

Short communication

Synthesis and characterization of Pt–Se/C electrocatalyst for oxygen reduction and its tolerance to methanol

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Received 7 March 2007; received in revised form 17 June 2007; accepted 24 June 2007

Available online 4 July 2007

Abstract

Pt–Se/C catalyst for oxygen reduction reaction (ORR) was prepared by a modified organic colloid method with sodium citrate and triphenyl phosphine as complexing agents. The active components were highly dispersed on the carbon black support. The addition of Se improved the dispersion of platinum significantly and reduced the particle size to be less than 1.8 nm. The catalyst showed similar activity compared to Pt/C catalyst, and had a higher tolerance to methanol than Pt/C catalyst. The catalyst was characterized with X-ray diffraction (XRD) and transmission electron microscope (TEM). Electrochemical measurements showed that the synthesized Pt–Se/C catalyst had a four-electron transfer mechanism for oxygen reduction. © 2007 Elsevier B.V. All rights reserved.

Keywords: Pt–Se/C catalyst; Oxygen reduction reaction; Methanol tolerance; Direct methanol fuel cells

1. Introduction

Direct methanol fuel cells (DMFCs) are the most attractive fuel cells compared to other types due to their ease, safe handling, distribution, storage of the fuel and high-energy density. The commercialization of DMFCs is, however, still hindered by a number of basic problems. One of the major problems, which decreases the efficiency of conversion of the chemical energy of the methanol to electrical energy in DMFCs, is the methanol crossover through the polymer electrolyte membrane [1,2]. The catalytic oxidation of methanol in the cathode is harmful to the fuel cell, resulting in not only decreasing fuel cell efficiency but also losing output power. To avoid this problem, one strategy is to develop novel membranes that have less methanol permeability or to modify the existing membranes. Unfortunately, no significant progress on the development of alternative electrolyte membranes with neither methanol crossover nor high proton conductivity has been made up to now. Another approach is to develop a novel cathode catalyst which has both high performance for oxygen reduction reaction (ORR) and high methanol tolerance.

Some interesting attempts for methanol tolerance catalysts without platinum have been reported in recent years; the cata-

lysts include chalcogenides [3–5] and macrocycles of transition metals [6,7]. Although these electrocatalysts showed high tolerance to methanol, their activities were still much lower than that of Pt/C catalyst, especially in methanol-free electrolytes. Carbon-supported platinum-based alloy catalysts, such as Pt–Fe/C [8], Pt–Co/C [9], Pt–Ni/C [10] and Pt–Cr/C [11], etc., had been widely investigated for oxygen reduction, but no obvious improvement for methanol tolerance had been observed. Recently, Gochi-Ponce et al. prepared a Pt–S/C catalyst, and they found that the catalyst showed a higher methanol tolerance than Pt/C catalyst, but its activity towards ORR was lower than that of the Pt/C catalyst [12].

In the present work, a novel selenium added Pt–Se/C catalyst was prepared by a modified organic colloidal approach. The catalyst showed very good methanol tolerance in methanol-containing electrolytes, while its activity for ORR was comparable with the Pt/C catalyst.

2. Experimental

2.1. Preparation of Pt–Se/C electrocatalyst

Vulcan XC-72R (Carbot Corp., BET: 237 m² g^{−1}, denoted as C) carbon black was used as support, and it was pretreated by washing with acetone, oxidized with 2 M HNO₃ and 30% H₂O₂, then washed with de-ionized water and dried overnight at 80 °C.

