Supported Mixed Metal Nanoparticles and PFA-Nafion Nanocomposite Membrane for Low Temperature Fuel Cells

Kwong-Yu Chan[a], Jiawen Ren[a], Jin Liu[b], Huanting Wang[c], Jie Ding[a], Kwok-Ying Tsang[a], and Tung-Chun Lee[a]

[a]Department of Chemistry, The University of Hong Kong
Pokfulam Road, Hong Kong.

[b]Department of Material Science and Engineering
Anhui Institute of Architectue and Industry
Hefei, Anhui, China 230022.

[c]Australian Key Centre for Microscopy & Microanalysis
Electron Microscope Unit
The University of Sydney
NSW, 2006, Australia

ABSTRACT

Performance of low temperature fuel cells depends critically on the nanostructures of the material components in the electrodes and membranes. Some studies are reported here for 1) mixed metal nanoparticles supported on mesoporous carbon and 2) modification of nanopores of Nafion via in-situ polymerization of furfuryl alcohol.

The anodic oxidation of small organic molecules such as alcohols in a low temperature fuel cell requires platinum based mixed metal electrocatalysts such as platinum-ruthenium. A number of techniques are now available for synthesizing mixed metal nanoparticles [1-3]. The challenge is to control both the size and composition of the mixed nanoparticles. The electrocatalysts are normally supported on activated carbon, such as Vulcan XC 72. A further challenge is to control the structure and properties of the support material. A number of novel carbon materials with well-defined nanostructures have been reported in the literature recently. We report here the synthesis of platinum and platinum-ruthenium nanoparticles supported on ordered mesoporous carbon CMK-3 [4]. The CMK-3 is synthesized from a template material SBA-15, an ordered mesoporous silica with uniform pores of a few nanometers in diameter. The mesoporous carbon supported Pt and Pt-Ru nanoparticles are characterized by HRTEM (Fig. 2) and EDX. The supported electrocatalysts are evaluated for electrochemical reduction of oxygen and electrocatalytic oxidation of methanol. A Pt-CMK-3 catalyst synthesized outperformed the commercial catalyst for oxygen reduction in a large area gas diffusion electrode. The Pt-Ru-CMK-3 catalyst did not perform as well, likely due to transport limitation in the long and narrow mesopores.

Methanol crossing over from anode to cathode has been a major barrier to the development of direct methanol fuel cells. Studies have been made to modify the polymer electrolyte membrane, Nafion. A novel approach is reported here using in-situ polymerisation of furfuryl alchol [5,6]. The monomer is hydrophilic and penetrates the nanopores of Nafion. Upon polymerisation catalysed by sulphuric acid, the polymer becomes hydrophobic. This increase in hydrophobicity increases the barrier to methanol. Improvement of the membrane performance in a methanol fuel cell is reported here. The methanol permeability and proton conductivity are measured as a function of methanol concentration. The performance of a membrane-electrolyte assembly at room temperature shows marked increase in current and power compared to the unmodified membrane (Fig. 5).

Keywords: mixed metal nanoparticles, mesoporous carbon support, PFA modified Nafion, fuel cell catalysts.

1 MIXED METAL NANOPARTICLES SUPPORTED ON MESOPOROUS CARON

Fuel cells using a safe liquid fuel and operating at temperature below 60°C are desirable for powering portable consumer products such as notebook computers and mobile phones. The performance of electrocatalysts, however, still falls below expectations for these applications in terms of power density and price per kW. Advances made in the nanostructuring of fuel cell catalysts are being made, most importantly in preparing mixed platinum based metal nanoparticles of uniform size and uniform composition and uniformly dispersed into a conducting carbon support. A number of synthetic methods are used to prepare uniform sized metal particles such as the colloidal method, the

microemulsion method, and the glycol method[3]. While nanosize control has been made readily, simultaneous control of uniform composition at the nanoparticle level has not been generally achieved. On the other hand, advances have been made in controlling the structure of carbon support, mainly through the ordered mesoporous silica templating technique [4]. A notable example is the CMK type carbon templated from SBA-15 silica with uniform pores of 2-15 nm. Typical structures of these carbons are shown in Fig. 1. The challenge is to prepare mixed metal nanoparticles and have them loaded uniformly into carbon support with control nanostructures. The details of the synthetic procedure are given in [4]. We achived the loading of Pt-Ru mixed metal nanoparticles into CMK-3 mesoporous carbon, as shown in Fig. 2.
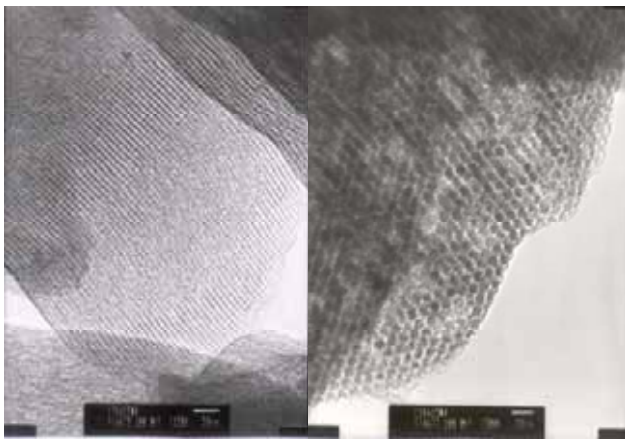

