

Mesocarbon microbeads supported Pt-Ru catalysts for electrochemical oxidation of methanol

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Abstract

The effects of mesocarbon microbeads support for platinum-ruthenium (Pt-Ru) catalysts on anode performance of the direct methanol fuel cell (DMFC) were investigated. The Pt-Ru catalyst with mesocarbon microbeads as support shows lower polarization characteristics than that with carbon black as support. The SEM of the cross-section of the catalyst layer with mesocarbon microbeads as support shows that there exist large pores and channels that are favorite for mass transfer in electrode reaction region. The effects of the cell operation temperature and the methanol concentration on the polarization curves of the anode electrode were also investigated.

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1. Introduction

The direct methanol fuel cell (DMFC) is one of the most desirable fuel cells for small-scale power unit [1–3]. To date, Pt-Ru alloy catalysts are still considered the most active catalysts to improve the effective polarization characteristics of methanol electrooxidation for DMFCs [4–10]. These catalysts are generally dispersed in small particles on conductive supports such as carbon blacks with a high specific surface area to obtain the optimum catalyst utilization for methanol electrooxidation in acidic electrolytes [11–17]. In order to improve the reaction rate in the cell, the mass transport in the anode should also be considered. To minimize the transport resistances in the electrochemical reaction, appropriate pore-forming additives [18,19] were introduced into the catalyst layer to increase the pore volume. In this paper, mesocarbon microbeads (MCMB) was used as catalyst support. Mesocarbon microbeads derived from petroleum residua is a kind of “hard” carbon with 1–40 μm in diameter and low specific surface area. By using MCMB as support, pores and channels in the electro-catalytic electrode may keep open and favorite for mass transport during the electro-catalytic reaction occurs.

2. Experimental

2.1. Preparation and characterization of supported Pt-Ru catalysts

MCMBs (Shanshan Inc., Shanghai, PR China) were boiled in 2 M KOH solutions boiling for 1 h before the supported catalyst preparation. The supported catalysts were prepared by liquid-phase reduction of chloroplatinic acid and ruthenium chloride with sodium dithionite. MCMB (3.7 g) was suspended in 200 ml of water at 80 °C. An aqueous solution (50 ml) containing 1 g chloroplatinic acid and appropriate amount of ruthenium chloride solution (Pt:Ru molar ratio equal to 3:1) were added slowly to the MCMB suspension and allowed for complete impregnation (lasting over 1 h). Then, 50 ml of 0.3 M Na₂S₂O₄ was added drop by drop. The resultant mixture was maintained at 80 °C for 3 h to allow complete reduction of Pt and precipitation of metallic oxides. Subsequently, the mixture was filtered, and washed copiously with hot distilled water to remove chloride ions. The catalyst was dried in an air oven at 80 °C for 5 h, and was heat-treated at 300 °C for 1 h.

Surface morphologies of the catalysts were examined by a thermal field emission scanning electron microscope (SEM LEO1530). X-ray diffraction (XRD: Rigaku X-ray diffractometer using a Cu target) was employed in order to study the crystal structure of the catalysts.

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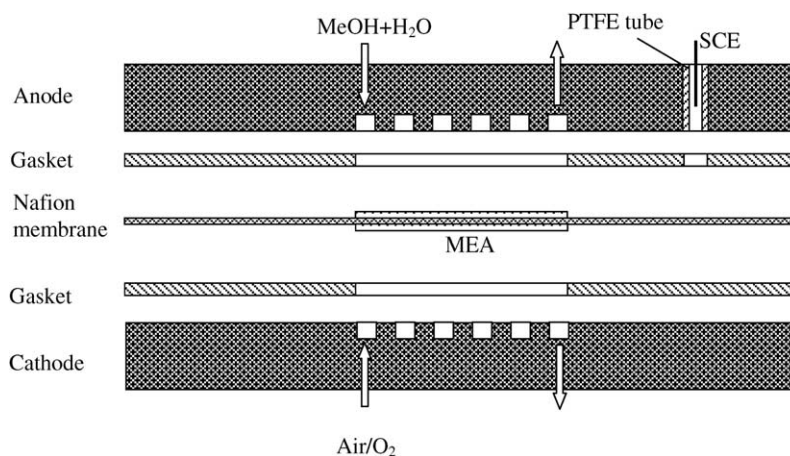


Fig. 1. Schematic diagram of the direct methanol fuel cell.