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The Pt–Se/C catalyst was prepared by a modified organic colloid method in an ethylene glycol solution. The detailed preparation process could be described as follows: chloroplatinic acid (H_2PtCl_6) and sodium citrate with atomic ratio of 1:2 were dissolved in ethylene glycol and then stirred for 0.5 h until the sodium citrate was completely dissolved. Then, it was mixed with a tetrahydrofuran (THF) solution of selenium and triphenyl phosphine. Carbon black Vulcan XC-72R (300 mg) was then added to the mixture (Pt metal loading: 20%, and Pt:Se = 2:1 in atomic ratio) whilst stirring. The pH of the system was adjusted to >10 by adding 5 wt% KOH/ethylene glycol solution dropwise with vigorous stirring. The mixture was then transferred to a teflon-lined autoclave and reacted at 160 °C for 6 h. After reaction, the mixture was neutralized by adding 10 wt% nitric acid solution to achieve a pH of <4, and then 5 ml of water was added, followed by sonication for 10 min. Thereafter the sample was recovered by filtering, washed with de-ionized water, dried in air at 90 °C, and thermally treated in a tubular furnace under a H_2/N_2 atmosphere at 200 °C for 2 h.

2.2. Material characterization

The characterization of the catalyst was carried out with a XD-3A X-ray diffraction (XRD) meter (Shimadzu, Japan) using filtered Cu $\text{K}\alpha$ radiation at 35 kV and 30 mA, and a Tecnai G220 S-TWIN transmission electron microscope (TEM) (Philips, The Netherlands) with 200 kV acceleration voltage.

2.3. Electrochemical measurements

The catalysts were evaluated electrochemically by cyclic voltametry (CV) and low sweep voltametry (LSV) using an IM6e electrochemical work station (Zahner, Germany) at room temperature in either N_2 -purged or O_2 saturated 0.1 M HClO_4 , and 0.1 M HClO_4 + 0.1 M CH_3OH solutions. A common three-electrode electrochemical cell was used for the measurements. A glassy carbon rotating disk electrode (RDE) with a diameter of 3.2 mm was used as working electrode, the rotating velocity was denoted as ω , and a saturated Ag/AgCl electrode and a platinum wire were used as reference and counter electrodes, respectively.

The catalytic electrode was prepared by the following procedures: the mixture of 5 mg catalyst and 1 ml 0.25% Nafion ethanol solution was sonicated for 30 min, 8 μl of the mixture was taken and dropped on the glassy carbon electrode, and dried at 70 °C for several minutes.

3. Results and discussion

3.1. Catalyst morphology

Fig. 1 shows powder XRD patterns of the Pt–Se/C and Pt/C catalysts with and without heat treatment in hydrogen/nitrogen atmosphere for 2 h at 200 °C. All the XRD patterns clearly showed the characteristic reflections of the face centered cubic (fcc) crystalline Pt, namely, the peaks at ca. 40°, 46°, 67.5° and 81.5° were reflected from Pt (1 1 1), Pt (2 0 0), Pt (2 2 0) and Pt

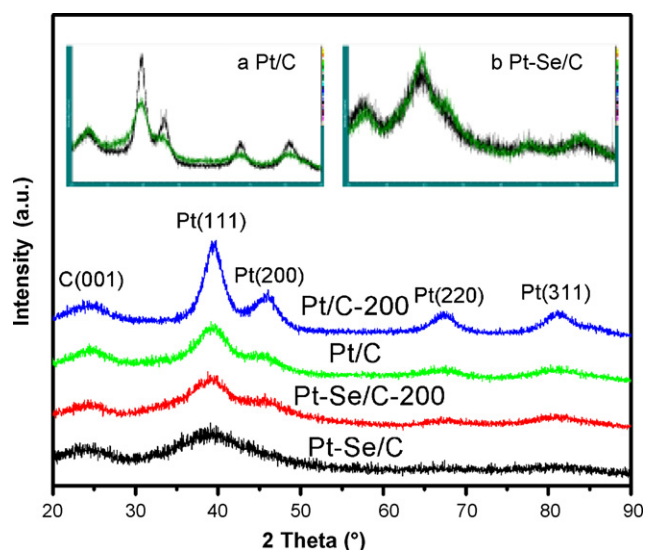


Fig. 1. XRD patterns for the Pt/C and Pt–Se/C catalysts with and without heat treatment in hydrogen/nitrogen atmosphere for 2 h at 200 °C. The insert shows the comparison of (a) Pt/C with (b) Pt–Se/C before and after heat treatment.

