/C, Ru₈₀Sₑ₁₀/C, Ru₇₅Sₑ₁₅/C, Ru₆₀Sₑ₂₀/C, Ru₅₅Sₑ₂₅/C, and Pt/C. In the Ru based catalysts, the Ru₆₀Sₑ₂₀/C catalyst showed the high-
RuSe Catalysts for Oxygen Electro-Reduction


Table 1. Summary of physical and electrochemical properties of the Ru/C, Ru95Se5/C, Ru90Se10/C, Ru85Se15/C, Ru80Se20/C, and Ru75Se25/C catalysts

<table>
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<tr>
<th>Physical characterization</th>
<th>Electrochemical characterization</th>
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<td>(110) Peak (°)</td>
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<tr>
<td>Ru/C</td>
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<td>Ru80Se20/C</td>
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<td>Ru75Se25/C</td>
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Figure 2. Electrochemical characterization: Cyclic voltammetry results (a) and ORR results (b) for the Ru/C, Ru95Se5/C, Ru90Se10/C, Ru85Se15/C, Ru80Se20/C, and Ru75Se25/C catalysts. Tafel plots for the ORR of Ru/C, Ru90Se10/C, and Ru80Se20/C catalysts (c). Methanol tolerance results for the Ru80Se20/C catalyst (d).

The mass activity of Ru80Se20/C was almost twice as large as that of the Ru/C. The above observations, optimum concentration of RuSe composition was the Ru80Se20/C which is similar with a previous study. Bron et al. suggested Ru80Se15 composition as the optimum concentration. This difference is caused by difference surface features such as amounts of Ru metal and Ru oxide originated from synthesis process. Se modified Ru catalysts showed the improved ORR activity which has been related to chemical stabilization of metallic Ru surface against oxidation. Babu et al. reported that Se on the Ru surface existed as metallic form due to charge transfer from Ru to Se. This charge transfer prevents the oxidation of Ru surface. In Fig. 2(c), the kinetic currents are calculated using the Koutecky-Levich (K-L) equation and Tafel plots. The RDE data are analyzed using the K-L equation:
\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_0} = \frac{1}{j_0} + \frac{1}{B_0^{0.5}} \tag{1}
\]

Where \( j \) is the measured current density, \( j_k \) is the kinetic current density, \( j_0 \) is the diffusion-limited current density, \( \omega \) is the rotation rate of the electrode and \( B \) is the Levich constant. The value of the \( B \) can be obtained from the slope of the K-L plot. The calculated kinetic currents \( j_k \) of Ru/C, Ru\(_{90}\)Se\(_{10}\)/C and Ru\(_{80}\)Se\(_{20}\)/C are displayed in semi-logarithmic plots versus the potential \( E \). The corrected \( j_k \) of three catalysts are compared at 0.7 V. The kinetic current densities at 0.7 V were 1.34, 1.47 and 1.80 mA cm\(^{-2} \) for the Ru/C, Ru\(_{90}\)Se\(_{10}\)/C and Ru\(_{80}\)Se\(_{20}\)/C.

The Ru\(_{80}\)Se\(_{20}\)/C catalyst showed the highest kinetic activity. As shown in the Tafel plot, Se modification of the Ru surface leads to increasing the catalytic activity of the Ru catalyst. The Ru\(_{80}\)Se\(_{20}\)/C catalyst showed significantly high methanol tolerant property compared to the Pt/C (Fig. 2(d)). The current density under methanol environment of Ru\(_{80}\)Se\(_{20}\)/C catalyst was \(-1.82 \) mA cm\(^{-2} \), which is 97.3\% performance of the activity without methanol. It is the reason that Ru catalyst has almost no methanol oxidation property. The high methanol property make Ru\(_{80}\)Se\(_{20}\)/C a powerful candidate as a cathode material of DMFCs. A summary of the electrochemical analysis results is tabulated in Table 1.

