

PtCeO_x/C as a novel methanol-tolerant electrocatalyst of oxygen reduction for direct methanol fuel cells

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Abstract A prominent methanol-tolerant characteristic of the PtCeO_x/C electrocatalyst was found during oxygen reduction reaction process. The carbon-supported platinum modified with cerium oxide (PtCeO_x/C) as cathode electrocatalyst for direct methanol fuel cells was prepared via a simple and effective route. The synthesized electrocatalysts were characterized by X-ray diffraction and transmission electron microscopy. It was found that the cerium oxide within PtCeO_x/C present in an amorphous form on the carbon support surface and the PtCeO_x/C possesses almost similar disordered morphological structure and slightly smaller particle size compared with the unmodified Pt/C catalyst.

Keywords Cerium oxide · Electrocatalyst · Methanol tolerance · Oxygen reduction reaction (ORR) · Direct methanol fuel cells (DMFCs)

Introduction

Direct methanol fuel cells (DMFCs) as promising portable power source systems have been extensively investigated for their advantages and attractive potential applications

in the past decade [1–3]. At present, there are several challenging problems obstructing the commercialization process of DMFCs [2, 3]; the serious one is related to methanol crossover from anode to cathode through proton exchange membrane, which leads to a dramatic loss in coulombic efficiency, voltage efficiency, and fuel conversion efficiency of a DMFC [2–8]. In such case, both methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) occur simultaneously at cathode compartment and subsequently produce mixed potential. This causes a negative potential shift at the cathode and a distinct decrease of performance of a DMFC [7–10]. An effective solution to the problem is to develop a methanol-tolerant cathodic catalyst which not only catalyzes ORR but also inhibits the oxidation reaction of the permeated methanol.

Transition metal catalysts were usually prepared by dispersing the active component on carriers with high surface area to achieve maximum specific metal surface area and high thermal stability [11]. More recently, a series of rare earth oxide exhibit excellent application prospect for DMFC's catalyst because of their oxygen storage capacity [13–15]. In particular, cerium oxide is an oxide with fluorite structure in which cation valence states can switch between +3 and +4, and it acts as an oxygen buffer because ceria can release oxygen reversibly [11–18]. Previous studies have proven that impregnating or mixing ceria into Pt/C catalyst could enhance the performance of a DMFC [14, 15].

The performance of the novel PtCeO_x/C cathodic nanocatalyst synthesized by a simple and effective process was reported in this preliminary investigation. The PtCeO_x/C electrocatalyst exhibited obvious higher methanol tolerance capacity during oxygen reduction process without reducing electrocatalytic activity for ORR than the unmodified Pt/C electrocatalyst.

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Experimental details

An appropriate amount of Vulcan XC-72 carbon (Cabot) and an excessive amount of NaOH were added into deionized water and which were stirred for 10 min. Then chloroplatinic acid (CPA, Aldrich), as a precious metal precursor, was added into the aqueous solution containing $\text{Ce}(\text{NO}_3)_3$. Afterwards, this mixed solution of CPA and $\text{Ce}(\text{NO}_3)_3$ was added into the vigorously stirred suspension of NaOH and Vulcan XC-72 carbon. Subsequently, excessive amount of NaBH_4 solution was added into the aforementioned suspension, and this mixture was continuously stirred for 6 h. Then, the precipitate PtCeO_x/C (40 wt.% Pt, 2.5 wt.% Ce) was filtered and washed with deionized water. For comparison, CeO_x/C (10 wt.% Ce) was prepared by mixing an appropriate amount of Vulcan XC-72 carbon and $\text{Ce}(\text{NO}_3)_3$ in a NaOH solution. Finally, the two washed precipitates were dried at 110 °C for 1 h and then calcined in muffle furnace at 300 °C for 2 h. The unmodified Pt/C (40 wt.% Pt) electrocatalyst was prepared by the similar precipitation method to the PtCeO_x/C preparation, except the relative procedures of cerium addition and the final precipitate was not treated by heating. All the chemicals used in this study were of analytical grade. All the solutions were freshly prepared with deionized water.