(3 1 1) planes, respectively, while a broad reflection observed at ca. 25° (2θ) was due to the amorphous carbon support.

It was interesting to note that no reflection peaks of Se or Pt/Se alloy were observed in XRD patterns, and the addition of Se caused no peak displacements. However, EDX spectra of the Pt–Se/C catalyst clearly showed the presence of Se. This may indicate that Se was either highly dispersed or in an amorphous state. Table 1 shows the lattice parameters calculated from XRD patterns with FullProf 98 software. It was found that the parameters of Pt–Se/C were slightly less than Pt/C; this might result from the incorporation of Se atoms into Pt lattice.

More importantly, the addition of Se could improve the dispersion of the active components remarkably. An extremely fine particle size was obtained for active components; for Pt–Se/C catalyst (20% Pt, Pt:Se = 2:1), the particle size of active components could be ca. 1.2 nm, estimated by the Sherrer equation.

Generally, heat treatment caused particle size of active components to increase; for catalyst Pt/C, as shown in the insert of Fig. 1, the particle size of active components increased significantly after being heated in reduction atmosphere at 200 °C, which size increase is reflected by the higher intensities of the diffraction peaks corresponding to metallic Pt and the lower background. On the other hand, for the Pt–Se/C catalyst, no particle size increase was observed by XRD after the heat treatment. The Pt–Se/C catalyst that was heat treated at 200 °C showed

Table 1
Particle size and lattice parameters of Pt/C and Pt–Se/C catalysts

Sample	Particle size (nm)	M–M mean bond distance (nm)	Lattice parameter (nm)
Pt/C	2.2	0.2664	0.3743
Pt/C-200 ^a	3.1	0.2668	0.3773
Pt–Se/C	1.2	0.2634	0.3724
Pt–Se/C-200 ^a	1.9	0.2641	0.3736

^a Heated at 200 °C for 2 h.

