Preparation, characterization of ZrO$_x$N$_y$/C and its application in PEMFC as an electrocatalyst for oxygen reduction

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Abstract

In this paper, a noble-metal-free electrocatalyst based on carbon-supported zirconium oxynitride (ZrO$_x$N$_y$/C) was prepared by ammonolysis of carbon-supported zirconia (ZrO$_2$/C) at 950 °C and investigated as cathode electrocatalyst towards oxygen reduction reaction (ORR) in PEMFCs. The electrocatalyst was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. The catalytic activity of the catalyst towards ORR was investigated by using the rotating disk electrode (RDE) technique in an O$_2$-saturated 0.5 M H$_2$SO$_4$ solution. The ZrO$_x$N$_y$/C electrocatalyst presented attractive catalytic activity for ORR. The onset potential of ZrO$_x$N$_y$/C electrocatalyst for oxygen reduction was 0.7 V versus RHE and the four-electron pathway for the ORR was achieved on the surface of ZrO$_x$N$_y$/C electrocatalyst. The ZrO$_x$N$_y$/C electrocatalyst showed a comparatively good cell performance to ORR in PEMFCs, especially when operated at a comparatively high temperature. © 2007 Elsevier B.V. All rights reserved.

Keywords: Zirconium oxynitride; Noble-metal free electrocatalyst; Oxygen reduction reaction; Cathode; Fuel cell

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are regarded as a possible alternative power source for stationary and mobile applications, due to their high-power density and near-zero pollutant emission [1]. However, there are several problems including the large overpotential of the ORR and the high cost of the electrocatalysts to be solved before commercialization can occur [2]. The reaction occurring at the cathode of the PEMFC is the reduction of oxygen in the presence of protons and electrons to produce water [Eq. (1)]:

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \tag{1}
\]

Currently, the common used cathode electrocatalysts for PEMFC are carbon-supported platinum. In order to improve the ORR activity of platinum electrocatalysts, platinum transition metal alloys have been well developed [3–5]. However, the stability of alloy electrocatalysts becomes a serious problem for long-term operation for transition metals tend to dissolve in acid electrolyte [6,7]. Moreover, the price of Pt is very high. So a strong motivation exists to find less expensive non-noble metal alternatives that are stable and exhibit catalytic activity comparable to that of Pt. Various materials have been proposed as non-noble cathode electrocatalysts for ORR. Such as, transition metal oxides [8], transition metal (e.g., Fe, Co) macrocyclic compounds [9], Ru-based chalcogenides [10] and etc. Unfortunately, neither of these electrocatalysts has reached the catalytic activity of Pt-based electrocatalysts and virtually none has sufficient stability in the acidic environment of PEMFC.

Transition metal nitrides as corrosion resistance materials have attracted much attentions over the years [11,12]. Transition metal nitrides have been studied as ORR electrocatalysts because of their high stability in acid medium and platinum-like catalytic behavior [13,14]. Herein we reported the results of a study on the electrocatalytic activity of zirconium oxynitride for ORR. The ZrO$_x$N$_y$/C electrocatalyst was prepared by ammonolysis of ZrO$_2$/C at 950 °C. The ORR activities of this electrocatalyst were evaluated by RDE measurements and single cell tests. The stability of the electrocatalyst was also investigated in the single cell test. The ZrO$_x$N$_y$/C electrocatalyst showed promising ORR activity and stability, and might have the possibility to be an alternative of the Pt-based electrocatalysts.
2. Experiment

2.1. Preparation of carbon-supported zirconium oxynitride electrocatalyst

The carbon-supported zirconium oxynitride electrocatalyst was prepared by ammonolysis of carbon-supported zirconia at 950°C as presented by Gilles and Collongues [15]. The preparation process of the electrocatalyst was composed of two steps: the preparation of ZrO2/C and the ammonolysis of ZrO2/C. The detailed process was as follows. One gram Vulcan XC-72 carbon powder (Cabot Corp., BET: 235 m² g⁻¹, denoted as C) was added to the 155 mL aqueous solution containing 5 mL ethanol and 150 mL water. The solution was mixed sufficiently before 0.5422 g ZrO(NO3)2·2H2O was added. The mixture was treated in an ultrasonic bath to form uniformly dispersed ink. The ink was then dried at 90°C. The dried mixture was heat-treated at 500°C in N2 for 3 h to get ZrO2/C (20 wt.% ZrO2). The carbon-supported zirconium oxynitride (ZrOxNy/C) was synthesized by heating ZrO2/C at 950°C in NH3 for 3 h. When the reaction was over, the sample was cooled to room temperature under N2 atmosphere and the electrocatalyst ZrOxNy/C (about 20 wt.% ZrO2Ny) was thus obtained.