Inductively coupled plasma optical emission spectrometry (ICP-OES; iCAP6300, Thermo Scientific, USA) was performed to determine the content of Pt and Ce in Pt/C and PtCeO_x/C electrocatalysts. X-ray diffraction (XRD) was employed to obtain information about the surface and bulk structure of the electrocatalysts and was carried out with a Philips Mode PW1729 X-ray diffractometer with the Cu K α ($\lambda = 0.15406 \text{ \AA}$) radiation generated at 40 kV and 200 mA. The transmission electron microscopy (TEM) measurements were performed on a JEOL 2010 microscope operating at 200 keV with nominal resolution. The samples for the TEM analysis were prepared as follows: The ultrasonicated suspension containing catalyst and ethanol was dropped onto copper grids covered with holey carbon film as a substrate and was dried in air.

The electrochemical performance of as-prepared PtCeO_x/C and Pt/C catalysts for the ORR was evaluated with an EG&G Park potentiostat/galvanostat model 273 A (Princeton Applied Research) and an EG&G Park Model-636 ring-disk electrode (RDE) system. The cyclic voltammetry (CV) and the linear scan voltammetry (LSV) were carried out in a conventional three-electrode electrochemical cell. Five milligrams of catalyst was dispersed ultrasonically in 1 mL ethanol solution with 0.05 mL of Nafion solution (5 wt.%, Aldrich). Then, 5 μL of this ink was transferred onto a freshly polished glassy RDE with 5-mm diameter by a syringe. After the solvent was evaporated, the prepared RDE was used as the working electrode. The platinum loading on

the RDE is 0.05 mg/cm². The Ag/AgCl electrode saturated with KCl was served as the reference electrode, and a platinum foil was used as the counter electrode. The Ag/AgCl electrode was placed in a different compartment to prevent the poisoning of the electrocatalysts by chloride anions, which was connected to the working electrode with a salt bridge filled with aqueous solution of saturated KCl. The LSV and CV curves were recorded with scan rate of 10 and 50 mV/s, respectively. All of the electrochemical measurements were conducted at ambient temperature ($20 \pm 1 \text{ }^\circ\text{C}$).

For the membrane electrode assembly (MEA), PtRu black (HiSPEC 6000, Alfa Aesar) was used as the anode catalyst. The cathode catalysts were as-synthesized PtCeO_x/C and Pt/C, respectively. The loading of PtRu in anode catalyst layer and the loading of Pt in cathode catalyst layer were both 4 mg cm⁻². The MEA is fabricated by pressing the anode and cathode onto the pretreated Nafion117 membrane for 150 s at 3 MPa and 130 °C. The active area of the MEA was 9.0 cm². To fabricate single passive DMFC, MEA was sandwiched between two current-collected meshes made of 316 stainless steels, which is placed between two current collectors made of 316 stainless steel plate with plurality of 3.0-mm circular holes designed for the fuel and air transfers. Then, the cell was fabricated between an aforementioned cathode current-collected plate and an anode fixture made of organic glass plate with 1.0-cm thickness. A 4.5 mL methanol solution tank was built in the anode fixture. Methanol from the tank through current collectors diffused into the anode catalyst layer, while oxygen from the surrounding air through the opening of the cathode plate transferred into the cathode catalyst layer. The performance of single passive DMFC was measured with a fuel cell test system (Arbin Instruments). A 1 M methanol solution was added into the anode tank. The passive DMFC operated at ambient temperature of 23–25 °C. The polarization curve of single passive DMFC can be obtained by recording the cell potential during a current hold for 3 min.

Results and discussion

The test result of ICP-OES shows that the weight percentage contents of Pt in the Pt/C and PtCeO_x/C catalysts are 40.09% and 37.81%, respectively. The contents of Pt in the two catalysts are almost close to the stoichiometric ratio 40 wt.%. The content of Ce in the PtCeO_x/C catalyst is 2.51 wt.%, which is nearly equal to the Ce content of the precursor salts.

The results of XRD for CeO_x/C, Pt/C, and PtCeO_x/C catalysts are shown in Fig. 1. For CeO_x/C (curve a), it can be observed that the characteristic diffraction peaks of (111), (220), and (311) located at 2θ values of 26.5°, 46.7°, and 56.5°, respectively.