2.2. Preparation and characterization of electrode

The diffusion electrodes were prepared for the investigation of the electrochemical oxidation methanol. First, the Pt-Ru/MCMB catalyst was suspended in Millipore conductivity water and agitated in an ultrasonic bath for 30 min. Subsequently, the slurry was mixed with perfluorosulfonic acid solution (5 wt.%, Nafion[®], Du Pont) and ethylene glycol and acetylene black (10 wt.%) under ultrasonic agitation for 1 h. In this manner, catalyst ink was obtained which was spread on a carbon paper (Toray). The Pt loading in the electrode was 0.5 mg cm^{-2} . The cathode was prepared with the same method of anode except not adding acetylene black. The catalyst loading in the cathode was 0.5 mg cm^{-2} Pt/C (20 wt.% Pt, E-TEK Inc.). The MEA was finally obtained by hot-pressing the anode and cathode on either side of a pre-treated Nafion-112TM membrane under a pressure of 50 kg cm^{-2} at $130 \text{ }^\circ\text{C}$ for 3 min. The MEA so formed was typically with the thickness about 1 mm.

The structure of cell for electrochemical measurement was shown in Fig. 1. The MEA was sandwiched between two blocks of condense graphite into which the gas/liquid flow channels were graved. The ridges between the channels provided the electrical contact to the carbon electrodes, and the total geometrical area of cell is 3 cm^2 . Electrical heaters were mounted at the rear of the graphite blocks in order to maintain the desired cell temperature, which was monitored by thermocouples buried in the blocks. A saturated calomel reference electrode (SCE, +242 mV versus normal hydrogen electrode (NHE)) port was machined into the anode block (Fig. 1). Current–voltage (I – V) curves were obtained using a Solartron potentiostat (Solartron 1287, Solartron Instruments), which was interfaced to a PC through National Instruments IEEE-488 GPIB card. Aqueous methanol solutions of various concentrations were supplied to the anode with the flow rate of 1 ml min^{-1} . The pressure of oxygen in cathode is about 1.5 atm.

3. Results and discussion

The XRD analysis was used to characterize the mesocarbon microbeads supported Pt-Ru catalysts (Fig. 2). The peak near $2\theta = 25^\circ$ in the pattern is corresponding to diffraction of mesocarbon microbeads. Platinum peaks are observed at 2θ values of ca. 39.7 , 46.2 , 67.6 and 81.3° , corresponding to platinum (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively. The crystal size of the supported catalysts, calculated from XRD peak widths [20], is 13.1 nm.

From the electron micrograph of the supported catalysts as shown in Fig. 3(a), the particle size of mesocarbon microbeads is ca. $10 \mu\text{m}$. The surface of spherules is not smooth. Many nodular lumps and pores can be observed on the surface of the mesophase spherules (Fig. 3(b)). The surface roughness increases the specific surface of the spherules, which is helpful for the adsorption of platinum alloy.

Fig. 3 also shows the morphology of noble metals deposited on the surface of the mesocarbon microbeads. Most of

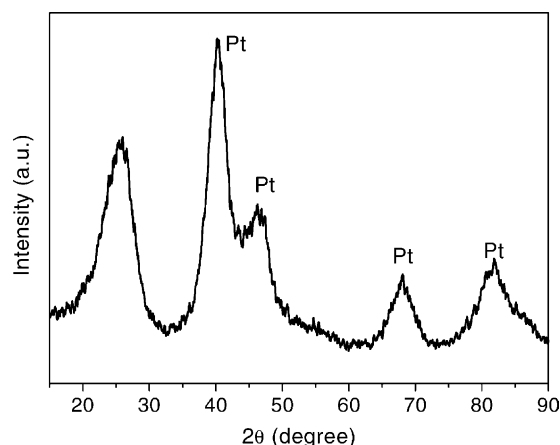


Fig. 2. XRD diffraction pattern of Pt-Ru/MCMB.