2.2. Physicochemical characterization

XRD measurements were conducted on a PAN-alytical powder diffrator (Philips X’Pert PRO) using Ni filtered Cu Kα radiation (λ = 1.54056 Å) to characterize the structures of XC-72 Carbon, ZrO2/C and ZrO2Ny/C electrocatalyst. TEM image was recorded on a JEOL JEM-2000EX microscope operated at 120 kV. The electrocatalyst powder was placed in a vial containing ethanol and then ultrasonically agitated to form homogeneous slurry. A drop of the slurry was dispersed on a holey polyvinyl formal microgrid for the TEM analysis. Two hundred particles were calculated to obtain the integrated information about the overall distribution of the electrocatalyst.

2.3. Electrochemical characterization

Eletrochemical measurements were carried out on CHI 660 electrochemical station (CH Corporation, USA) with a RDE system (EG&G model 636). A standard three-electrode cell was used. A Pt foil was served as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. The electrocatalyst layer on the glassy carbon electrode (GCE) (4 mm in diameter) was prepared as follows: a mixture containing 1 mL of ethanol, 5 mg of XC-72 carbon or ZrO2/C or ZrO2Ny/C or Pt/C (20 wt.%, Johnson Matthey) and 50 μL of Nafion solution (5 wt.%) was homogenized for 30 min in a ultrasonic bath. 25 μL of the mixture was cast on the clean GCE surface and dried in air. The electrochemical measurements were carried out in 0.5 M H2SO4 solution at room temperature. All potentials shown in the figures were quoted to RHE. The cyclic voltammetry (CV) curves were recorded in the potential range from 0.05 to 1.2 V versus RHE with a scan rate of 100 mV s⁻¹ after bubbling high-purity nitrogen through the electrolyte for 30 min. The RDE curves were obtained in the scan range from 1.0 to 0.05 V versus RHE with a scan rate of 5 mV s⁻¹ after O2 bubbling for 30 min.

To validate whether Pt from the counter electrode will contaminate the working electrode and invalidate the results, we carried out the CV and RDE measurements on ZrO2Ny/C electrocatalyst in the three-electrode system by the use of graphite rod as the counter electrode.

2.4. Preparation of membrane electrode assembly and single cell test

The electrode was prepared as follows: mixing ZrO2Ny/C electrocatalyst, 5% Nafion and ethanol to form a homogeneous mixture, spraying the mixture onto the wet-proofed carbon paper (SGL, 39% PTFE). The ZrO2Ny loading in the electrode was about 1 mg cm⁻² and the dry Nafion loading was about 0.5 mg cm⁻². This electrode was used for the cathode. The ZrO2/C or Pt/C cathode was prepared by the same procedure. The ZrO2 loading in the ZrO2/C cathode was about 1 mg cm⁻² and the dry Nafion loading was about 0.5 mg cm⁻². The Pt loading in the Pt/C cathode was about 0.4 mg cm⁻² and the dry Nafion loading was about 0.2 mg cm⁻². The anode adopted the commercial 46.7% Pt/C electrocatalyst (TKK Co.) with Pt loading of 0.37 mg cm⁻² and Nafion 117 (175 μm, Du Pont) was used as the membrane. The MEA was fabricated by hot-pressing the anode and the cathode to the membrane at 140°C and 1 MPa for 1 min and fitted into a test station. The active area of the MEA was 5 cm². The single cell performance was tested at 80, 60 and 40°C with saturated humidification level. The single cell was fed with pure hydrogen and oxygen and operated at 0.2 MPa. Fifty-hour stability tests of single cells with ZrO2Ny/C and Pt/C as cathode electrocatalysts were also carried out at 80°C with a constant current density of 200 mA cm⁻².

