

Research article

Modification of carbon support to enhance performance of direct methanol fuel cell

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Abstract

Carbon black powder is modified by applying a coating of a proton-conducting polymer electrolyte (ionomer), namely, perfluorosulfonic acid. The carbon is intended for use as a catalyst support in the preparation of Pt-Ru catalysts for direct methanol fuel cell. The aim is to extend the interfacial area between the catalytic metal particles and the proton-conducting ionomer. Ionomer incorporation is found to reduce the micropore volume and thus the BET surface-area of the carbon. Single-cell performance tests on a DMFC show that Pt-Ru catalyst supported on modified carbon exhibits superior performance to that on plain carbon.

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1. Introduction

In spite of intensive work on catalysts in recent years, carbon supported and unsupported Pt–Ru alloys are still considered to be the best electrocatalysts for methanol oxidation in direct methanol fuel cells (DMFCs) [1–8]. Significant efforts have been made to find an appropriate synthesis procedure for production of these catalysts with suitable dispersions. The main requirement of a good electrode is a three-phase boundary [9] between the supply of reactants on the one hand and the catalyst particle and the protonic conductor on the other hand. The catalyst particles must be in direct contact with an electronic conductor to ensure that the electrons are supplied to, or taken away from, the reaction site. Electronic conductivity is usually provided by a carbon substrate on which the catalyst particles are supported. An effective reaction zone in a catalyst layer is made by impregnating the catalyst powder with some ionomeric binder before pressing the electrode onto a polymer electrolyte membrane to ensure good contact with the membrane. Usually, the catalyst powder is made into an ink with a solvent and then mixed with

a binder material. The catalyst ink can be cast directly onto a membrane or a gas-diffusion medium. The effect of binder content on the performance of the electrodes has been studied both for PTFE and ionomeric binders [10–12]. The ionomer (proton-conducting polymer electrolyte) was incorporated into a catalyst ink to increase the catalyst utilization [13–20]. In all studies, the platinum utilization, even in the best-performing electrodes, was very low (10–25%). Such attempts aimed at maximizing the catalyst utilization must also satisfy other criteria such as reactant access, product removal, and protonic and electronic path continuity.

In perfluorosulfonic acid (PFSA) ionomer, the sulfonic acid micelles have an approximate diameter of 4–200 nm [21] and hence would be excluded from carbon pores with diameters less than 4 nm. Accordingly, part of the platinum particles deposited within the micropores of the carbon support may be inaccessible to the polymer electrolyte in a catalyst layer. A diagrammatic representation of this aspect is given in Fig. 1(a). This shows that the interaction between the catalyst metal particles and the ionomer in the electrode is poor when plain carbon powder is employed as a support material. We have evolved a new technique to extend the three-phase boundary in a catalyst layer by coating carbon powder with ionomer followed by incorporation of catalyst metal particles. Fig. 1(b) shows the

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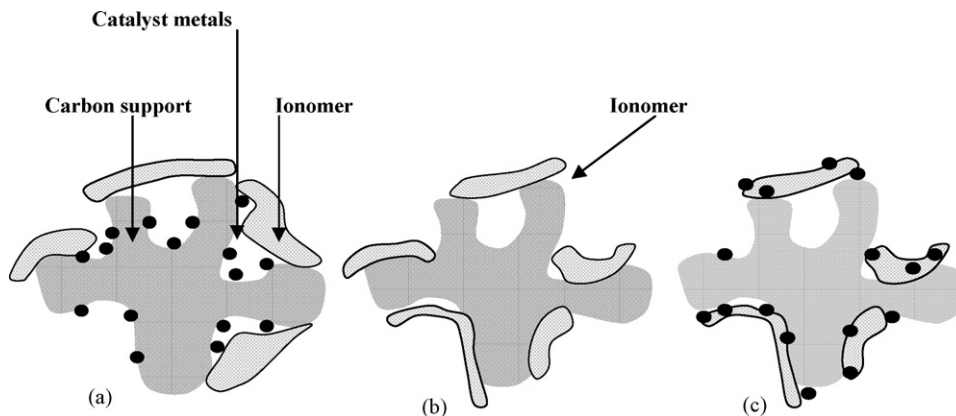


