

Electrochemical characteristics and performance of CoTMPP/BP oxygen reduction electrocatalysts for PEM fuel cell

Zi-Feng Ma ^{a,*}, Xian-Yu Xie ^a, Xiao-Xia Ma ^a, Dong-Yun Zhang ^a, Qizhi Ren ^a,
Natascha Heß-Mohr ^b, Volkmar M. Schmidt ^b

^a Department of Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

^b Department of Process Engineering and Chemical Technology, Mannheim University of Applied Sciences, Mannheim, D-68163, Germany

Received 12 December 2005; received in revised form 22 December 2005; accepted 31 December 2005

Available online 2 February 2006

Abstract

Microwave synthesis method was applied to prepare CoTMPP/BP oxygen reduction electrocatalysts. The influence of the pre-treatment of BP2000 carbon supports by 6 M HNO₃ and 30 wt% H₂O₂ on the activity of electrocatalysts for oxygen reduction was investigated by means of the measurements of their electrochemical characteristics and performances. Levich–Koutecky plot shows that the number of transferred electrons during oxygen reduction on CoTMPP/BP is found to be between 2 and 4. The observed evidence indicated that the production of hydrogen peroxide has occurred during oxygen reduction in two electrons, and further oxidation of hydrogen peroxide involving two other electrons in the higher potential may also occur. The fuel cell performance of single cells with the different CoTMPP/BP electrocatalysts was examined under actual PEM fuel cell conditions. For hydrogen–oxygen fuel cell system, the maximal output power density reached 150 mW/cm² at 50 °C. Life test was carried out at a constant of the output current density of 200 mA/cm² for CoTMPP/BP electrocatalyst, the single cell output voltage maintains at about 0.5 V for more than 900 min, there was no obvious performance degradation under fuel cell conditions.

© 2006 Elsevier B.V. All rights reserved.

Keywords: CoTMPP; N4-metal macrocycles; Electrocatalyst; Oxygen reduction reaction; Fuel cell

1. Introduction

Polymer electrolyte membrane (PEM) fuel cell is an attractive power generation system for the transportation and residence applications due to their high energy densities, low operating temperature, low polluting emissions and long life times [1–3]. PEM fuel cell is also one of the solid electrolyte membrane reactors for selective hydrogenation of unsaturated organic compound [4–6]. The reduction reaction on the cathode is a key reaction for PEM fuel cells or PEM reactor. The development of novel cathode electrocatalysts is required for different reduction reactions. Oxygen reduction reaction (ORR) is the control step for fuel cell system. On the

widely used platinum electrocatalysts, the ORR is kinetically slow, and cathodic polarization of the ORR is usually about 0.3–0.4 V under typical PEM fuel cell operating conditions. So far, the replacement of platinum as an electrocatalyst for the ORR to reduce cost in fuel cell technology has been carried out in several research groups worldwide for almost four decades. A variety of Pt/M alloys (M = Fe, Pd, Ni, Cr, Mn and Ir) [7–10] carbide and [11] materials have been developed to alternate pure platinum as ORR electrocatalyst for PEM fuel cell, but less new electrocatalyst materials that have been mentioned before have been applied to practical fuel cell system until now.

Since the pioneering work of Jasinsky using Co phthalocyanine [12], N4-metal macrocyclic compounds have been appearing as promising electrocatalysts for the reduction of oxygen; the essential structures employed are phthalocyanines, porphyrines, Schiff bases and related derivatives

* Corresponding author. Tel.: +86 21 54742894; fax: +86 21 54741297.
E-mail address: zfma@sjtu.edu.cn (Z.-F. Ma).

[13]. Savinell and Gojković et al., [14,15] investigated the kinetics of oxygen reduction on heat-treated FeTMPP-Cl/BP electrocatalysts, and the influence of H_2O_2 that was released during ORR on the decay in the activity of the electrocatalyst was concluded. D. Guay and J.P. Dodelet group [16–20] focused on the oxygen reduction over Fe-based N4 macrocycles electrocatalysts, the activity and active site structure information of the Fe-based electrocatalysts, and the effect of H_2O_2 on the stability of the electrocatalyst was studied in detail. The roles of carbon supports and preparation technique were also concerned in their work. The selectivity of oxygen reduction at pyrolyzed FeTPP-Cl on carbon black was studied in acidic electrolyte using the rotating ring disk electrode (RRDE) [21].