3. Results and discussion

3.1. XRD and TEM characterization of carbon-supported zirconium oxynitride

Fig. 1 shows the XRD patterns of XC-72 carbon, ZrO2/C and ZrO2Ny/C electrocatalyst. As shown in Fig. 1, the first peak at the low 2θ range (2θ = 25°) was associated with the XC-72 carbon support. ZrO2/C showed the typical tetragonal zirconia crystal structure with some monoclinic phase impurities [16]. The structure of ZrO2Ny/C was β''-phase zirconium oxynitrides with non-regular succession of the basic building units of β-phase Zr7O8N4 and monoclinic phase ZrO2 [17].

Fig. 2a shows the typical TEM image of the ZrO2Ny/C electrocatalyst and the histogram of the particle size distribution was shown in Fig. 2b. The amorphous carbon appeared as the gray areas and the ZrO2Ny particles appeared as the black particles. Due to the high temperature heat treatment, the ZrO2Ny particles size distribution is very broad and ranges between 6 and 14.5 nm. The mean particle size is about 9 nm.
3.2. Electrochemical measurements of the electrocatalysts

The CVs from the first to the tenth cycle of the ZrO$_x$N$_y$/C catalyst under nitrogen atmosphere was shown in Fig. 3. The ZrO$_2$/C sample showed almost the same CV behavior. The oxidation and reduction peaks at about 0.6 V was responsible for the carbon support. No other specific oxidation and reduction current peaks were observed. The CVs soon approached to a steady state. The anodic and cathodic charges of the CV were 24.0 and 24.5 mC cm$^{-2}$, respectively. These results indicate that ZrO$_x$N$_y$ is stable in acid solution at least in the potential range from 0.05 to 1.2 V.

In order to investigate the electrocatalytic activities of the electrocatalysts for ORR, RDE measurements were carried out both in N$_2$ and O$_2$ atmosphere, respectively. Fig. 4 shows the linear scan voltammogram (LSV) curves of electrodes (a) bare GCE, (b) XC-72 R/GCE, (c) ZrO$_2$/C/GCE and (d) ZrO$_x$N$_y$/C/GCE in 0.5 M H$_2$SO$_4$ electrolyte saturated with N$_2$ and O$_2$ at room temperature. As shown in Fig. 4, very low currents were observed in the potential range for all the electrodes under the N$_2$ atmosphere. Comparatively, the reduction currents increased for all the electrodes under the O$_2$ atmosphere. The potential at which the reduction current with bare GCE under O$_2$ increased more than that under N$_2$ was about 0.55 V. Unfortunately, the reduction current was very low owing to the scarce active sites for ORR on bare GCE. The ORR onset potentials for the XC-72 carbon and ZrO$_2$/C were about 0.55 and 0.56 V, respectively. The reduction current on the ZrO$_2$/C/GCE electrode was a little higher than that on the XC-72 R/GCE electrode.

The above two electrodes showed higher reduction current than bare GCE, but the reduction current was still very low. However, as shown in Fig. 4d, the reduction current with ZrO$_x$N$_y$/C under O$_2$ started at about 0.7 V. Because such a reduction current was not observed under N$_2$ atmosphere, the reduction current should be due to the oxygen reduction. ZrO$_x$N$_y$/C had attractive ORR activity and the reduction current was the highest among the four tested electrodes. Liu et al. [18] and Doi et al. [19] investigated the ORR activities of sputtered ZrO$_2$ and ZrO$_x$N$_y$. 

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Fig. 1. XRD patterns of XC-72 Carbon, ZrO$_2$/C and ZrO$_x$N$_y$/C electrocatalyst. m: m-ZrO$_2$, t: t-ZrO$_2$, r: β-phase Zr$_7$O$_8$N$_4$.

Fig. 2. TEM image (a) and histogram (b) of the particle size distribution of the Zr$_x$N$_y$/C electrocatalyst.

Fig. 3. TEM image (a) and histogram (b) of the particle size distribution of the Zr$_x$N$_y$/C electrocatalyst.