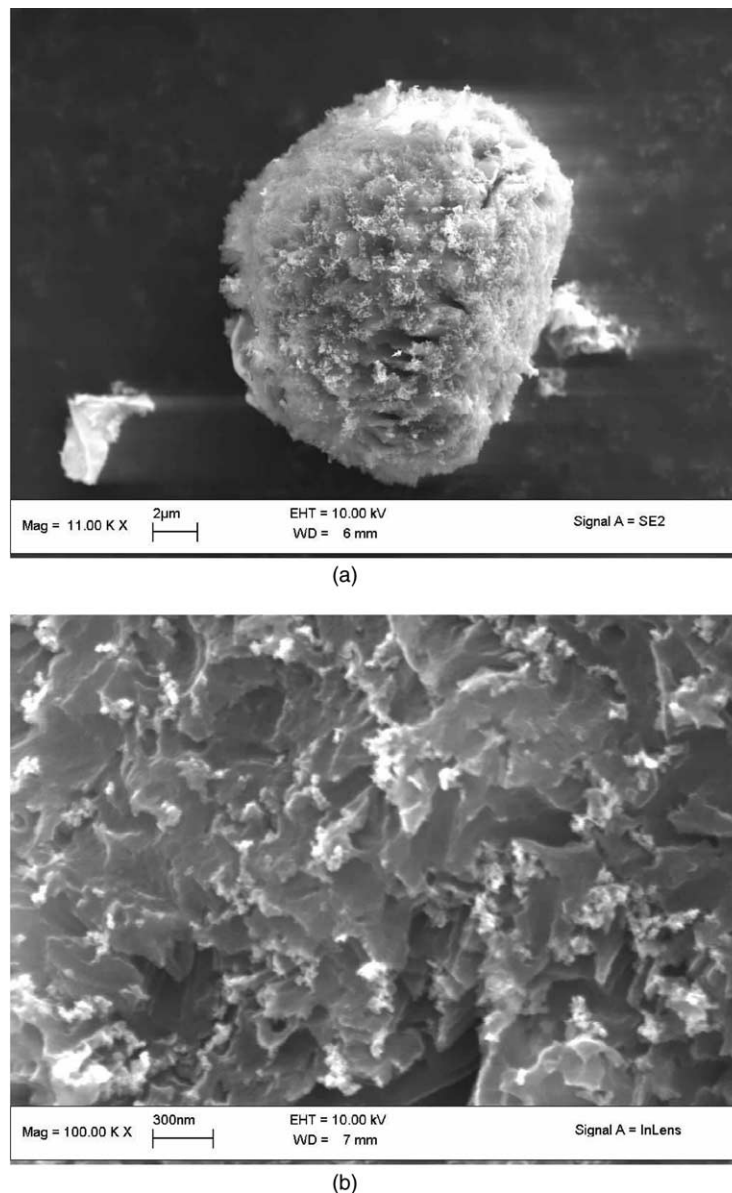


Fig. 3. SEM photograph of Pt-Ru/MCMB.

the noble metals are spread over the lumps of the surface. The size of the particles determined by SEM are ca. 12 nm, which is very close to the value calculated by the Scherrer formula as shown above. The Pt particle size is larger than that of catalyst prepared with carbon black. For example, the Pt size of the supported catalyst Pt/Vulcan XC-72R is 3.0 nm [13].

Fig. 4 shows a comparison of anode polarization curves of Pt-Ru/Vulcan XC-72 (E-TEK) and Pt-Ru/MCMB electrodes with 1.0 M methanol at 90 °C. The two electrodes were prepared and measured with the same method except that some acetylene black was added into the slurry during preparing the Pt-Ru/MCMB electrode.

The electrode with Pt-Ru/MCMB shows lower polarization performance than that of Pt-Ru/Vulcan XC-72. For example,

the overpotential of Pt-Ru/MCMB electrode is 0.39 V (versus SCE) at 300 mA cm⁻², which is 70 mV lower than that of Pt-Ru/Vulcan XC-72 electrode. The result indicates that meso-carbon microbeads supported Pt-Ru catalyst exhibits a high catalytic activity for methanol electrochemical oxidation at low Pt loadings. The high catalytic activity of Pt-Ru/MCMB may be due to the change of the structure of catalyst layer when compared with the usual carbon black supported catalysts. Fig. 5 shows the morphologies of cross-section of the interface of electrolyte and catalyst layer. It can be seen that the carbon black supported catalyst contacts the Nafion membrane tightly (Fig. 5(a)) and some Pt alloy particles may be covered by the support. These may hinder the mass transfer in the catalyst layer of electrochemical reaction. However, there still exists large pores or channels in the catalyst layer

