

Iron(III) tetramethoxyphenylporphyrin(FeTMPP) as methanol tolerant electrocatalyst for oxygen reduction in direct methanol fuel cells

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Carbon supported iron(III) tetramethoxyphenylporphyrin (FeTMPP) heat treated at 800 °C under argon atmosphere was used as catalysts for the electroreduction of oxygen in direct methanol polybenzimidazole (PBI) polymer electrolyte fuel cells that were operated at 150 °C. The electrode structure was optimized in terms of the composition of PTFE, polymer electrolyte and carbon-supported FeTMPP catalyst loading. The effect of methanol permeation from anode to cathode on performance of the FeTMPP electrodes was examined using spectroscopic techniques, such as on line mass spectroscopy (MS), on line Fourier transform infrared (FTIR) spectroscopy and conventional polarization curve measurements under fuel cell operating condition. The results show that carbon supported FeTMPP heat treated at 800 °C is methanol tolerant and active catalyst for the oxygen reduction in a direct methanol PBI fuel cell. The best cathode performance under optimal condition corresponded to a potential reached of 0.6 V vs RHE at a current density of 900 mA cm⁻².

Keywords: oxygen electrocatalysts, gas diffusion electrode, PEM fuel cells, PBI polymer electrolyte

1. Introduction

Fuel cells employing solid polymer electrolytes such as perfluorosulfonic acid polymer membranes (Nafion[®]) have received increasing attention due to their promise as a high energy density power plant for both stationary and mobile applications [1–4]. The main features of the polymer electrolyte fuel cell (PEFC) are pollution free operation, less corrosion and high power density. Recently, there is an increasing motivation to develop a direct methanol/oxygen fuel cell (DMFC) [5–8]. Using methanol as fuel has several advantages compared to hydrogen. Methanol is a relatively plentiful liquid fuel that can be easily handled, stored and transported. Moreover, the infrastructure built for gasoline can be used, if the methanol/oxygen fuel cell is used in transportation. However, there are at least two technical challenges impeding direct methanol/oxygen fuel cell commercialization. One is lack of a sufficiently active anode catalyst, though Pt–Ru alloy is still recognized as the best catalyst for direct methanol oxidation. The other is that the solid polymer electrolytes currently available, such as Nafion[®], have a large methanol crossover rate. The methanol permeates across the membrane to the cathode and not only wastes fuel but also causes excess polarization of the oxygen electrode, consequently lowering the energy efficiency

and cell performance. To overcome these problems, Savinell *et al.* [9] proposed to raise the cell operating temperature by using a new polymer electrolyte, polybenzimidazole (PBI). Operating a fuel cell at elevated temperature can enhance the electrode reaction kinetics, depress the electrode poisoning, and reduce methanol crossover rate.

Another approach to overcome these problems is to use an active oxygen reduction electrocatalysts which is unaffected by the presence of methanol or its oxidation products.

Since Jasinski [10] first reported the effectiveness of metallophthalocyanines as catalysts for the cathodic reduction of oxygen in alkaline solutions, there have been many efforts to yield materials which exhibit high activity for the electrochemical oxygen reduction [11–15]. These catalysts were prepared by the dispersion of certain transition metal macrocycles on high area carbons followed by a heat treatment in an inert atmosphere at temperatures ranging from 600 to 1000 °C. The advantages for the use of macrocycle catalysts are that they are nonprecious metal based and they are expected to be methanol tolerant.

The purpose of this work was to optimize the FeTMPP electrode structure and to examine effects of methanol permeation on electrode performance. The catalytic activity for oxygen reduction was examined by conventional polarization curve measurements. Spectroscopic techniques, such as online mass spectroscopy (MS) and Fourier transform infrared (FTIR) spectroscopy under fuel cell condition were

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also used to monitor and analyse the products emanating from the cathode.

2. Experimental details

2.1. Catalyst preparation

The iron(III) tetramethoxyphenylporphyrin (FeTMPP) in the form of FeTMPP-Cl was obtained from Aldrich Chemical Company and was used without further purification. The catalysts for oxygen reduction were prepared by dissolving specific amount of FeTMPP-Cl into solvent and mixing with un-deashed RB carbon (Calgon Corp., Pittsburgh, PA) in acetone. The resulting mixture was mixed by a magnetic stirrer for about 20 h and then was filtered rapidly through a nuclepore polycarbonate membrane (1 μm pore size). The concentration of the FeTMPP in the filtrate was measured spectrophotometrically and thus the amount of the FeTMPP adsorbed on the carbon was calculated. The solid samples were then heat-treated in a horizontal tube furnace at 800 °C (HT 800) for 2 h under continuous flow of purified argon (Matheson, H.P. grade), and allowing to cool while still under flowing argon.

