



Short communication

Fuel cell performance of templated Ru/Se/C-based catalysts

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ABSTRACT

The catalytic activity of highly porous Ru/Se/C-based catalysts was investigated. Fuel cell measurements were carried out in a 5 cm² cell using pure hydrogen and oxygen at a temperature of 75 °C and ambient pressure. Maximum power densities of 100, 144 and 150 mW cm⁻² were observed for membrane electrode assemblies (MEA) containing of 0.04, 0.12 and 0.22 mg cm⁻² ruthenium, respectively. The catalysts were further characterized by high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS).

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1. Introduction

Several platinum-free catalyst systems have been reported for the use as alternative cathode catalysts in polymer electrolyte membrane fuel cells (PEMFC) [1,2]. One of the first non-noble metal electrocatalysts for the oxygen reduction reaction (ORR) was reported by Jasinski about 40 years ago [1]. The author describes the use of cobalt phthalocyanine as cathode catalyst in fuel cells. Since his discovery, extensive research work on Fe-N-C-type and Co-N-C-type non-noble metal catalysts (NNMC) was done and is still undergoing today [3,4]. Another type of a platinum-free cathode catalysts are chalcogenide based materials such as Ru/Se/C. The catalytic activity of these transition metal chalcogenides for oxygen reduction was first reported by Alonso-Vante and Tributsch [2]. Various approaches about the synthesis of transition metal chalcogenides supported on carbonaceous materials are reported in literature [5,6]. Recently, we have reported a new method for the preparation of highly porous Ru/Se/C electrocatalysts applying template assisted synthesis route [7].

In this study, templated Ru/Se/C electrocatalysts have been investigated in a fuel cell and they were found to exhibit comparable activity to the Ru/Se/C catalysts reported in the literature. This demonstrates the utility of the template assisted synthesis route.

2. Experimental

2.1. Catalyst preparation

A detailed description for the preparation of templated Ru/Se/C catalysts is given elsewhere in literature [7]. Briefly, a mesoporous silica gel was impregnated with an aqueous solution of RuCl₃·xH₂O, SeO₂ (0.1, 0.3 or 0.6 M; with a molar ratio of 1:1) and sucrose. Afterwards, the composite material was carbonized and reductively annealed at elevated temperature. The resulting carbon/silica gel composites were treated with 40% hydrofluoric acid in order to liberate the catalyst material from the composite materials. Three catalyst samples with different Ru and Se contents were prepared. The composition of the resulting catalysts samples was tested using electron microprobe (Table 1).

2.2. Electrochemical characterization

PEM fuel cell measurements were carried out using a fuel cell technologies (FCT) test station with a 5 cm² fuel cell. Anodes (50 wt.% platinum on carbon, E-Tek Inc.) and cathodes containing Ru/Se/C catalysts were prepared according to the procedure reported in Ref. [8]. Briefly, 10 mg of each Ru/Se/C catalyst were suspended in a mixture of nanopure water and 5% Nafion solution. The three catalyst suspensions were blended ultrasonically for 45 min. The different cathode catalyst slurries were deposited and spread uniformly on 2.3 × 2.3 cm² pieces of 3M-fabricated gas diffusion layer (GDL). Anode pieces were prepared with 50 wt.% platinum on car-

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Table 1

Ruthenium concentration of each synthesis batch and ruthenium content of corresponding MEAs.

	Initial Ru concentration (M)	Ru content (mg cm^{-2}) of MEA
$\text{Ru}_{0.02}\text{Se}_{0.02}\text{C}_{0.90}\text{O}_{0.06}$	0.1	0.04
$\text{Ru}_{0.06}\text{Se}_{0.06}\text{C}_{0.84}\text{O}_{0.04}$	0.3	0.12
$\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$	0.6	0.22