Fig. 1. Diagrammatic representation of: (a) catalyst–ionomer interaction in electrode using plain carbon as a support; (b) ionomer-coated carbon support; (c) catalyst–ionomer interaction on ionomer-coated carbon support.

ionomer-coated carbon support which is prepared by mixing carbon black powder with a perfluorosulfonic acid ionomer solution, followed by drying and crushing into fine powder. This modified carbon material offers an enhanced interfacial region with protonic continuum from the ionomer. Hence, a favourable and facilitating situation is readily available to the incoming catalyst particulates while they are dispersed during catalyst preparation steps on such modified carbon support materials. Fig. 1(c) shows an improved catalyst–ionomer–carbon interaction, i.e., a typical enhancement of the three-phase boundary required for an efficient reaction when the modified carbon material is used as a support, instead of a plain carbon. Consequently, a greater utilization of catalyst particles is also feasible.

This paper presents the results of a study of the employment of ionomer-coated carbon powder as a support for Pt–Ru catalyst towards methanol oxidation to extend the reaction area of the three-phase boundary and hence improve the utilization of catalyst particulates in direct methanol fuel cells.

2. Experimental

Carbon black powder (Vulcan XC-72R, Cabot International) with a specific surface-area (BET) of $217 \text{ m}^2 \text{ g}^{-1}$ was used as a support for the anode catalysts. Modified carbons were prepared by dispersing carbon powder and perfluorosulfonic acid ionomer (5% Nafion solution, Du Pont) in ethanol, stirring for 24 h, and then heating in a water bath at 80°C . The resulting solution was dried in oven at 65°C . The modified carbon agglomerates were crushed and apportioned with a screen and preserved over molecular sieves No. 140. The perfluorosulfonic acid ionomer content in the carbon was varied as 1, 2 and 5 wt.% and the samples were designated as 1, 2 and 5% MC (MC stands for modified carbon); 0% MC stands for a plain carbon support without any modification. The Pt–Ru catalysts were prepared by a colloidal method [22] on a plain carbon or modified carbon as a support. Their performance was compared with commercial 40 wt.% Pt–Ru/C catalysts from E-TEK. Commercial 46.5 wt.% Pt/C (Tanaka) was used as a cathode catalyst for all the experiments carried out in this study.

The BET surface-areas of the anode catalyst supports were measured by nitrogen adsorption using a Micromeritics ASAP2010 apparatus. X-ray diffraction (XRD) measurements were recorded on a Rint-Dmax 2500, Rigaku instrument, with a nickel-filtered $\text{Cu K}\alpha$ (0.15418 nm) source. The morphologies of the catalysts were examined by scanning electron microscopy (SEM) (S-4200, Hitachi) as well as by transmission electron microscopy (TEM) with a Phillips-CM30 electron microscope.

Gas-diffusion electrodes were prepared by spray coating a required amount of catalyst ink onto teflonized carbon paper substrates (Toray TGPH-060, 20% PTFE). The catalyst inks were prepared by dispersing appropriate amounts of catalysts, de-ionized water, isopropyl alcohol (IPA), and 5 wt.% Nafion solution (1100 EW, Du Pont). The catalyst ink was sprayed onto 10 cm^2 of carbon paper and an additional ionomer solution was sprayed onto the catalyst layer of each electrode in order to decrease the contact resistance with polymer electrolyte membrane (Nafion[®] 117). The amount of ionomer content in the anode was varied from 15 to 60 wt.% based on the catalyst, but the amount of ionomer in the cathode was fixed at 30 wt.%. In this paper, the ionomer content in the electrode is defined as: ionomer content (wt.%) = $W_{\text{ion}}/W_{\text{catal}} \times 100$, where W_{ion} is the weight of dry ionomer and W_{catal} is the weight of bulk catalyst including metal and carbon support contained in the electrode. A membrane–electrode assembly was fabricated by placing a Nafion[®] 117 membrane between a PtRu (3 mg cm^{-2}) anode and a Pt (3 mg cm^{-2}) cathode followed by hot-pressing at 140°C , 70 MPa for 150 s.