Fig. 1. TEM micrograph of ordered mesoporous carbon templated from SBA-15 silica.
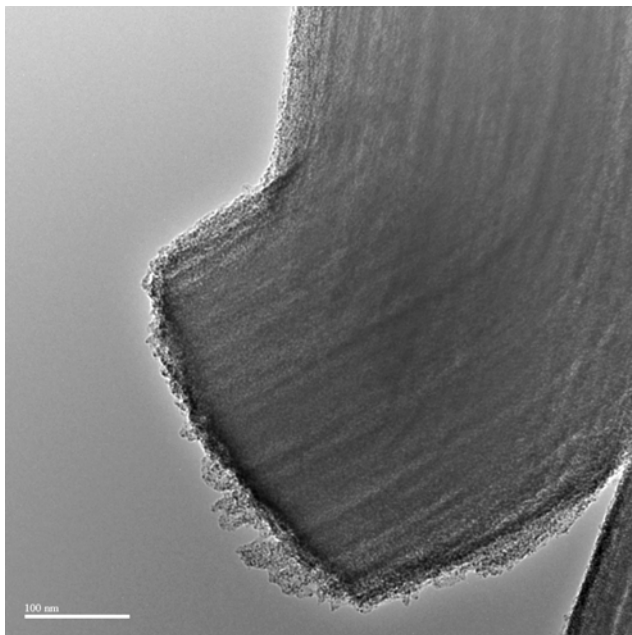

Fig. 2(a). TEM micrograph of Pt-Ru nanoparticles supported on mesoporous carbon templated from SBA-15 silica (CMK-3). The scale bar is 100 nm.
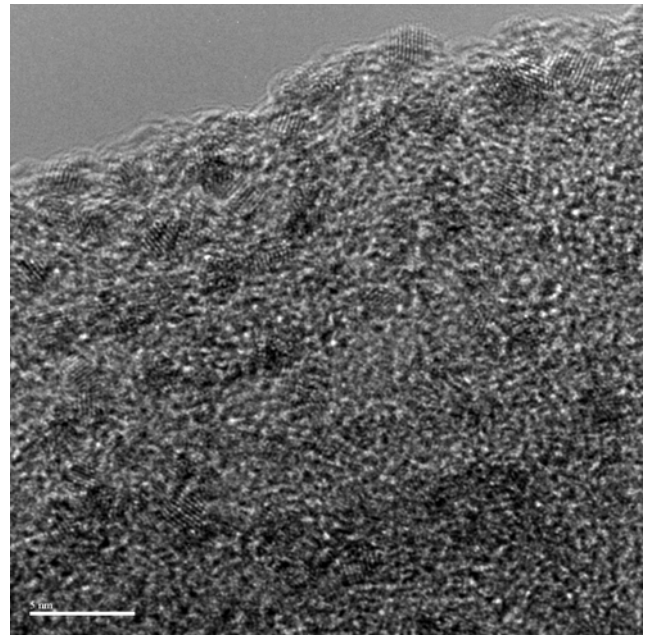

Fig. 2(b). HRTEM micrograph of Pt-Ru nanoparticles supported on mesoporous carbon templated from SBA-15 silica (CMK-3). The scale bar is 5 nm.

The performance of these Pt-Ru-CMK3 catalysts was tested for anodic oxidation of methanol in sulphuric acid at room temperature (20°C). As shown in Fig. 3, low activation polarization is indicated at low current. At higher current, however, polarization increases steadily, indicating ohmic and transport limitations. The interesting feature is some oscillatory V-I behaviour at high current. This may be due to the unsteady mass transfer in the long and narrow channels of CMK-3 carbon. Typical sizes of these CMK-3 particles are over a few hundred nanometers. One possible improvement is to produce smaller particles of these CMK-3 powders to about 50 nm of less in diameter.
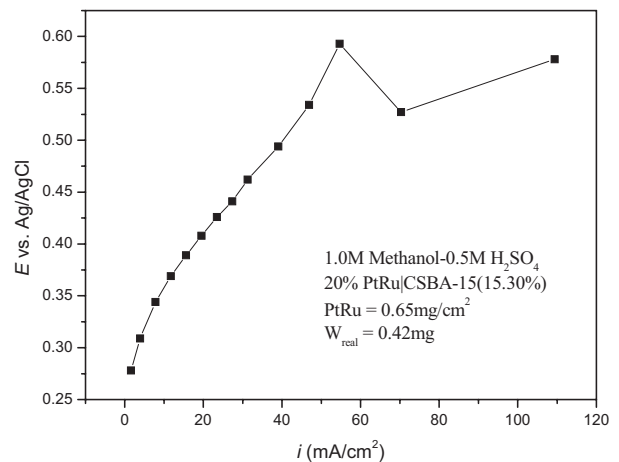

Fig. 3. Polarization curve of methanol oxidation on Pt-Ru/CMK-3 carbon electrode obtained from data of steady-state current discharged.