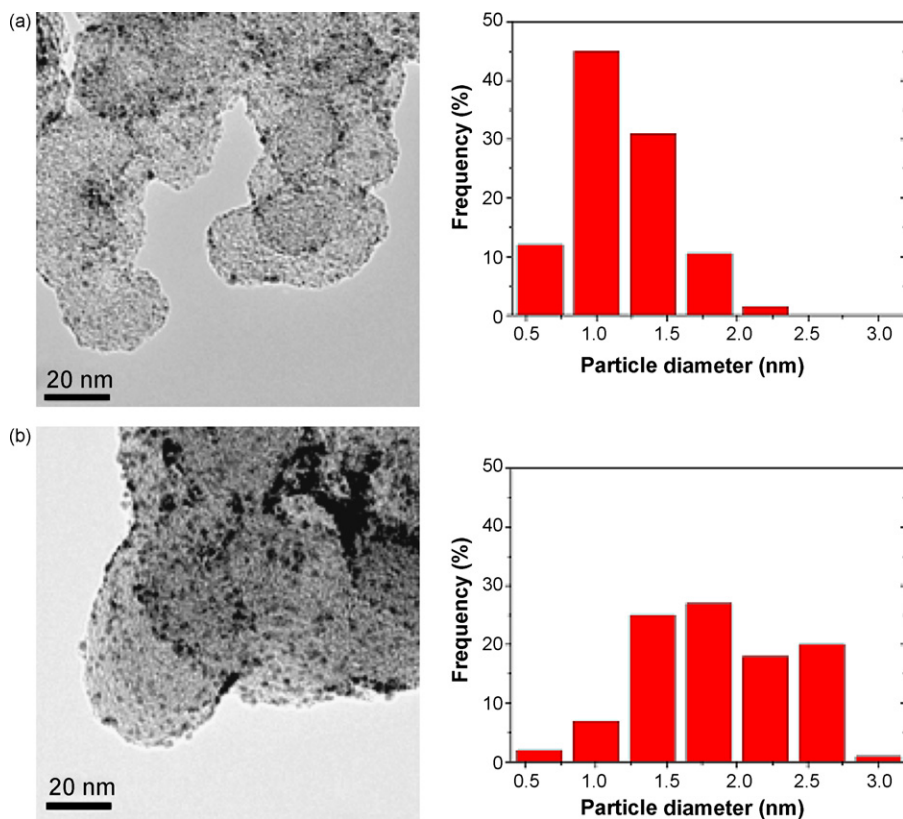


Fig. 2. TEM images and the corresponding particle size distribution histograms for the Pt–Se/C catalysts before (a) and after (b) heat treatment in hydrogen/nitrogen atmosphere for 2 h at 200 °C.

almost same XRD pattern as that without heat treatment. It implied that the addition of selenium could prevent the aggregation and growth of platinum nanoparticles supported on carbon black, and the prevention of aggregation was very helpful to obtain high catalytic performance catalyst [13].

Fig. 2 shows TEM images and the corresponding particle size distribution of the Pt–Se/C electrocatalysts based on the observation of 200 nanoparticles before and after heat treatment in hydrogen/nitrogen atmosphere for 2 h at 200 °C. It can be observed from Fig. 2 that the active components were highly dispersed on the carbon support and the particle size distribution was quite homogeneous. The average particle size of active components calculated from the TEM image of a heat treated sample was ca. 1.8 nm, and it was just slightly larger than that of the sample without heat treatment (ca. 1.2 nm). These results were quite consistent with those observed and calculated from XRD data.

3.2. The activity of Pt–Se/C catalysts for oxygen reduction

Fig. 3 shows representative cyclic voltammograms in N₂-purged 0.1 M HClO₄ electrolyte, recorded on (a) Pt/C and (b) Pt–Se/C electrocatalysts from –0.2 to 1.0 V versus Ag/AgCl, the data were obtained at 300 rpm of RDE and at a scan rate of 40 mV s^{–1}. The potential of plot (a) showed the well-known electrochemical fingerprint of platinum Pt/C. The anodic peak at –0.1 V is attributed to hydrogen desorption from the Pt surface. The small and broad anodic current due to adsorption of water-

related species, such as hydroxyl species, began at 0.1 V and was amplified at 0.6 V to form Pt surface oxide and adsorption of hydrogen on Pt. Plot (b) showed a typical CV of the Pt–Se/C electrocatalyst. The hydrogen desorption peak (–0.2 to 0.1 V) observed in the case of the Pt/C catalyst was completely suppressed in the case of the Pt–Se/C catalyst, indicating that Se significantly modified the electrode surface. Similarly, adsorp-

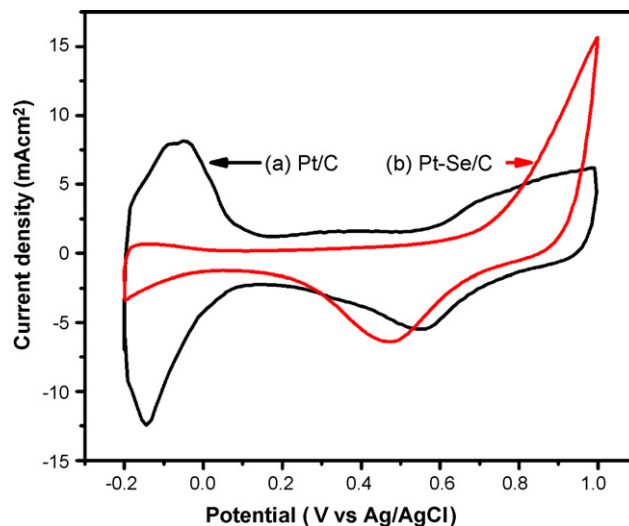


Fig. 3. Cyclic voltammograms of the 20 wt% Pt/C and Pt–Se/C electrodes (RDE at 300 rpm) measured in N₂-purged 0.1 M HClO₄ electrolyte, at room temperature and at a sweep rate of 40 mV s^{–1}.