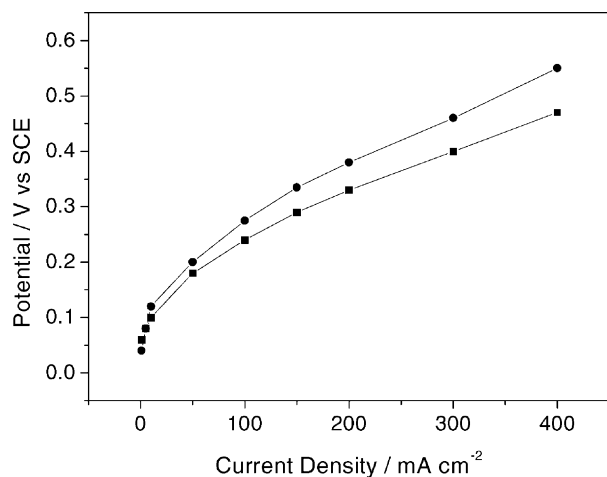


Fig. 4. Anode polarization curves for various supported electrodes in 1 M CH_3OH at 90 °C. Pt loading: 0.5 mg cm^{-2} . (■), Pt-Ru/MCMB electrode; (●), Pt-Ru/Vulcan XC-72 (E-TEK) electrode.

with Pt-Ru/MCMB due to the large size of the MBMC support (Fig. 5(b)). Meanwhile, the Pt alloy particles are not covered by the support and are exposed to the electrolyte. In this case, it is not only helpful for the access of the reactant into the catalyst layer and the product removal, but also improving the utility of the catalyst.

Fig. 6 shows the temperature dependence of the polarization curves with different concentration aqueous methanol (0.5–2.0 M) as the fuel. The improvement of the anode performance with temperature is due to the improved charge transfer kinetics at higher temperature. The result is consistent with the result obtained with the carbon black supported catalysts. It has been reported that from 60 to 90 °C, the power density of the cell doubles [21].

Fig. 7 shows the concentration dependence of the anode performance using MCMB supported Pt-Ru catalyst. The anode polarization decreased with the methanol concentration increase. The influence of methanol concentration on