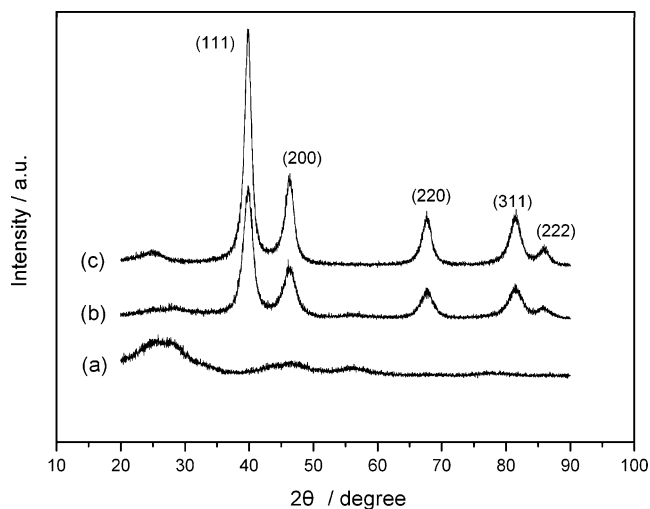
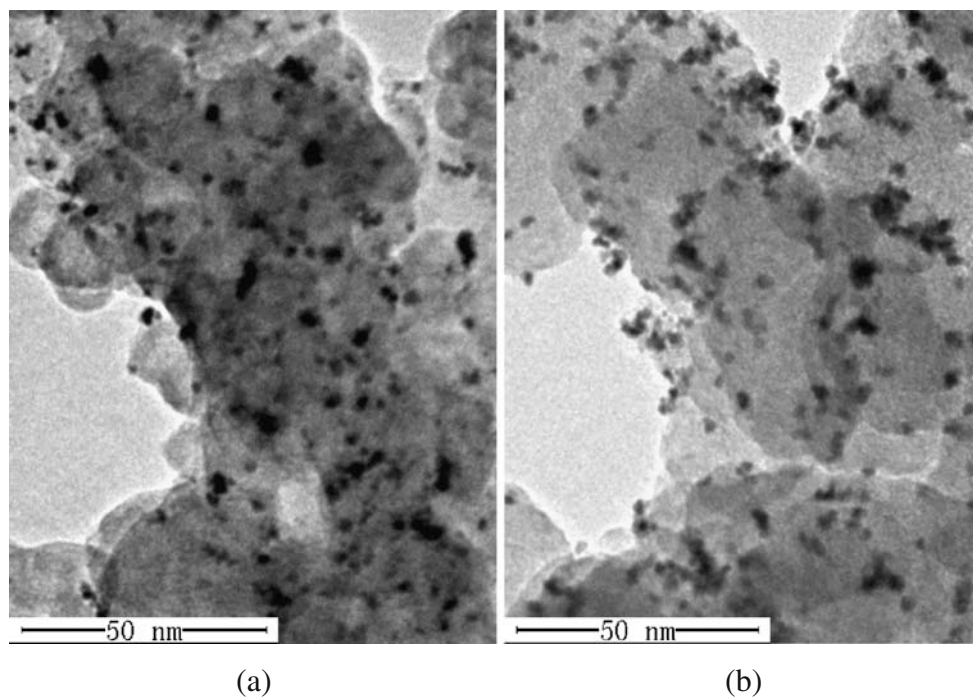


Fig. 1 XRD patterns of CeO_x/C (a), PtCeO_x/C (b), and Pt/C electrocatalysts (c)

and 56.1° , respectively. These values are similar to the results of fluorite structure for cerium oxide reported in literature [12]. The XRD pattern of PtCeO_x/C catalyst (curve b) exhibits five main characteristic peaks of the face-centered cubic of Pt, namely, the planes (111), (200), (220), (311), and (222). It can be seen that the shape and position of these five diffraction peaks are similar to those of the unmodified Pt/C catalyst (curve c), whereas the intensity of Pt(111) peak for Pt/C is higher than that for PtCeO_x/C . As reported in literature [19], MOR process is favored on a Pt (111) surface, which possesses the nearest reasonable Pt–Pt inter-atomic distance. Thus, the poisoning effect of methanol crossover should be more obvious on the Pt(111) surface.

Fig. 2 TEM images of Pt/C (a) and PtCeO_x/C (b) electrocatalysts



Accordingly, the permeated methanol possesses lower reaction activity on PtCeO_x/C in comparison with Pt/C catalyst. From the XRD curve of PtCeO_x/C , it can be observed that there is no peak shift compared to the corresponding peaks of Pt/C, indicating that there is no PtCe alloy formation in the PtCeO_x/C catalyst. No diffraction peak of cerium oxide was found in the PtCeO_x/C curve. Therefore, the cerium oxide modified in PtCeO_x/C likely presents in an amorphous form on the carbon support surface. All the diffraction peaks of Pt/C catalyst are sharper than those of PtCeO_x/C catalyst, implying a larger platinum particle size in Pt/C than that in PtCeO_x/C . The average sizes of platinum particles in Pt/C and PtCeO_x/C catalysts were calculated to be 3.6 and 3.3 nm, respectively, based on the Scherrer equation [21] from the (220) diffraction peak width after correction for instrumental broadening.