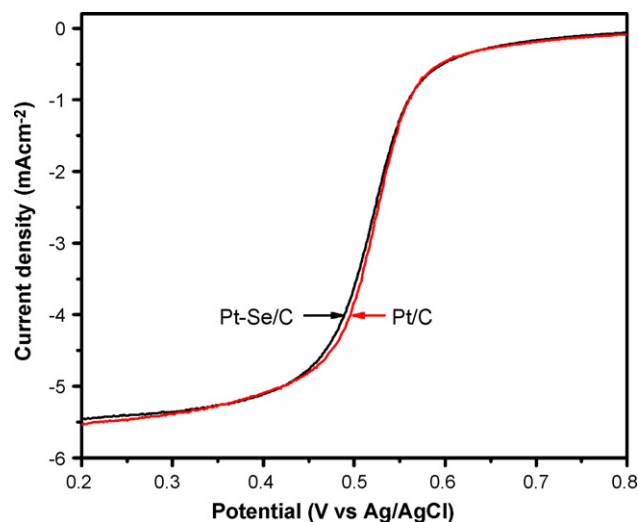


Fig. 4. Polarization curves for the ORR on Pt–Se/C and Pt/C catalysts in 0.1 M HClO₄ at a sweep rate of 5 mV s⁻¹, rotating velocity of 1800 rpm, and room temperature.

tion of water-related species that began at 0.1 V for the Pt/C catalyst was also suppressed by the addition of Se.

We believed that the oxidation current that began at 0.65 V in plot (b) in Fig. 3 might correspond to the oxidation and partial dissolution of the Se overlayers according to the redox reaction: $\text{Se} + 3\text{H}_2\text{O} = \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^-$ [4]. Even if this current overlapped with the Pt oxidation current, the major shift in the surface oxidation threshold due to Se was confirmed. The cathodic peak attributed to the oxide reduction was diminished and shifted to more negative potentials. It seemed that the addition of Se to the catalysts inhibited electrochemical oxidation of Pt. On the other hand, we noticed that the anodic charge for Pt–Se/C was not compensated by the cathodic counterpart, and it might be attributed to the slight dissolution of Se.

Fig. 4 displays the ORR polarization curves for Pt/C and Pt–Se/C in oxygen saturated 0.1 M HClO₄ solution at room temperature and at a sweep rate of 5 mV s⁻¹; the rotating rate of rotating disk electrode was 1800 rpm. It was found that the curve obtained in the case of the Pt–Se/C catalyst was similar to that of the Pt/C catalyst; the half-wave potentials were about 0.56 V (versus saturated Ag/AgCl). It indicated that the Pt–Se/C catalysts have an activity toward ORR similar to that of the Pt/C catalyst.

3.3. The methanol tolerance of Pt–Se/C catalysts

Fig. 5 shows the slow sweep voltammograms obtained for the Pt/C and Pt–Se/C in 0.1 M HClO₄ + 0.1 M methanol under an oxygen atmosphere at a rotating speed of 1800 rpm. The Pt/C exhibited a large anodic current at ca. 0.6 V versus Ag/AgCl because of the oxidation of methanol on Pt/C catalyst, which caused the onset of a net cathodic current to shift cathodically by ca. 250 mV. This result was attributed to the formation of a mixed potential, which was caused by the simultaneous reaction of the methanol oxidation and oxygen reduction on the surface of the Pt/C catalyst [14]. Such a mixed potential at the