2. MODIFICATION OF NANOPORES OF NAFION VIA IN-SITU POLYMERIZATION OF FURFURYL ALCOHOL

The direct methanol fuel cell is a promising device to replace existing batteries for high energy density operation of portable electronic products. Current technology of direct methanol fuel cells uses a polymer electrolyte membrane between the anode and cathode to separate the anode and cathode contents, to prevent internal electronic current between the two electrodes, and most importantly to provide ionic conductivity within the fuel cell. Nafion© , a perfluorosulfonic polymers is the best proton electrolyte membrane developed for fuel cells because of its outstanding chemical, mechanical and thermal stability and high proton conductivity. In the operation of direct methanol fuel cells (DMFCs), however, high methanol permeation through Nafion membranes significantly lowers fuel efficiency and cell performance, and thus impedes the commercial development of DMFCs. Significant efforts have been made to modify Nafion by inserting a variety of materials such as palladium and its alloys, polyvinyl alcohol, polypyrrole, zeolite, silica, molybdophosphoric acid, and montmorillonite. The strategy of forming Nafion composite membranes has sometimes proven to be effective for reducing methanol permeation. However, either proton conductivity is undesirably affected, or additional costs and instability prevent their practical applications in DMFC.

Here, we describe a novel approach to the modification of solid polymer electrolyte membrane by in situ polymerization of an initially hydrophillic monomer, furfuryl alcohol to form the more hydrophobic polyfurfuryl alcohol (PFA) within the solid polymer electrolyte membrane porous domains. Furfuryl alcohol monomer is miscible with water and alcohols. It can be readily incorporated into hydrophilic zones of the internal pores of Nafion. After acid catalysed polymerization, PFA becomes more hydrophobic. The polymerization and change of hydrophobicity alter the microstructures and nanostructures of the polymer electrolyte and make it more impermeable to methanol. A homogenous PFA-Nafion nanocomposite membrane is demonstrated to be highly impermeable to methanol. In addition, PFA is chemically stable and relatively inexpensive. Conventional polymeric modifications to Nafion usually involve blend of polymers into the Nafion matrix and in effect filling either the hydrophillic or hydrophobic domains of the microstructures.

We found that the PFA-Nafion nanocomposite membrane outperforms the conventional Nafion membrane by more than a factor of two in the presence of methanol. Table 1 shows the reduced methanol permeability in several PFA-Nafion composite membranes with the appropriate weight percentages of PFA. The actual performance in an anode-membrane-cathode assembly (MEA) with 10% (vol) methanol in water as fuel is shown in Figures 3-4 under ambient air at room temperature and at an elevated temperature. The peak power density in the PFA modified MEA is more than two times higher than the MEA using an unmodified Nafion membrane.

A commercial Nafion 115 membrane was first sodium exchanged by boiling in 0.5 M NaOH solution and rinsed with deionized water. The dried membrane with an area of 2 cm x 2 cm was immersed in a mixture of 6 g furfuryl alcohol (FA, 98%, Lancaster), 12 g isopropanol, and 6 g deionized water. The fully swollen and saturated Nafion membrane was transferred into 1.0M sulphuric acid at room temperature for 2 min. Subsequently, the polymerization of furfuryl alcohol was carried out at 80 °C in an oven. The membrane was washed with ethanol, and boiled with 1.0M sulphuric acid to obtain the acidic form. The dark brown membrane was finally treated at 140° C for 10 min allowing for microstructural rearrangements of the membranes. The resulting PFA-Nafion membrane contains approximately 2.0 % by weight of PFA. Repeating the monomer loading and polymerization procedure can increase the final weight percentage of PFA to the desirable level.