Figure 2 shows TEM images of Pt/C and PtCeO_x/C catalyst. From Fig. 2a, it can be noticed that the unmodified Pt/C exhibits relatively uniform platinum particles dispersion on the carbon support surface, but a portion of platinum particles with spherical and irregular shapes still agglomerate. The average size of Pt particle in Pt/C is about 3.6 nm. It can be seen from Fig. 2b for the PtCeO_x/C catalyst that the platinum particles with a very narrow particle size distribution are uniformly dispersed on the surface of carbon support. The mean particle size is approximately 3.1 nm, which is close to 3.3 nm that is the calculated value based on the XRD data. The presence of cerium oxide in the PtCeO_x/C catalyst appears to have some effect on the platinum particle size and its distribution. Discussions in literatures [19, 20], especially studies concerning carbon-supported Pt

electrocatalysts for oxygen reduction, showed that the electrocatalytic activity of these electrocatalysts depends on the mean particle size. The mass activity for oxygen reduction reaches a maximum at a particle size of 30 Å. Therefore, the PtCeO_x/C particle size is much more favorable to the electrocatalysis for ORR compared with Pt/C particle size. The detailed discussion of this phenomenon required further research.

Figure 3 shows the linear sweep voltammogram of the nanosized PtCeO_x/C and Pt/C electrocatalysts in the 0.1 M HClO₄ + 1 M CH₃OH solution saturated with oxygen. From Fig. 3, it can be seen that there was an obvious methanol oxidation peak ($j_p = 6.2 \text{ mA}\cdot\text{cm}^{-2}$) on Pt/C electrocatalyst, while there was no methanol oxidation peak on PtCeO_x/C electrocatalyst, indicating that the methanol oxidation was inhibited on the PtCeO_x/C catalyst compared with that on Pt/C catalyst [22]. Moreover, the onset potential of the ORR on Pt/C shifted by approximately 150 mV towards the negative direction in comparison to that on PtCeO_x/C. Therefore, it can be concluded that the PtCeO_x/C catalyst possesses higher methanol tolerance characteristic and higher electrocatalytic activity for the ORR than Pt/C catalyst in perchloric acid solution containing methanol.

Figure 4 shows cyclic voltammograms of MOR on Pt/C and PtCeO_x/C catalysts in the nitrogen-saturated 0.1 M HClO₄ + 1 M CH₃OH solution. The voltammetric features are typical for the electrooxidation of methanol on platinum, which is consistent with literature [23]. It can be found that the current density of MOR on PtCeO_x/C catalyst is much lower (approximately 70%) than the total oxidation current density recorded on Pt/C catalyst under the same conditions, indicating that PtCeO_x/C catalyst is obviously tolerant for methanol oxidation compared to Pt/C catalyst. Thereby, it can be affirmed that the modification of cerium

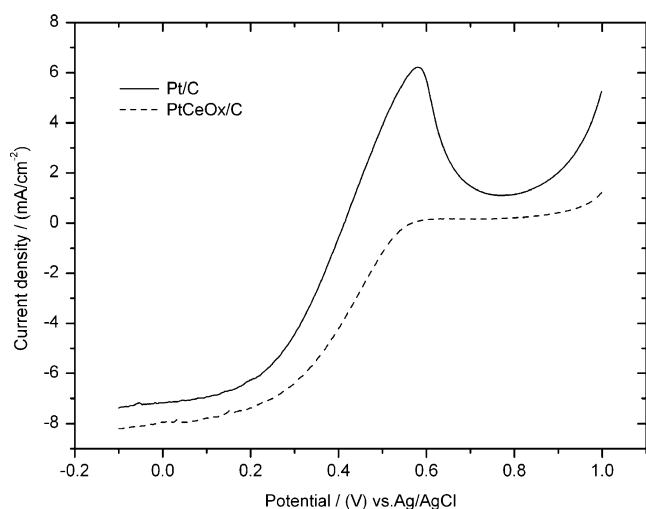


Fig. 3 Linear sweep voltammograms of Pt/C and PtCeO_x/C catalysts in 0.1 M HClO₄+1 M CH₃OH solution saturated with pure oxygen at a scan rate of 10 mV/s and a rotation speed of 2,400 rpm