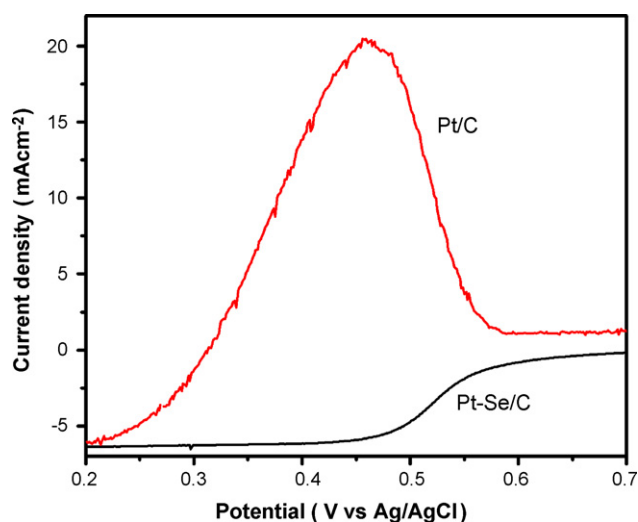


Fig. 5. Polarization curves for Pt/C and Pt–Se/C in 0.1 M HClO₄ + 0.1 M CH₃OH under oxygen atmosphere and at a sweep rate of 5 mV s⁻¹, rotating velocity of 1800 rpm, and room temperature.

cathode should negatively affect the cathode performance of the DMFCs.

It was important that there was no obvious increase in overpotential of the ORR in the presence of methanol for Pt–Se/C catalyst. It was thus clear that the Pt–Se/C was inactive to methanol, and the activity of the Pt–Se/C catalyst to ORR in methanol-containing electrolyte was much higher than that of the Pt/C catalyst at the same conditions. This implied that the Pt–Se/C catalyst might be a good potentially active cathodic catalyst for application in the direct methanol fuel cell.

3.4. Oxygen reduction kinetics of Pt–Se/C catalyst

To obtain kinetic information on this process, the reaction was carried out under steady-state conditions at a rotating disk electrode (RDE). Fig. 6 presents the polarization diagrams for the ORR at the Pt–Se/C electrode at several rotation speeds in oxygen saturated 0.1 M HClO₄ solution at room temperature, with a sweep rate of 5 mV s⁻¹. These types of curves normally show three distinct regions of interest. In the present case the kinetic control region was approximately from 0.7 to 0.6 V versus Ag/AgCl, the diffusion-limited region was from 0.48 to 0.2 V and the mixed control region was from 0.48 to 0.6 V.

In the diffusion-limited region the current increased with the rotation velocity. According to the Koutecký–Levich analysis [15], the total current I during the oxygen reduction comprised the diffusing part and the kinetic part, and could be expressed as follows:

$$j^{-1} = j_k^{-1} + j_d^{-1} \quad (1)$$

where j is the disk electrode current density, j_d the diffusion limited current density owing to the mass transport and j_k is the kinetic current density determined by the charge transfer. For the RDE, in the laminar flow regime, the diffusion current density is a function of the rotational velocity and hence Eq. (1) may be

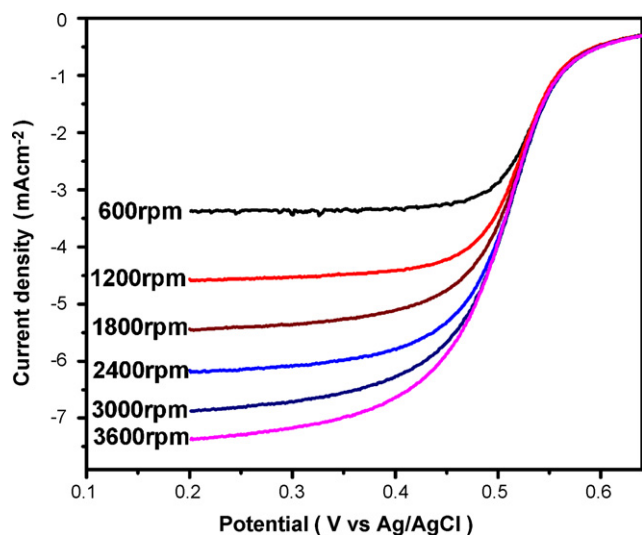


Fig. 6. Oxygen reduction reaction on Pt–Se/C electrode in 0.1 M oxygen saturated HClO₄ solution and at room temperature and different rotating rates. The sweep rate was 5 mV s⁻¹.