All experiments, including the electrochemical measurements, were conducted with cells that consisted of an MEA sandwiched between two graphite flow-field plates. For all studies conducted in a fuel cell mode, 2 M methanol solution was pumped through the anode side at a flow rate of $5 \text{ cm}^3/\text{min}^{-1}$ and oxygen to the cathode side at a flow rate of 250 sccm. The temperature and pressure of single cells were held at 90°C and 1 atm, respectively. The oxygen gas was passed through a humidifier maintained at a temperature of 65°C .

Current–voltage curves were measured galvanostatically by means of an electronic load (Daegil 500P). Cyclic voltammetry

was conducted with a conventional, air-tight, three-electrode cell that contained 0.5 M H₂SO₄ electrolyte in 1 M methanol at 25 °C. The working electrode was formed using a Pt-Ru/C catalyst that was applied to a graphite electrode with Nafion[®] solution as the binder. Platinum mesh and a saturated calomel electrode served as the counter and reference electrodes, respectively. Before each recording of cyclic voltammograms, pure nitrogen was bubbled through the cell to deoxygenate the solutions. The temperature was maintained at 25 ± 0.2 °C by circulating water from a thermostat through the double wall of the cell. A potentiostat–galvanostat (EG & G 273 A) was used for the measurements and all data were transferred to a PC controlled by a GPIB interface.

3. Results and discussions

Pore-size distributions and specific BET surface-areas were measured for plain carbon (Vulcan XC-72R) and for modified carbons with various amounts of ionomer Nafion (PFSA) incorporation. The pore-size distributions of the modified carbon samples are presented in Fig. 2. An increase in ionomer content decreases the pore size of the carbon texture and also decreases the pore volume, especially in the micropore regions (<4 nm). The BET surface-areas of carbon with ionomer contents of 0, 1, 2 and 5 wt.% are 217, 189, 178 and 161 m² g⁻¹, respectively. The sequential decrease in BET surface-area indicates that the ionomer is distributed well on the pores of the carbon powder.

The forward sweeps of cyclic voltammograms of the electrodes using a home-made 40 wt.% Pt-Ru catalyst supported on the plain and ionomer-coated carbons are given in Fig. 3. An improved activity for methanol oxidation is found with the 2% MC catalyst, but the 5% MC catalyst exhibits a poor activity compared with the plain carbon catalyst. The increased activity by using modified carbon as a support is attributed to enhancement of the three-phase boundary of the catalyst layer that leads to an increased utilization of the catalytic particulates. It is speculated that a considerable portion of the catalytic particulates

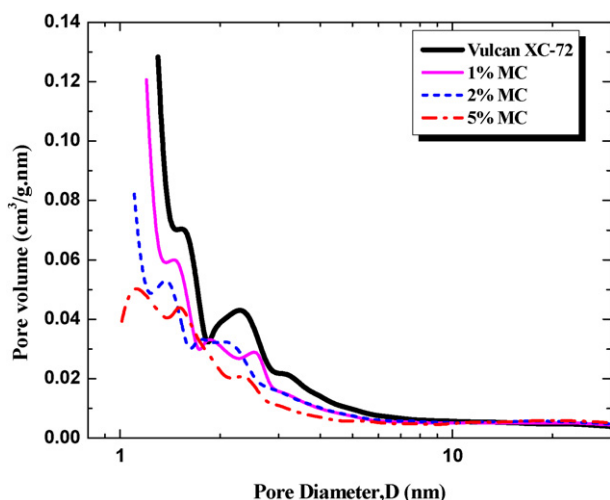


Fig. 2. Pore-size distribution of plain Vulcan XC-72 carbon and various ionomer-coated Vulcan XC-72R carbons.