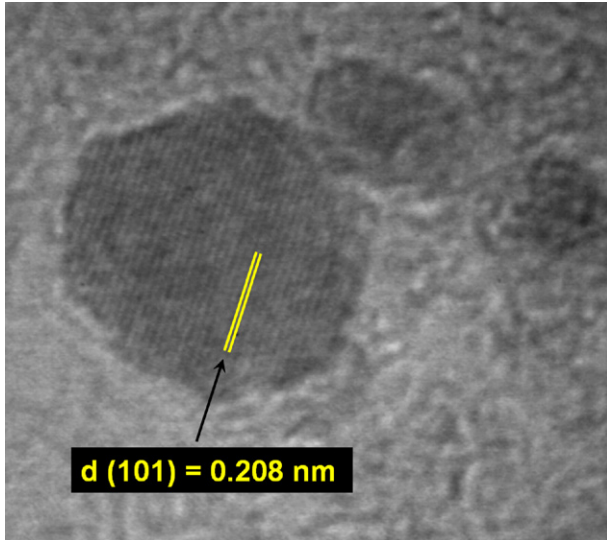


Fig. 1. High resolution transmission electron micrograph of sample $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$.

bon, (E-Tek Inc.) 20 mg of Pt/C were suspended in 0.8 ml of nanopure water and 0.5 ml of 5% Nafion solution and blended in the ultrasonic bath. 300 μl of the anode catalyst suspension was applied to a $2.3 \times 2.3 \text{ cm}^2$ piece of the GDL material and spread uniformly.

The ruthenium content of the prepared cathodes is given in Table 1. MEAs were hotpressed using 3 M ionomer membrane under 190 bar at 140°C for 45 s. For comparison purposes MEAs with different cathode catalysts were prepared. Corresponding MEAs were made with templated Fe-N-C-type catalyst [9] and 5 wt.% platinum on carbon (E-Tek Inc.), respectively. The Fe loading was $1.9 \times 10^{-2} \text{ mg cm}^{-2}$ for the Fe-N-C-type catalyst and the Pt loading was $5 \times 10^{-2} \text{ mg cm}^{-2}$ in case of 5 wt.% Pt/C. The detailed protocol for the fuel cell measurements are given elsewhere in literature [8]. Briefly, fuel cell measurements were carried out at 75°C using hydrogen/oxygen at atmospheric pressure. Humidified hydrogen and oxygen gas flows were maintained at 200 and 450 sccm, respectively. An initial pretreatment was performed for 1 h at open circuit potential (OCP). Polarization curves were obtained by varying an applied potential between OCP and 50 mV. The potential was

changed at 50 mV steps with a 10 s hold at each potential step. Durability tests were carried out by holding the potential at 0.6 V and recording the current over a 20 h period.

2.3. High resolution transmission electron microscopy

The structure of the nanoparticles in the catalyst sample $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$ was investigated using a transmission electron microscope (Philips CM-200 microscope). The images were taken at 200 kV accelerating voltage and 0.23 nm point resolution.

2.4. X-ray photoelectron spectroscopy

The surface composition of the catalyst sample $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$ was studied using a VG Microtech Multilab XPS system (Thermo Electron Corporation) equipped with a CLAM-4 hemispherical analyzer. The analyzer was operated in constant pass energy mode (50.0 eV) with a Mg K_{α} radiation (1253.6 eV; 15 kV and 20 mA) source.

3. Results

3.1. High resolution transmission electron microscopy

In our earlier work we have shown that templated Ru/Se/C catalysts consist of nanosized clusters (2–5 nm), which are embedded in the carbon matrix [7]. High resolution transmission electron microscopy (HRTEM) images were recorded in the present study and a resulting HRTEM image is given in Fig. 1. The digitally recorded HRTEM image of sample $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$ shows what could be a ruthenium nanocrystal embedded into carbon. Lattice planes whose spacings match those of Ru are clearly visible. The lattice spacings indicated in Fig. 1 could correspond to the $d(101) = 0.208 \text{ nm}$ of hexagonal ruthenium. Amorphous clusters are also visible at the grain boundary/surface of the nanocrystal as shown in Fig. 1, which may consist of selenium or selenium oxide among other possibilities.