written as follows:

$$j^{-1} = (nFkC_{O_2})^{-1} + (B\omega^{1/2})^{-1} \\ = (nFkC_{O_2})^{-1} + (0.62nFA C_{O_2} D_{O_2}^{2/3} \nu^{-1/6} \omega^{1/2})^{-1} \quad (2)$$

where k is the reaction rate constant, n the number of electrons exchanged per O₂ molecule, F the Faraday constant, A the electrode geometric area (0.08 cm²), C_{O_2} the bulk oxygen concentration (1.26 × 10⁻⁶ mol cm⁻³), D_{O_2} the diffusion coefficient of molecular oxygen (1.93 × 10⁻⁵ mol cm⁻³), ν the cinematic viscosity of the electrolyte (0.01009 cm² s⁻¹) [16] and ω is the electrode rotation speed ($=2\pi f = 2\pi$ rpm number/60) [17].

Eq. (2) establishes a linear relation between I^{-1} and $\omega^{-1/2}$ with a y -intercept equal to the inverse of the kinetic current and a slope ($B = 0.62nFA^{-1}C_{O_2}D_{O_2}^{2/3}\nu^{-1/6}$) whose inverse was proportional to the number of electrons transferred per oxygen molecule. By determining this slope, the number of electrons transferred per oxygen molecule during the ORR can be determined. From the data of Fig. 6, the Koutecky–Levich plots (I^{-1} versus $\omega^{-1/2}$) were drawn (Fig. 7). From the slopes of the Koutecky–Levich plots, i.e., the constant B , the number of electrons exchanged in the reduction of an oxygen molecule could be obtained.

The experimental value of $B = 0.51$ mA cm⁻² rpm^{-1/2}, evaluated from Fig. 7, agreed well with the calculated value of $B^0 = 0.55$ mA cm⁻² rpm^{-1/2}. From these results, we suggest that the ORR may proceed via the overall four-electron transfer reaction to form water.

Further kinetic information on the electron transfer reaction mediated by the catalysts Pt–Se/C and Pt/C were compared in Fig. 8. It showed corrected mass transfer Tafel polarization curves of Pt/C and Pt–Se/C electrodes for ORR at room temperature and in 0.1 M HClO₄ and 0.1 M HClO₄ + 0.1 M

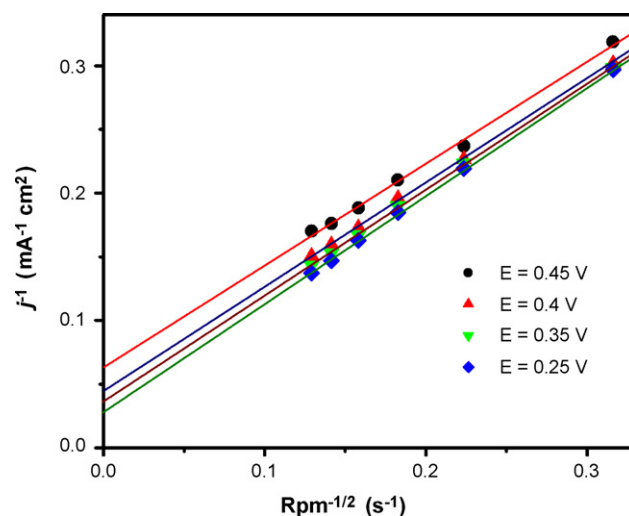


Fig. 7. Koutecky–Levich plots prepared from data in Fig. 6 at different potentials.

CH₃OH solution saturated by oxygen, respectively. The data were obtained at 1600 rpm of rotating velocity based on a cathodic sweep from 1.0 to 0.2 V (versus Ag/AgCl) at a sweep speed of 5 mV s⁻¹.