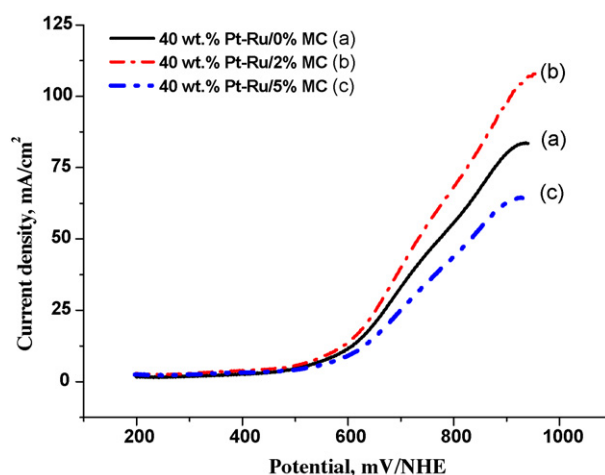


Fig. 3. Forward sweep of cyclic voltammograms of: (a) 40 wt.% Pt-Ru/0% MC (plain carbon), (b) 40 wt.% Pt-Ru/2% MC, and (c) 40 wt.% Pt-Ru/5% MC on glassy carbon electrode in 0.5 M H₂SO₄/1 M CH₃OH at a scan rate of 50 mV s⁻¹.

that enter into the pores of the plain carbon support remain inaccessible for the ionic conduction provided by ionomer in the catalyst layer, as depicted in Fig. 1(a). This is because the Nafion ionomer agglomerates in solution have diameters ranging from 4 to 200 nm and thus the ionomer is excluded from carbon pores with diameters less than 4 nm. In the case of the ionomer-coated carbon support, however, the catalytic particulates do not deposit in the micropores of carbon but deposit in the larger pores or in the vicinity of the ionomer and hence remain accessible for reactants and provide a proton conduction path in the catalyst layer, as shown in Fig. 1(c). On the other hand, when an excessive amount of ionomer is incorporated in the carbon powder, the larger portion of the pores can be blocked and thus the carbon powder cannot offer sufficient surface-area to disperse catalyst particulates fully and thus achieve maximum catalytic activity. This may be the reason why the 5% MC catalyst exhibits a poor activity compared with the catalyst supported on plain carbon.

Preliminary experiments have been conducted to determine the effect of ionomer content on the performance of a DMFC with a commercial 40 wt.% Pt-Ru/C (E-Tek) catalyst by varying the ionomer content in the anode catalyst layer, namely, 15, 30, 45, 60 and 80 wt.%. The corresponding values of the maximum power density values are 68, 126, 123, 158 and 66 mW cm⁻² respectively for a supply of 2 M methanol and oxygen at 90 °C and 1 atm. These data confirm that the maximum performance is obtained with an ionomer content of 60 wt.% in the catalyst layer. Comparative studies have been conducted with catalysts supported on modified carbons to investigate the influence of the modified carbon on the total amount of ionomer required in the anode catalyst layer.

Fig. 4 shows the performance of a single-cell DMFC with 40 wt.% Pt-Ru/2% MC and various amount of electrode ionomer, i.e., 15, 30, 45 and 60 wt.%. The maximum power density values obtained are 52, 168, 75 and 13 mW cm⁻², respectively. It can be seen that the best performance is exhibited by Pt-Ru catalyst supported on modified carbon with a 30%

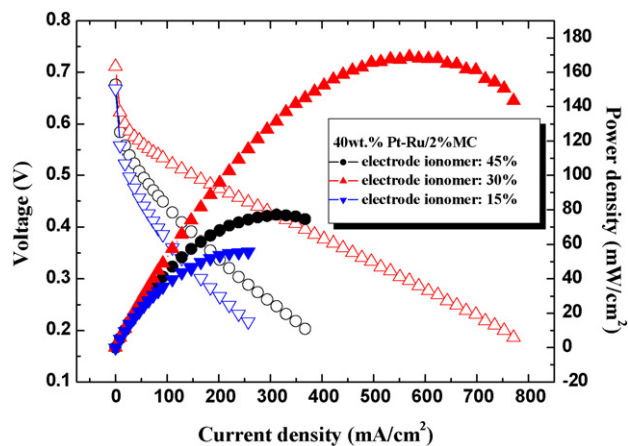


Fig. 4. Single-cell performance of DMFC with 40 wt.% Pt-Ru/2% MC with various contents of ionomer in catalyst layer at 90 °C, 2.0 M CH₃OH 5 cm³/min⁻¹, humidified O₂ 250 sccm.