3.2. X-ray photoelectron spectroscopy

The obtained X-ray photoelectron spectroscopy (XPS) spectra of catalyst sample $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$ are shown in Fig. 2. The elements found in this sample are carbon, ruthenium, selenium and oxygen. The C1s and Ru3d element spectra overlap with regard to their binding energy values ranging from 280 to 290 eV [10,11]. The Ru 3d_{5/2} spectrum was fitted with two component peaks. The first peak having a binding energy of 280.3 eV can be assigned to ruthenium in the metallic state [11]. The second component peak located at a binding energy value of 281.3 eV was attributed to ruthenium species in RuO_2 [11,12].

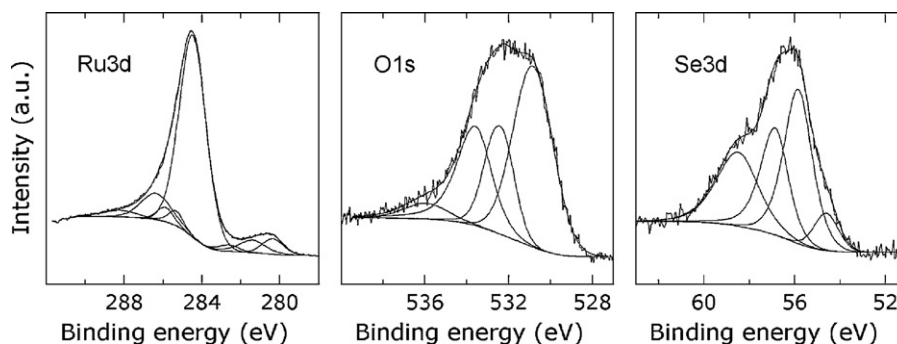


Fig. 2. XPS spectra of sample $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$. Ru3d, O 1s and Se 3d regions are indicated.