Fig. 4. TEM image (a) and histogram (b) of the particle size distribution of the Zr$_x$N$_y$/C electrocatalyst.
Apparent oxygen reduction currents were observed below ca. 0.9 and 0.75 V versus RHE for sputtered ZrO$_2$ and ZrO$_x$N$_y$, respectively. The onset potential for the ORR on ZrO$_x$N$_y$/C electrocatalyst prepared in our study was about 0.7 V versus RHE, which was comparable to the sputtered ZrO$_2$ and ZrO$_x$N$_y$ samples.

The Pt counter electrode is widely used in the conventional three-electrode system to test the electrocatalytic activities of non-precious catalysts as described in the Refs. [20,21]. The potential range of the CV test performed in this work is from 0.05 to 1.2 V versus RHE in the CV test. The Pt counter electrode is very stable in this potential range. As reported by the DOE report 2005 [22], the dissolved platinum equilibrium concentrations form a polycrystalline platinum wire immersed in room-temperature non-adsorbing electrolyte under the voltammetric cycling is below 1E-07 when the high potential adopted in the cyclic voltammogram is 1.2 V versus RHE. So the dissolved Pt during the CV test will hardly contaminate the working electrode and nearly cannot make the CV results incorrect. Also, the electrolyte is replaced every time when a new catalyst is tested. This will further decrease the influence of the dissolved Pt on the working electrode.

In order to verify whether Pt from the counter electrode will contaminate the working electrode and invalidate the results, we carried out the CV and RDE measurements on ZrO$_x$N$_y$/C electrocatalyst in the three-electrode system by the use of graphite rod as the counter electrode. Fig. 5a and b shows the cyclic
voltammograms and linear scan voltammograms on ZrO$_x$N$_y$/C electrocatalyst that were processed by using Pt foil and graphite rod as the counter electrodes. The CV and LSV for ORR on ZrO$_x$N$_y$/C electrocatalyst that were processed by using graphite rod as the counter electrodes is nearly the same as the test that using Pt foil as the counter electrode. These results truly revealed that Pt from the counter electrode hardly contaminated the working electrode and invalidated the results.

In order to compare the ORR activity more distinctly, the LSV curves of the bare GCE, XC-72 carbon, ZrO$_2$/C and ZrO$_x$N$_y$/C at a constant rotation speed of 2500 rpm in O$_2$-saturated 0.5 M H$_2$SO$_4$ at room temperature were presented in Fig. 6 along-side the LSV curve of 20 wt.% Pt/C (Johnson Matthey). We used negative-going sweeps in our experiment as adopted in Ref. [23]. As described in Ref. [24], Pt surface oxidation will be presented in the negative-going sweeps, which will cause a low activity. But in our work, as elucidated in Fig. 3 (CVs), no specific oxidation and reduction current peaks about the zirconium oxynitride were observed. The negative-going sweeps is very commonly applied in the detection of polarization curve for a reduction reaction. Meanwhile, all the LSV curves presented in this work were all measured using the negative-going sweeps. So the comparison of the ORR activities among the tested catalysts is unified and the results are credible. As shown in Fig. 6, the bare GCE showed nearly no ORR activity and the ORR activity of ZrO$_x$N$_y$/C was far higher than that of XC-72 carbon and ZrO$_2$/C. Though ZrO$_x$N$_y$/C had a clear ORR activity, the onset electrode potential for oxygen reduction catalyzed by ZrO$_x$N$_y$/C was much more negative than that catalyzed by Pt/C electrocatalyst. To assure the readers that the experimental setup is functioning properly, the benchmark activity of Pt/C was compared with the Pt activity reported in Refs. [18,24]. The ORR activity of Pt/C reported in this paper is similar to that reported in Ref. [24] and is higher than that reported in Ref. [18]. The tested commercial Pt/C catalyst in this work and the Pt/C catalyst used in Ref. [24] are all carbon-supported Pt catalysts. They both have the similar mean particle size and size distribution. But the Pt catalyst used in Ref. [18] is sputtered Pt and the mean particle size is 30 nm. On the basis of the above comparison of the activities of Pt catalyst, we believe we gave an exact benchmark for the comparison of the ORR activity between the Pt/C catalyst and the synthesized non-noble ZrO$_x$N$_y$/C catalyst. The ORR activity of ZrO$_x$N$_y$/C could be further improved by optimization of the electrocatalyst composition and the electrochemical active surface.