ionomer content in the catalyst layer. Given that a maximum performance with a plain carbon catalyst was obtained with an ionomer content of 60 wt.% in the catalyst layer, it is interesting to find that the incorporation of ionomer in carbon particulates greatly reduces the amount of ionomer required in the catalyst layer by half.

When the ionomer content in the carbon support was increased to 5 wt.%, drastic changes were observed in the single-cell performance. The 40 wt.% Pt-Ru/5% MC catalyst with varied additional ionomer content in the catalyst layer such as 15, 30 and 60 wt.% shows maximum power densities of 160, 70 and 50 mW cm⁻², respectively. In the previous case (Fig. 4), with a 2% modified carbon an ionomer content of 15 wt.% was insufficient to provide adequate electrolytic conductance inside the catalyst layer and consequently the DMFC performance was low. When, however, the ionomer content is raised to 5 wt.% in the carbon support, the performance increases three-fold, even with a low ionomer content of 15 wt.% in the catalyst layer. By contrast, an opposite trend is observed with 30 wt.% ionomer content, as the ionomer content in the carbon is increased from 2 to 5 wt.%.

The single-cell performances for the best performed ionomer compositions with various modified carbon supports is shown in Fig. 5 and compared with the single-cell performance exhibited by the commercial 40 wt.% Pt-Ru/C (E-Tek). Among the homemade catalysts with these compositions, there is no significant difference in the performance exhibited by each of them in low current density region, though a slightly higher performance is shown by the catalyst supported on 2% MC in the high current density region. The performance in low current density region is not improved appreciably with the modified-carbon catalysts contrary to our expectation. This observation is similar, however, to the fundamental studies of Nakagawa and Xiu [23] on the electrode performance of a DMFC with different loadings of anode catalyst. They did not observe a significant change in performance in low potential region, but a noticeable difference in performance was found in the high potential region, as in our present investigation. Thus, the slightest addition of ionomer

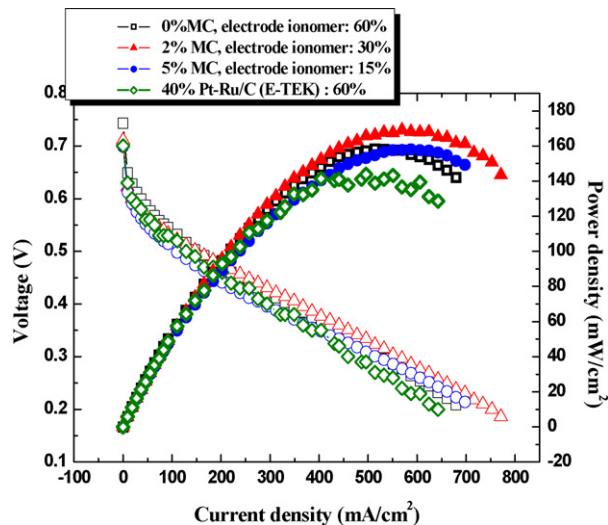


Fig. 5. Single-cell performance with 40 wt.% Pt-Ru supported on plain carbon and various ionomer-coated carbons with optimized electrode ionomer content at 90 °C, 2.0 M CH₃OH 5 cm³/min⁻¹, humidified O₂ 250 sccm.

content in the carbon greatly reduces the amount of ionomer that otherwise would be required in the catalyst layer to yield the comparable performance. The modified carbon catalyst also exhibits higher performance than a commercial catalyst from E-Tek. In conclusion, the results in Figs. 4 and 5 show that there is an optimum combination between the inner ionomer that is on the carbon particles and the outer ionomer in the catalyst layer.