Two Tafel slopes, i.e. ca. -60 mV dec⁻¹ in the low current region and -180 mV dec⁻¹ in the high current region, were observed for the two catalysts. For the Pt/C, the low and high Tafel slopes were in good agreement with the literature [18]. The Tafel slopes of the Pt–Se/C were almost similar to that of Pt/C; it could be explained in terms of the coverage of adsorbed oxygen, which follows a Temkin isotherm (high coverage) at low overpotentials and a Langmuir isotherm (low coverage) at higher overpotentials. It implied that the rate determining step (rds) for the ORR is unchanged at both skin-layer Pt over Pt–Se/C and Pt/C catalysts, despite some differences in their electrocatalytic activities.

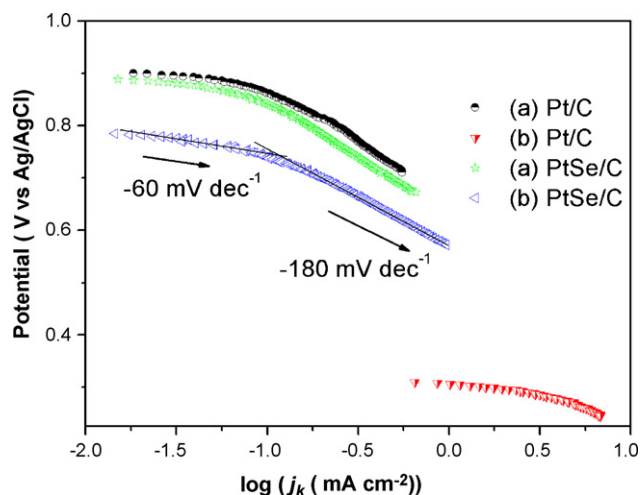


Fig. 8. Corrected mass transfer Tafel polarization curves of Pt/C and Pt–Se/C electrodes for ORR (room temperature, 1600 rpm, sweep velocity of 5 mV s⁻¹ in: (a) 0.1 M HClO₄ and (b) 0.1 M HClO₄ + 0.1 M CH₃OH solution saturated by oxygen.

Although Pt–Se/C catalyst showed much better performance than Pt/C catalyst in 0.1 M HClO₄ + 0.1 M CH₃OH solution, two catalysts showed similar catalytic activity for ORR in 0.1M HClO₄ solution without methanol at low overpotentials (activation region, see Fig. 8), it indicated that the catalytic mechanism of Pt–Se/C catalyst for ORR might be the same as that of Pt/C, and the kinetics for ORR was not perturbed by the addition of selenium onto platinum in methanol-containing or methanol-free solutions.

4. Conclusion

The Pt–Se/C electrocatalyst was synthesized by a modified organic colloid method in an ethylene glycol solution. The addition of Se could improve the dispersion of active components significantly. The particle size of active components of Pt–Se/C catalyst could be as small as 1.2 nm as determined by XRD and TEM. The catalyst showed good activity for oxygen reduction similar to that of Pt/C in methanol-free solution, and much better activity than Pt/C catalyst in methanol-containing solution; it implied that Pt–Se/C catalyst exhibited an especially high methanol tolerance in comparison to the Pt/C catalyst. Besides, the addition of Se could prevent the aggregation and growth of platinum nanoparticles in the thermal heating process effectively. On the basis of electrochemical experiments data, a multielectron charge transfer process ($n = 4e^-$) for the ORR on Pt–Se/C catalyst was determined. The higher activity and good tolerance to methanol poisoning of the Pt–Se/C catalyst make it a potentially suitable cathode catalyst for application in DMFCs.

Acknowledgments

We would like to thank the State Natural Science Foundation of China and Guangdong Provincial Natural Science

Foundation for financially supporting this work (Project Nos. 20476034, 20673040, 03665). And thanks to Dr. Leslie Petrik of University of the Western Cape in South Africa for her assistance.

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