Table 1 Properties of PFA-Nafion Nanocomposite

Sample	Nafion 115	Nafion-3.9PFA	Nafion-8.0PFA	Nafion-12.4PFA
Proton conductivity (S/ cm)	0.095	0.089	0.070	0.056
Methanol permeability ($\mu mol/cm^2 min$)	4.66	2.16	1.72	4.35

The microstructures of Nafion 115 membrane and Nafion-PFA nanocomposite membrane were examined with a scanning electron microscope (SEM, Philips Cambridge S360). The membranes were freeze-fractured in liquid N2 for SEM observations. A low voltage (5 kV) was operated to lower electron beam energy and avoid damage to the membranes. The representative cross-sectional images of the samples are shown in Figure 4. A protruded or rugged texture is observed from the plain Nafion 115 (Fig.4a). Flake-interlaced compact morphology develops when PFA is incorporated, and uniformly dispersed in Nafion structures (Fig.4b). The dimension of cluster aggregates evidently increases, and the thickness of interstitial regions in Nafion significantly decreases as the amount of PFA increases.
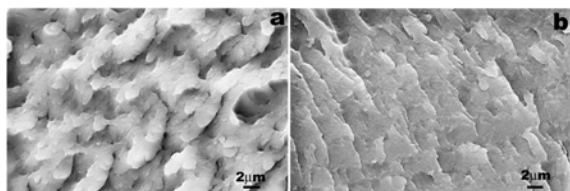
Fig. 4. SEM micrographs of cross-sections of fractioned unmodified Nafion membrane (a) and PFA-Nafion membrane (b)

The cathode electrode for the membrane –electrode assembly (MEA) was prepared by pasting a mixture of the required amount of the carbon-supported 60 wt% Pt catalyst (E-TEK) and 5 wt% Nafion solution (Aldrich) onto a teflonized carbon cloth (E-TEK) and drying in air at 80°C for 1 h. The anode was prepared by pasting a mixture of the required amount of the carbon-supported 60 wt% $Pt_{50}Ru_{50}$ onto a non-wet-proofing carbon cloth (E-TEK) and drying in air at 80°C for 1 h. Both electrodes prepared were then coated with Nafion solution (5wt% Nafion solution, Aldrich) and dry at 80°C. The metal loadings in cathode and anode were 2.5 mg cm^{-2} and 2 mg cm^{-2}, respectively. MEAs were fabricated by hot-pressing the made anode and cathode onto a pretreated Nafion or a polyfurfuryl alcohol modified Nafion 115 membrane at 140°C for 3 min. The performances of MEAs were evaluated with a self-made single cell test system with 4 cm^2 active geometrical area using galvanostatic technique. A 10 vol % methanol solution was supplied to the anode at 10 ml/min and an atmospheric dry air was flowed to the cathode. The performance at room temperature and 60° C of the MEAs is shown in Figs. 5.

REFERENCES

[1] 1. X. Zhang and K.-Y. Chan, "Microemulsion Synthesis and Electrocatalytic Properties of Platinum-Ruthenium Nanoparticles", Chemistry of Materials, 15(2) (2003) 451.

[2]. X. Zhang, K.Y. Tsang, and K.Y. Chan, "Electrocatalytic Properties of Supported Platinum-Cobalt Nanoparticles with Uniform and Controlled Composition", J. Electroan. Chem., 573 (2004) 1.

[3]. K.Y. Chan, J. Ding, Jiawen Ren, S.A. Cheng, and K.Y. Tsang, "Supported Mixed Metal Nanoparticles for Fuel Cell Electrode", J. Mater. Chem, 14 (2004) 505.

[4]. Jie Ding, Kwong-Yu Chan*, Jiawen Rena, and Feng-shou Xiao, "Platinum and Platinum-Ruthenium Nanoparticles Supported on Ordered Mesoporous Carbon and their Electrocatalytic Performance for Fuel Cell Reactions", Electrochimica Acta, to appear in 2005.

[5]. J. Liu, H.T. Wang, S.A. Cheng, and K.Y. Chan, "Nafion-polyfurfuryl alcohol nanocomposite membranes with low methanol permeation", Chem. Comm., 2004, 728.

[6]. J. Liu, H. Wang, S. Cheng, and K.Y. Chan, "Homogenous Nafion-polyfurfuryl alcohol nanocomposite membranes for direct methanol fuel cells", J. Membr. Sci., 246 (2005) 95.
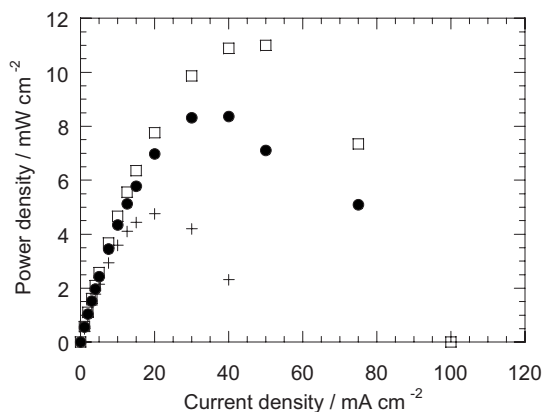
Fig.5. Cell performance of DMFC single cell made with unmodified Nafion 115 (crosses) membrane and two Nafion-PFA nanocomposite membranes operating at 60°C and ambient air.