A decrease in the required optimum ionomer content in the catalyst layer can be explained as follows. The ionomer in the catalyst layer plays several roles: it acts as a pathway for the protons to migrate from the catalyst particles to the polymer electrolyte membrane and as a binder for the catalyst particles to be attached firmly to the polymer electrolyte membrane. On the other hand, it is an electronic insulator and hence may hinder the transport of the electrons produced at the catalyst surfaces to the current-collector. Further, the amount and the distribution of the ionomer can modify the porosity and pore size of the catalyst layers and thus influence the mass transport rates of the reactants and the products [24]. Therefore, an appropriate amount of ionomer is needed in the catalyst layer to achieve higher performance. In case of catalysts supported on modified carbons, the interfacial area between the catalyst particles and the ionomer significantly widens and thus the catalyst layer needs only a small amount of additional ionomer compared with the case with the plain carbon catalyst. Therefore, further increase of ionomer content in the catalyst layer could increase the resistance to mass transport and electronic conduction.

In summary, the enhanced performance by the catalysts supported on ionomer-coated carbon is attributed to the formation of an extended three-phase boundary which increases the catalyst utilization for the same metal loading without increasing the mass transport and electronic resistances in the catalyst layer.

An examination was made on the microstructure of the anode catalyst layer. X-ray diffraction patterns of the catalysts (data

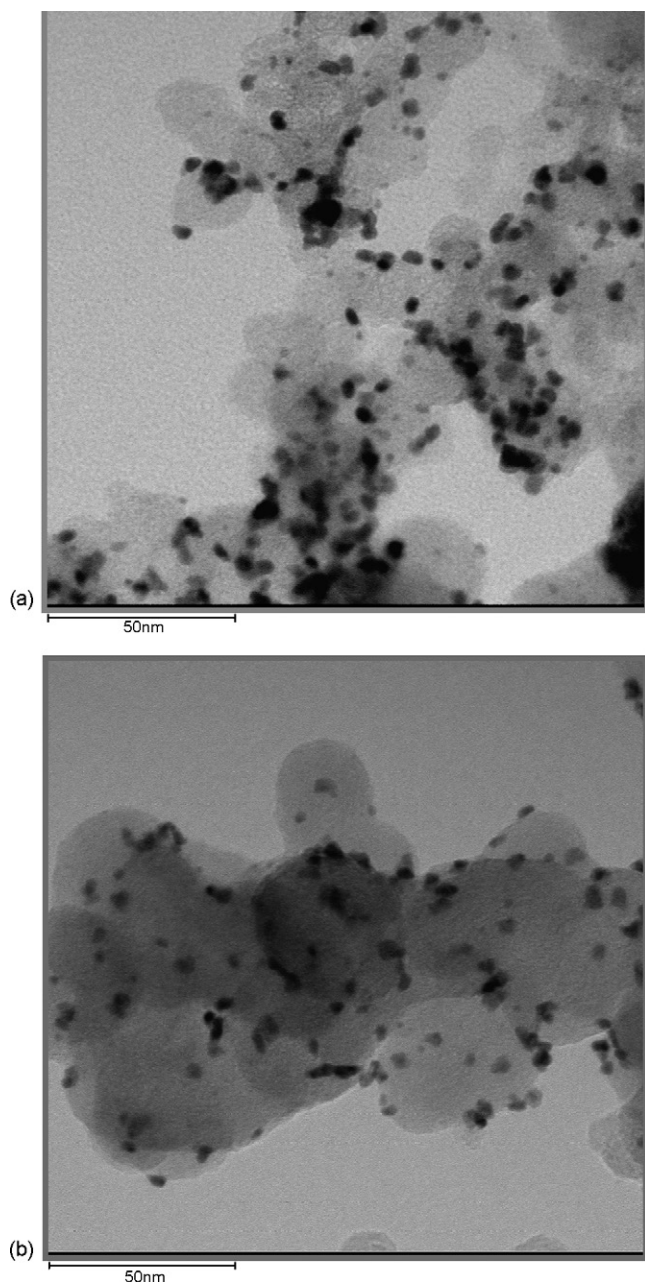


Fig. 6. Transmission electron micrographs of: (a) 40 wt.% Pt-Ru/0% MC and (b) 40 wt.% Pt-Ru/2% MC.