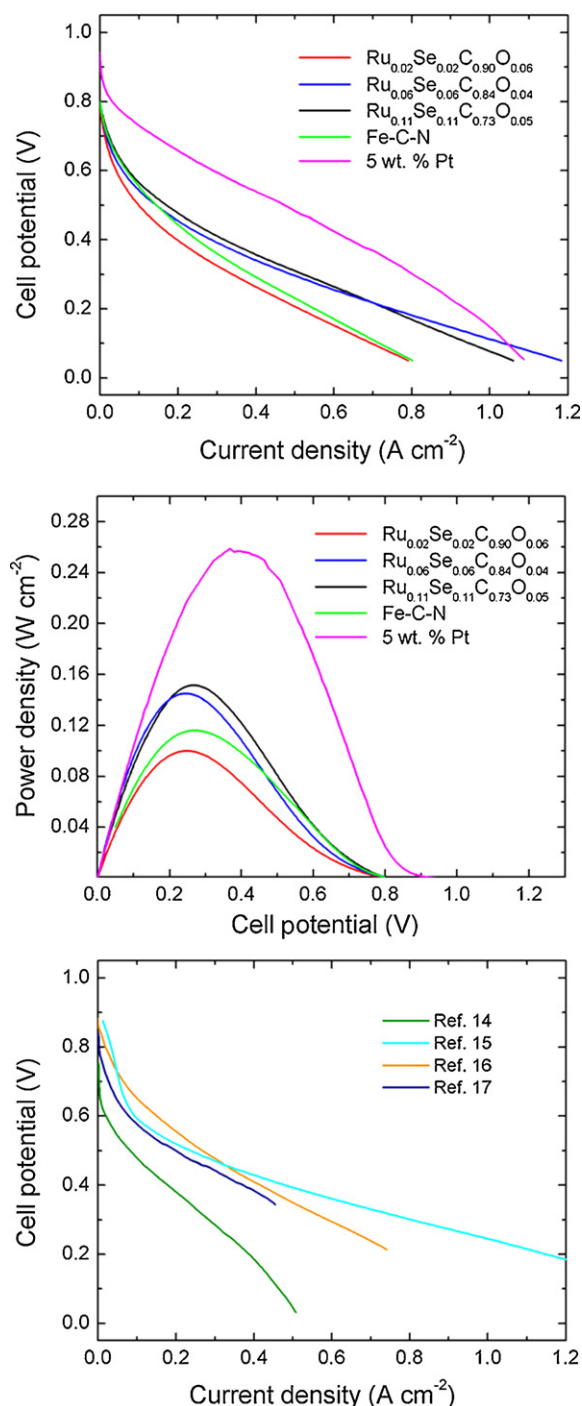


Fig. 3. $\text{H}_2\text{-O}_2$ polarization curves (75°C) for templated Ru/Se/C, templated Fe-N-C and 5 wt.% Pt/C.

The fitted O 1s spectrum has four components peaks. According to Fiechter et al. the peaks with binding energies ranging from 530.1 to 532.5 eV may originate from oxygen species in RuO_2 , RuO_3 and $(\text{SeO}_3)^{2-}$, respectively [13]. The peak at 530.7 eV may also be related to oxygen in phenyl carbonyl groups [10]. Carbonyl oxygen atoms in esters and anhydrides give binding energies around 532.5 eV. The peak at 533.6 eV can be assigned to oxygen of phenol groups or hydroxyl oxygen of carboxyl groups [10]. The peak at 536.1 eV is related to adsorbed water.

The Se 3d spectrum was deconvoluted into four peaks located at binding energies of 54.5, 55.7, 56.9 and 58.5 eV, respectively. Apparently, selenium is present in different oxidation states. Component

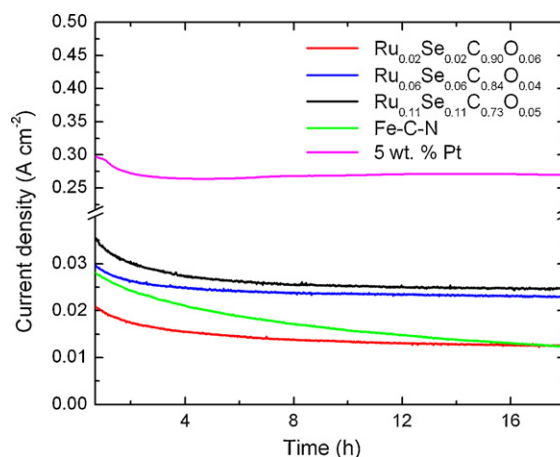


Fig. 4. Current versus time during potential hold experiments (0.6 V) for templated Ru/Se/C, templated Fe-N-C and 5 wt.% Pt/C.

peaks at lower binding energy (54.5 and 55.7 eV) may be attributed to elemental selenium or selenide species such as RuSe_2 . Corresponding species are likely generated during the heat treatment and reductive annealing procedure in hydrogen atmosphere [13]. Selenium is also present in highly oxidized states such SeO_2 , H_2SeO_3 or SeO_3^{2-} , which correspond to the peak component at 58.5 eV [11,13].

In our opinion, the information that can be gleaned, with certainty, from these XPS studies is limited. This is because of the broad featureless XPS lines which are fitted with numerous overlapping peaks. The fits are certainly not unique. In addition, assigning the fitted peaks to chemical surface species is also fraught with difficulty due to the large number of species that give binding energies in the same ranges.

Our work, although consistent with previous studies, does not further the understanding of the nature of the catalytic sites in these materials but shows that Ru/Se/C catalysts prepared by the template assisted route have similar surface chemistry to samples prepared by other methods.