Pyrolyzed carbon supported cobalt porphyrin is used most frequently as N4-metal macrocycles electrocatalyst for ORR in fuel cell condition besides Fe-based electrocatalyst. After data collected from H_2SO_4 solutions under fuel cell conditions were presented by Yeager [22] using cobalt tetramethoxyphenylporphyrin (CoTMPP or $\text{TpOCH}_3\text{PPCo}$) and hydrogen or cobalt dibenzotetraazaannulene supported on carbon black, many efforts have been taken for the catalysis of ORR over pyrolyzed carbon supported cobalt porphyrin. Oxygen electrocatalysis of $\text{TpOCH}_3\text{PPCo}$, TpCF_3PPCo and CoTTA under fuel cell conditions was carried out by Biloul et al. [23]. Electrochemical and oxygen reduction characteristics of several cobalt porphyrins of CoTPP, CoOEP, CoPPIX, CoTPyP [24], CoTCPP, CoTMPyP [25], CoTMPP [26–30] and CoTPP-PAP [31] were investigated systematically by using various electrochemical methods. It was found that the origin of the pyrolyzed carbon supported cobalt porphyrin electrocatalyst activity is the simultaneous presence of metal precursor, active carbon and a source of nitrogen. Nevertheless, the electrochemical and life test performances of the pyrolyzed carbon supported cobalt porphyrin electrocatalyst in fuel cell system were less reported. Herein, the pyrolyzed carbon supported cobalt tetramethoxy-phenylporphyrin (CoTMPP) electrocatalyst was prepared by applying microwave method. The electrochemical characteristics of the prepared electrocatalyst were measured. In particular, under fuel cell system conditions, the electrochemical and life test performances of the electrocatalyst were investigated.

2. Experimental details

Tetramethoxy-phenylporphyrin (TMPP) was synthesized by using the experimental protocol described in the literature [16]. High surface area carbon Black Pearls 2000 (BP2000, Cabot Corp.) was used as carbon support. To avoid the H_2O_2 detrimental effect on the fuel cell stability test, the carbon support has to be treated with H_2O_2 or HNO_3 solution beforehand. The pyrolyzed carbon supported CoTMPP/BP electrocatalysts were prepared by applying microwave method. A dispersion consisting in porphyrin monomer (TMPP), cobalt acetate (p.a., Fluka) and carbon support with a low Co content of 2–3% w/w

loading was prepared by dissolving in ice acetic acid, and then blending ultrasonically for 15 min. The resulting dispersion was heated and refluxed in microwave bath for 90 min in argon atmosphere and cooled down, the amount of CH_3OH was added into the dispersion, and then placed into a refrigerator overnight. The dispersion was filtered and washed with CH_3OH several times. The residual mixtures were dried in a vacuum oven at 70°C for 12 h, and ground in to powder. Thermal treatments of the electrocatalysts were performed at 900°C for 2 h under argon atmosphere.

An ink-type electrode was applied to the measurements of electrochemical characteristics. Ink was made by mixing 16 mg of CoTMPP/BP with 0.6 mL of deionized water and 0.2 mL of a 5 wt% Nafion in alcohol–water solution (Aldrich) in an ultrasonic bath for 20 min. 5 μL of the ink was dropped onto a vitreous carbon disk electrode as the substrate (4 mm diameter), dried for 10 min at 70°C , and then cooled down for 10 min in air.

A three-compartment glass cell system was used. The counter electrode was a Pt wire and the reference electrode was Ag/AgCl electrode ($\phi_{00} = 196\text{ mV}$ vs. RHE). The electrolytes were 0.5 M H_2SO_4 solution. Prior to each experiment the electrolytes were first saturated with oxygen. The Cyclic voltammograms (CV) were recorded by applying a scan rate of $d\phi/dt = 50\text{ mV/s}$ in acid electrolytes between 0 V and 0.9 V. The line scan voltammograms (LSV) for RDE measurements were recorded at $d\phi/dt = 10\text{ mV/s}$. The rotating speed for the disk electrode is from 0 to 4000 rpm.

The electrochemical and life test performances of the electrocatalyst under fuel cell conditions were measured in a PEM single cell that was incorporated in a test station (ElectroChem Inc., USA) with temperature controller, humidification, volume mass flow control of hydrogen and oxygen, and pressure regulator. During the performance evaluation, the fuel cells were connected with an electric load; cell voltage versus output current densities was recorded. The cell temperature was 50°C at gas pressures of 0.2 MPa for hydrogen and oxygen. Both reaction gases were fully humidified. The geometric areas of the anode and the cathode were 5 cm^2 .

For the performance evaluation, an anode with a Pt loading of 0.35 mg cm^{-2} was purchased from E-TEK Inc. The anode was coated by 5 wt% Nafion® solutions with a final loading of about $1\text{ mg Nafion}^\circ\text{ cm}^{-2}$ before MEA preparation. For cathode preparation, an electrocatalyst ink was made by the dispersion of 85.5 mg CoTMPP, 1.2 mL of deionized water and 1.2 mL of 5 wt% Nafion® solution ultrasonically for 1 h, and then dispersed on the uncatalyzed ELAT gas diffusion electrodes (ETEK) uniformly. The anode and cathode incorporated together with the pretreated Nafion® 115 membrane at 2 kN for 1 min at room temperature to form sandwich-like MEA. The MEA was hot pressed at 130°C for 2 min at 2 kN. Before incorporation into the PEM fuel cell, the MEA was soaked in deionized water at room temperature.

Download English Version:

<https://daneshyari.com/en/article/182709>

Download Persian Version:

<https://daneshyari.com/article/182709>

[Daneshyari.com](https://daneshyari.com)