not shown) revealed the formation of Pt–Ru alloy particles in a size range of 3.5–4.0 nm. Transmission electron microscopy (TEM) photographs of two different catalysts used in this study is shown in Fig. 6. The semi-transparent clusters are aggregates of carbon black particles and the black dots are the dispersed metal particles. The particle-size distribution of the metal is uniform in both the cases, with an average particle size of 3.5–4.0 nm. No significant agglomerates of metal particles is observed. Scanning electron micrographs of the catalyst layers are presented in Fig. 7. The images do not show any special structural changes when using a modified carbon-supported catalyst.

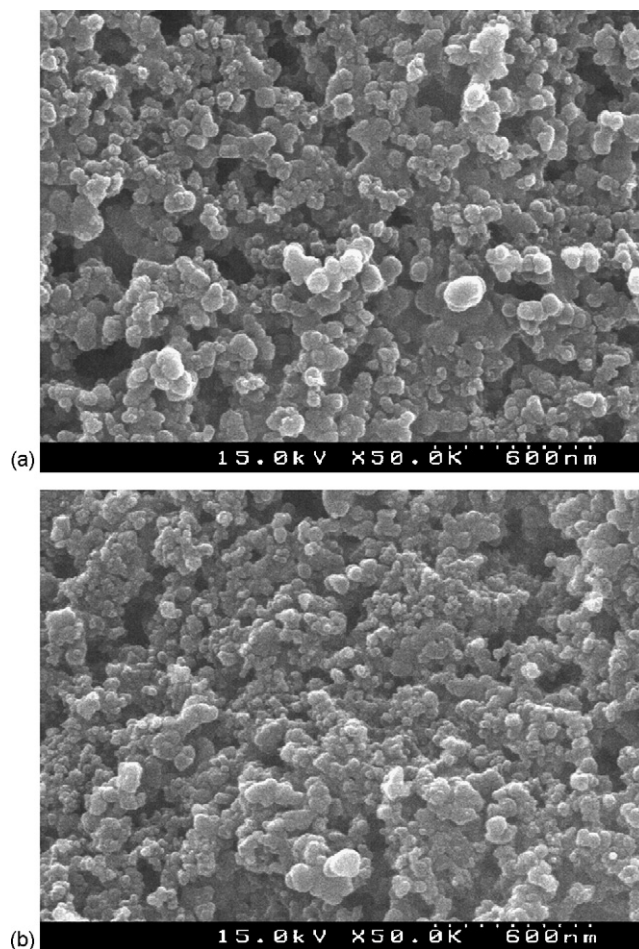


Fig. 7. Scanning electron micrographs of: (a) 40 wt.% Pt-Ru/0% MC and (b) 40 wt.% Pt-Ru/2% MC.

4. Conclusions

The major findings from the present investigation of using ionomer-coated carbons as support material for Pt–Ru anode catalysts in direct methanol fuel cell applications are as follows. The ionomer incorporation induces changes in the pore-size distribution of the carbon support and this leads to the suppression of undesirable micropores. The required optimum ionomer content in the catalyst layer is much less than that in a plain carbon catalyst and is influenced by the amount of ionomer incorporated in the carbon particles. The Pt–Ru catalysts supported on modified carbon give better performance than the catalyst supported on the plain carbon. This improvement is achieved through increased catalyst utilization and extension of the three-phase boundary in the catalyst layer.

In conclusion, incorporation of ionomer in the carbon support enhances the contact area between the catalyst particles and ionomer and reduces the total amount of ionomer required in the anode catalyst layer. The reduced total ionomer content in the anode facilitates the mass transport of reactants and products. Optimization of the fabrication process could render further gains in fuel cell performance.

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