3.3. Fuel cell tests

Fig. 3 shows the polarization and power density curves obtained from single cell measurements for MEAs with templated Ru/Se/C catalysts, a templated Fe-N-C catalyst [9] and a MEA prepared using 5 wt.% platinum on carbon. In addition, selected polarization curves of Ru-based catalysts reported in literature are also given in Fig. 3. Corresponding polarization curves have been measured under similar conditions. The polarization curves of the catalysts $\text{Ru}_{0.02}\text{Se}_{0.02}\text{C}_{0.90}\text{O}_{0.06}$, $\text{Ru}_{0.06}\text{Se}_{0.06}\text{C}_{0.84}\text{O}_{0.04}$ and $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$ show current densities of 0.42, 0.60 and 0.63 A cm^{-2} at 0.25 V, respectively.

The maximum power densities of the templated Ru/Se/C catalysts range from 100, 144 and 150 mW cm^{-2} for the corresponding catalyst samples. Fig. 3 shows that the catalytic activity increases as the ruthenium and selenium content in the prepared catalyst samples increases. The catalytic activities, inferred from the polarization curve(s), of the templated Ru/Se/C samples are similar to the catalytic activity of templated Fe-N-C. Both types of non-platinum catalysts exhibit an onset potential of 0.75 to 0.8 V in the present fuel cell study. However, the current densities of both catalysts do not exceed 0.17 A cm^{-2} at cell potentials above 0.5 V. The Fe-N-C-type catalyst exhibits a current density of 0.47 A cm^{-2} at 0.25 V and a maximum power density of 117 mW cm^{-2} was obtained. In contrast, the MEA prepared with 5 wt.% platinum delivered a current density of 0.87 A cm^{-2} at $E_{\text{cell}} = 0.25\text{ V}$ and a maximum power density of 256 mW cm^{-2} . The present results show that the tem-

plated Ru/Se/C catalysts have a much lower output performance than dispersed platinum on carbon. The maximum power density of the MEA prepared with templated Ru/Se/C catalysts is around 45% lower than the result obtained with the platinum-containing MEA. Similar results have been reported by Solorza-Feria and co-workers who were investigating Ru-based clusters (Ru, Ru/Se and Ru/Fe/Se) as cathode catalysts in fuel cells [14,15]. By looking at the catalytic activities of other Ru-based catalysts described in the literature it can be seen that the activity of our templated Ru/Se/C catalysts compares well with reported data. The polarization curves of Ru/Se/C catalysts described by Liu et al. [16], Solorza-Feria and collaborators [14,15] and Wieckowski and coworkers [17] are displayed in Fig. 3. Corresponding data were obtained with comparable cathode catalyst loadings.

Fig. 4 shows the obtained current densities recorded during potential hold experiments at 0.6 V. After an initial drop (during the first 4 h) the observed currents of templated Ru/Se/C catalysts remained relatively constant over the following 14 h period. In contrast, we observed a pronounced current decay for the templated Fe-N-C-type catalyst as illustrated in Fig. 4. These results show one advantage of the templated Ru/Se/C catalysts over the templated Fe-N-C-type catalyst. Templated Ru/Se/C catalysts reveal higher stability and durability during constant operation at 0.6 V. The current density observed for the MEA prepared with 5 wt.% platinum on carbon is about ten times higher during the potential hold at 0.6 V in comparison to the catalyst sample $\text{Ru}_{0.11}\text{Se}_{0.11}\text{C}_{0.73}\text{O}_{0.05}$.

4. Conclusion

Templated Ru/Se/C-based catalysts were investigated in a 5 cm² fuel cell, which was operated using pure hydrogen and oxygen. The prepared catalyst samples delivered maximum power densities between 100 and 150 mW cm⁻² at a cell temperature of 75 °C under ambient pressure. The fuel cell performance of our templated catalyst is comparable to that observed for Ru/Se/C catalysts reported in literature. Durability tests at 0.6 V have shown a higher stability

of templated Ru/Se/C in comparison to templated Fe-N-C catalyst. The structural analysis confirmed the existence of nanocrystals embedded in carbon. Amorphous clusters were also observed at the surface of the ruthenium nanocrystals. XPS measurements suggest that metallic ruthenium and ruthenium oxide may exist along with selenide and oxidized selenium species.

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