As seen from Fig. 6, the ORR curve of the thin film ZrO$_x$N$_y$/C electrode has no obvious limited current. But we can derive the limited current from Fig. 6. Firstly, the kinetic current at any given potential can be obtained by Koutecky–Levitch ($j_{\text{kin}}$ versus $\omega^{-1/2}$) plots, then, according to the following equation:

$$MA = i_{\text{kin}} = \frac{i_{\text{lim}}}{i_{\text{lim}} - i_{\text{obv}}}$$

where $i_{\text{lim}}$ is the limited current density, $i_{\text{kin}}$ is the kinetic current density, and $i$ is the current density derived from LSV curve.
\( I_{\text{lim}} \) can be calculated accordingly. From above procedure, the calculated limited current density of the ZrO\(_2\)/C electrode (rotation speed: 2500 rpm) is about 7 mA cm\(^{-2}\), which is higher than that presented in the Ref. [24] (5.5 mA cm\(^{-2}\)) at the same rotation speed. But as to ZrO\(_2\)/C electrode, it is difficult for us to measure the limited current directly. We can only make comparisons by the calculated limited current.

Fig. 7 shows the Tafel plots of the ORR on XC-72 carbon, ZrO\(_2\)/C, ZrO\(_N\)/C, Pt/C and GC electrodes. As seen from Fig. 7, the GC electrode showed nearly no electrocatalytic activity for the ORR. The Tafel slopes of the ORR on XC-72 carbon and ZrO\(_2\)/C are 293 and 233 mV dec\(^{-1}\), respectively. The above two samples showed poor electrocatalytic activity for the ORR. ZrO\(_N\)/C was found to have a clear electrocatalytic activity for the ORR as we mentioned above. The Tafel slope of the ORR on ZrO\(_N\)/C is 109 mV dec\(^{-1}\). However, the Tafel slope of the ORR on Pt/C is 56 mV dec\(^{-1}\). In comparison with Pt/C, the ORR activity of ZrO\(_N\)/C should be further improved.

To testify the oxygen reduction mechanism of ZrO\(_N\)/C, the Koutecky–Levich equation [21] was used to determine the number of electrons transferred per O\(_2\) molecule.

\[
-I = -I_k + \frac{1}{0.62nFAD^{1/3}c_v^{-1/6}\omega^{1/2}}
\]

where \( I_k \) is the kinetic current; \( \omega \) is the rotation rate; \( n \) is the number of electrons involved in the reaction; \( F \) is the Faraday constant; \( A \) is the geometric area of the disk electrode; \( D \) and \( c \) are the diffusion coefficient of dissolved oxygen and the concentration of dissolved oxygen in 0.5 M H\(_2\)SO\(_4\), respectively; \( v \) is the kinematic viscosity of the electrolyte. Fig. 8 shows Koutecky–Levich (\( j^{-1} \) versus \( \omega^{-1/2} \)) plots for O\(_2\) reduction on ZrO\(_N\)/C electrodes at different electrode potentials in 0.5 M H\(_2\)SO\(_4\). The inset in Fig. 8 shows the LSV curves of the ZrO\(_N\)/C electrocatalyst obtained at various rotations rates on a GCE. The number of electrons transferred per O\(_2\) molecule was determined by Eq. (2) according to the data of the inset figure in Fig. 8. The linearity of the plots confirmed the applicability of Eq. (2) to analysis of the behavior at the electrocatalyst layer. The calculation of \( n \) was performed using the values: \( F, 96485 \text{C mol}^{-1}; A, 0.1256 \text{cm}^2; D, 1.93 \times 10^{-5} \text{cm}^2 \text{s}^{-1}; c, 1.13 \times 10^{-6} \text{mol cm}^{-3}; v, 9.5 \times 10^{-3} \text{cm}^2 \text{s}^{-1} \) [25]. The number of electrons is 3.8, close to 4. This suggested that the molecular oxygen was directly reduced to water on the surface of ZrO\(_N\)/C. Further investigation using a rotating ring-disk electrode will be reported in the future work to confirm the four-electron pathway.