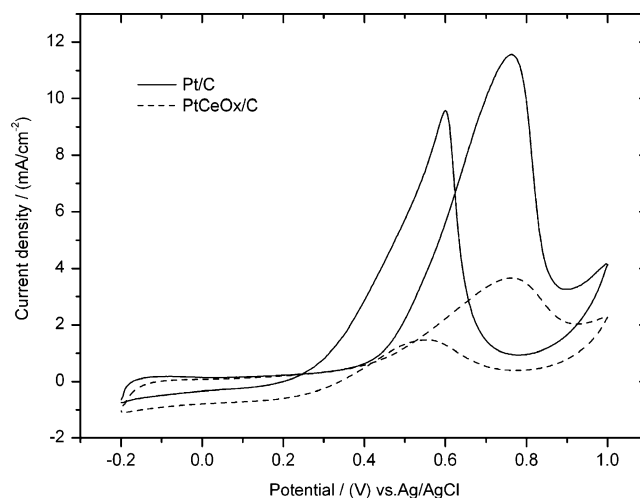


Fig. 4 The CVs of methanol oxidation on Pt/C and PtCeO_x/C catalysts in nitrogen saturated 0.1 M HClO₄+1 M CH₃OH solution at a scan rate of 50 mV/s

oxide on Pt/C catalyst can prominently inhibit the oxidation of methanol, meaning the high methanol tolerance performance of PtCeO_x/C during the ORR.

Figure 5 shows the polarization curves and power density curves of single passive DMFCs for Pt/C and PtCeO_x/C as the cathode catalyst. It can be obviously observed that two passive DMFCs possess similar open circuit voltage (about 0.72V). At low current density, the two cell voltages are a little different, while with the current density increase, the voltages of cell using PtCeO_x/C electrocatalyst become gradually larger than that using Pt/C electrocatalyst. The maximum power density (8.39 mW/cm²) of passive DMFC using PtCeO_x/C electrocatalyst is higher than that (6.31 mW/cm²) using Pt/C electrocatalyst. These results indicate that the performance of the single passive

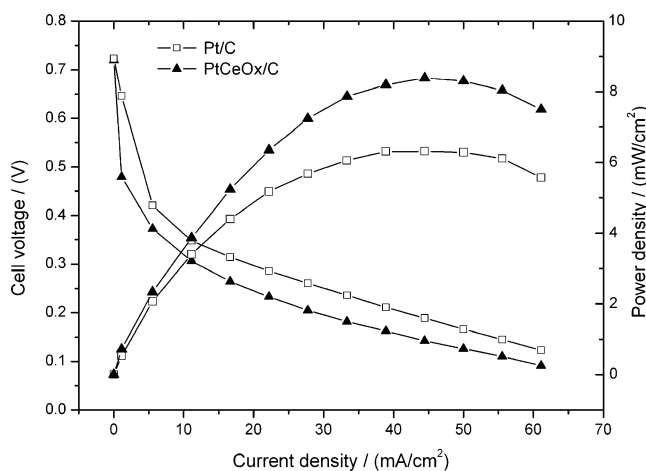


Fig. 5 The polarization curves and power density curves of single passive DMFC using PtCeO_x/C and Pt/C as cathode electrocatalysts with 1 M methanol solution at ambient temperature of 23–25 °C

DMFC with the PtCeO_x/C electrocatalyst is better than that with the Pt/C electrocatalyst. This resulted from much higher methanol tolerance capability of PtCeO_x/C electrocatalyst for ORR. The mechanism of the obvious methanol tolerance for PtCeO_x/C electrocatalyst is underway.

Conclusion

The preliminary investigation demonstrated that PtCeO_x/C electrocatalyst was an effective electrocatalyst with high methanol tolerance performance for ORR. Physical characterizations indicate that PtCeO_x/C exhibits the disordered state with a different micro-surface structure and proper platinum particle sizes for ORR compared with Pt/C. Electrochemistry and single passive DMFC tests show that PtCeO_x/C catalyst presented significantly enhanced methanol tolerance capacity for ORR compared with Pt/C catalyst, which makes PtCeO_x/C promising as a candidate cathode catalyst for the commercialization of DMFCs.

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