Fig. 3 exhibits the XPS results of Ru 3d core level for Ru\(_{80}\)Se\(_{20}\)/C (Fig. 3 (a)) and Ru\(_{80}\)Se\(_{20}\)/C (Fig. 3(b)). The results of all catalysts for Ru 3d core level are summarized in Table 1. The prepared catalysts were supported by Vulcan XC72R carbon material which shows the large C 1s peak in 284.5 eV. The metallic Ru doublet with 3d\(_{5/2}\) and 3d\(_{3/2}\) components shows peaks at 280.1 eV and 284.3 eV, respectively.\(^{51}\) From peak deconvolution, the Ru surface was composed of a metallic Ru and an oxide form. The RuO\(_2\) doublet with 3d\(_{5/2}\) and 3d\(_{3/2}\) components exhibit peaks at 281.3 eV and 285.5 eV, respectively.\(^{52,53}\) The Ru/C catalyst was composed of 38\% metallic Ru and 62\% RuO\(_2\). The Ru\(_80\)Se\(_{20}\)/C was observed. It has good agreement with previous study. As mentioned above, Se modification on Ru surface makes Ru surface metallic. Lewera et al. suggested that the oxygen in the Ru surface is strongly bonded to Ru, and Se is weakening the Ru-O bond.\(^{54}\) In Fig. 3(c), the XPS result of Se 3d core level for Ru\(_{80}\)Se\(_{20}\)/C is exhibited. The results of all catalysts for Se 3d core level are summarized in Table 1. The binding energy peak for Se 3d\(_{5/2}\) peak appear at 55.2 eV. The Se 3d\(_{3/2}\) peak for oxidized form appears at about 58.5 - 59.0 eV.\(^{52,53}\) The Ru\(_{80}\)Se\(_{20}\)/C catalyst was composed of 61.0\% elemental Se and 39.0\% oxidized Se. Other catalysts show similar results to Ru\(_{80}\)Se\(_{20}\)/C. All catalysts appeared the large amount of oxidized Se. In a previous study, Zhu et al. reported that elemental Se powder were synthesized by polyol method in similar conditions.\(^{55}\) It means that reduction of the Se was affected by the Ru species. The oxidized Se on the RuSe catalysts should be affected by the charge transfer from Ru to Se on Se modified Ru surface.

Fig. 4 shows the single cell performance of Ru\(_{80}\)Se\(_{20}\)/C catalyst. The commercial Pt/C was prepared for comparison. MEA1 was composed of PrRu/C (anode) and Pt/C (cathode) and MEA2 was composed of PtRu/C (anode) and Ru\(_{80}\)Se\(_{20}\)/C (cathode). The open circuit voltages (OCV) of MEA1 and MEA2 were 0.62 V and 0.70 V, respectively. The MEA2 showed improved OCV due to outstanding methanol tolerant property of Ru\(_{80}\)Se\(_{20}\)/C which is exhibited in electrochemical study. As expected, MEA1 showed much higher max power density, 73.5 mW cm\(^{-2} \) than MEA2. Max power density of MEA2 was 39.5 mW cm\(^{-2} \). The Ru\(_{80}\)Se\(_{20}\)/C which is non-Pt cathode material showed 53.6\% max power density and the improved OCV when comparing with Pt/C. This is suitable for cathode material to substitute Pt but the improved ORR activity of RuSe catalysts is essential.
The Se modified Ru catalysts were synthesized via a polyl method. By adding Se component, amounts of metallic Ru surface were increased and improvement of ORR activity was achieved. Optimum concentration of RuSe composition was the Ru$_{80}$Se$_{20}$/C which is almost twice as higher than Ru/C in mass activity. Furthermore, the Ru$_{80}$Se$_{20}$/C showed prominent methanol tolerant property. Electrochemical characterization and single cell measurement showed that the Ru$_{80}$Se$_{20}$/C is suitable for cathode material of DMFCs.

Conclusions

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