There has been considerable interest in the electrocatalytic properties of transition-metal nitrides and they were found to have high activities similar to those of noble metal electrocatalysts in isomerization, hydrogenation, dehydrogenation and water gas shift reactions [26,27]. The noble metal-like properties of the ZrO\(_N\)/C electrocatalyst is of major importance for the attractive ORR activity. Meanwhile, zirconium oxide has been found to have some ORR activity [18]. The crystallinity of ZrO\(_N\)/C was better than ZrO\(_2\)/C, this would be one of the factors to affect the catalytic activity for ORR [19].

3.3. Single cell tests

The single cell performances achieved at 40, 60 and 80°C with ZrO\(_N\)/C as cathode electrocatalyst were shown in Fig. 9. The cell performances of ZrO\(_2\)/C and Pt/C as cathode electrocatalyst at 80°C were also shown in Fig. 9 for giving a good comparison. The ZrO\(_2\)/C sample showed the worst cell performance among the three tested catalysts with the maximum power density of 10.7 mW cm\(^{-2}\). The maximum power density (50 mW cm\(^{-2}\)) of the single cell based on ZrO\(_N\)/C as cathode electrocatalyst achieved at 80°C was far lower than the single cell based on commercial Pt/C as cathode electrocatalyst (570 mW cm\(^{-2}\)). In addition, as described by Jaouen et al. in ref. [28], the state-of-the-art non-Pt ORR catalyst (nitrogen-doped carbon-supported Fe) also showed a better cell performance than ZrO\(_N\)/C catalyst in this work. The ORR activity of the ZrO\(_N\)/C catalyst should be further improved. However, as shown in Fig. 9, the MEA operated at 80°C gave a better per-
Cell with saturated humidification. Flow rates of H₂ and O₂ are 50 ml min⁻¹.

**Fig. 9.** Performance curves of single cell adopting ZrO₂/C, ZrOₓNᵧ/C and Pt/C as cathode electrocatalyst at different temperatures. Anode: the commercial TKK 46.6% Pt/C electrocatalyst with Pt loading of 0.37 mg cm⁻². Cathode: ZrO₂ and ZrOₓNᵧ loading are all 1 mg cm⁻²; Pt loading is 0.4 mg cm⁻². H₂/O₂ = 0.2 MPa/0.2 MPa. Pure hydrogen and oxygen are put into the cell with saturated humidification. Flow rates of H₂ and O₂ are 50 ml min⁻¹ and 100 ml min⁻¹, respectively.

**Fig. 10.** Stabilities of the single cells using ZrOₓNᵧ/C and Pt/C as the cathode electrocatalysts at a constant current density of 200 mA cm⁻². For the Pt/C electrocatalyst, the cell voltage changed a little during the whole operating time. For the ZrOₓNᵧ/C electrocatalyst, the cell voltage decreased about 25 mV in the initial 20 h. Then, the cell voltage maintained almost the same value during the following test time. It should be noted that the parameters for the cathode electrocatalyst layer formation were not optimized. The parameters are, for instance, the loading of the ZrOₓNᵧ/C electrocatalyst and the proton conducting electrolyte, the microstructures of the diffusion layer and the electrocatalyst layer. These parameters would influence the stability of the cell performance [29]. In addition, the optimization of nitrogen content in zirconium oxynitride and zirconium oxynitride loading on the carbon support would also improve the activity and durability. Further studies are required and are currently underway.

### 4. Conclusion

In this work, carbon-supported zirconium oxynitride as a noble-metal-free ORR electrocatalyst was prepared by ammonolysis of ZrO₂/C at 950 °C. This non-noble electrocatalyst showed a good stability in acid media and presented a promising electrocatalytic activity for the ORR with an approximate four-electron process. The performance achieved by the H₂/O₂ single cell is most related to the intrinsic properties of the ZrOₓNᵧ/C electrocatalyst, and could be improved by the optimization of the electrocatalyst preparation process, the MEA manufacture and the operating conditions. Further optimization for the electrocatalyst preparation and the long-term single cell test are under way. The zirconium oxynitride might possibly be a substitute material for the platinum cathode of PEMFCs.

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### References