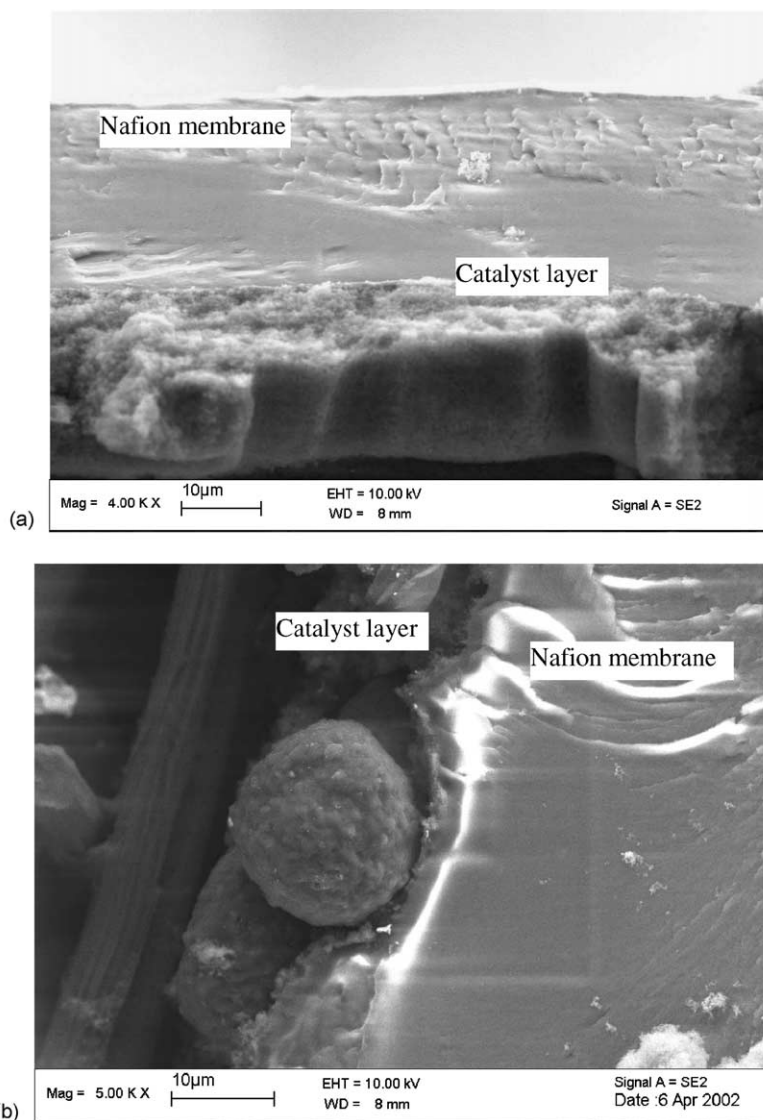


Fig. 5. SEM photograph of cross-section of the interface of electrolyte and catalyst layer. (a) Pt-Ru/Vulcan XC-72 (E-TEK) electrode; (b) Pt-Ru/MCMB electrode.

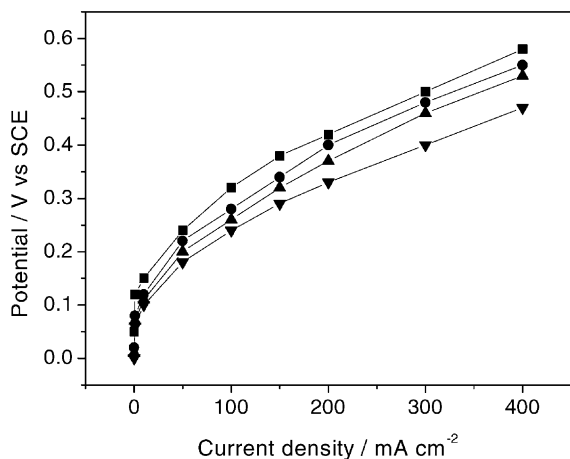


Fig. 6. Temperature dependent anode polarization curve for Pt-Ru/MCMB in 1 M CH₃OH. Pt loading: 0.5 mg cm⁻². Cell temperature: (■), 60 °C; (●), 70 °C; (▲), 80 °C; (▼), 90 °C.

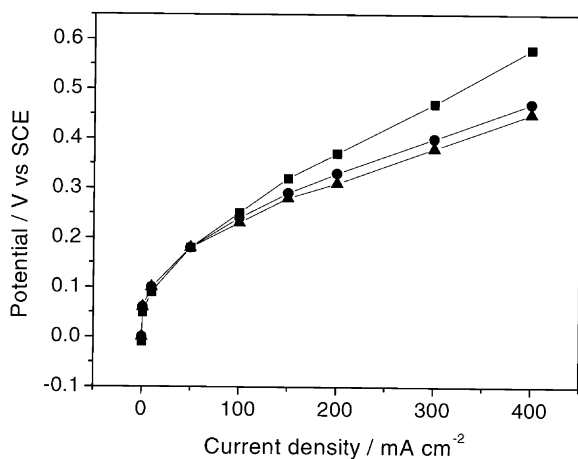


Fig. 7. Concentration dependent anode polarization curve for Pt-Ru/MCMB. Pt loading: 0.5 mg cm⁻². Methanol concentration: (■), 0.5 M; (●), 1.0 M; (▲), 2.0 M.

the cell performance needs to be further studied for the reason of methanol crossover. It has been reported that the selection of methanol concentration, for maximum cell power density, depends upon the current density [22].

4. Conclusion

Mesocarbon microbeads supported Pt-Ru catalyst exhibits a high catalytic activity for methanol electrochemical

oxidation than that with carbon black as support. The Pt particle size dispersed on the MCMB is larger than that of catalyst prepared with carbon black as support because of the lower specific surface area of the MCMB. The lower anode polarization characteristic may be due to the improvement of the mass transport ability. Further work is ongoing to reduce the Pt particle size of the supported catalyst and to study the performance of the fuel cell used the MCMB supported catalyst as the anode catalyst.

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