2.2. Electrode preparation

Platinum black (Johnson Matthey) and carbon supported FeTMPP were used as anode and cathode catalysts, respectively. The cathodes and anodes were prepared as follows. The desired amount of catalyst and PTFE suspension (ICI Fluoropolymer) were mixed with distilled water. The resulting mixture was filtered through a polycarbonate filter membrane (1 μm pore size) to remove water. After most of the water was removed, a thin, uniform catalyst layer remained on the filter membrane. In order to reduce cracking of the catalyst layer in the drying process, a small amount of glycerol was added on the top of the catalyst layer. The glycerol was then filtered through the catalyst layer that replaced the residual water in the catalyst layer. Lightly pressing the catalyst layer onto the gas backing, and then carefully peeling off the filter membrane transferred the catalyst layer onto a gas backing material (Spectracarb 2050 carbon paper). The electrode was dried at room temperature in a vacuum oven for 4–5 hours, then further dried at 60 °C in a vacuum oven overnight. Finally, the electrode was treated in a nitrogen atmosphere at 200 °C for 2 h to decompose the surfactant in the PTFE suspension.

2.3. E&M assembly

Polybenzimidazole (Hoechst Celanese) films were cast from a solution of the high molecular weight PBI (25 000 amu) in trifluoroacetic acid (TFA) with approximately six phosphoric acid molecules per polymer repeat unit. The film thickness was about 0.008 cm. The membrane/electrode (M&E) assem-

blies were formed by hot pressing the electrodes on a phosphoric acid doped PBI membrane at 150 °C, 2.2×10^4 kPa for 10 min. The M&E assemblies were then impregnated with phosphoric acid by adding 15 and 21 μl of 5 M H_3PO_4 solution on the gas backing side of the anode and the cathode, respectively, and allowing the acid solution to penetrate into the electrode structure.

2.4. Electrochemical experiments

All the electrochemical experiments were carried out in a single cell test station as described in [6]. Figure 1 shows the fuel cell hardware which consisted of two PTFE blocks supported by two steel plates at the outsides. The gas distribution channels and feed throughs were machined into the PTFE blocks. The whole unit was held together by four threaded studs and nuts. At one side, a reference electrode was held against the membrane. With this reference electrode, the potential of the cathode or the anode can be separately measured. The reference electrode consisted of an E-TEK electrode (0.5 mg cm^{-2} Pt on carbon), which was fed continuously with humidified hydrogen gas during the experiment. Its potential was assumed to be equal to that of the reversible hydrogen electrode (RHE), and all potentials reported are with respect to this reference electrode. The fuel cell hardware was placed in an oven and heated to 150 °C. Humidified oxygen or air was fed to the cathode chamber. Gas humidification was achieved by bubbling the gases through distilled water at room temperature. Humidified hydrogen or a liquid mixture of methanol and water was fed to anode chamber. In the case of the liquid mixture of methanol and water feeding, the liquid was first vapourized in the oven and then fed to the anode chamber. The fuel cell was operated at atmosphere pressure and the gas flow-rates were in large excess of stoichiometric requirements. The cell resistance between anode and cathode was measured using the current interrupt method. The typical cell resistance measured was about 0.3–0.5 Ωcm^2 . All of the electrode polarization curves reported in this paper are iR corrected.

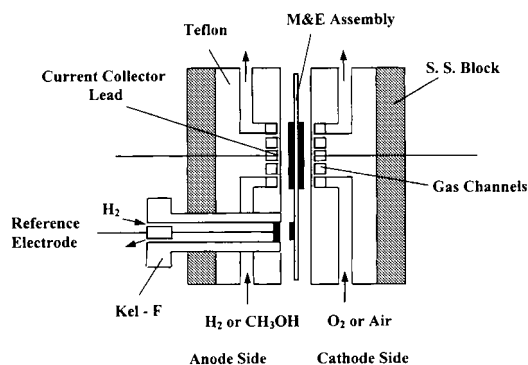


Fig. 1. Schematic of single cell with an electrode area of 1 cm^2 .

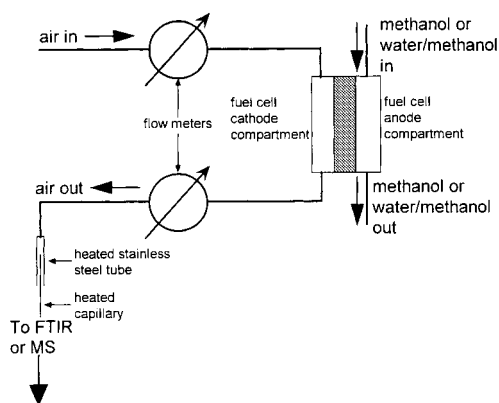


Fig. 2. A schematic of the combination of multipurpose electrochemical mass spectrometry (MS) or Fourier transform infrared spectroscopy (FTIR) with the prototype direct methanol PBI fuel cell (DMFC).

2.5. Online FTIR measurement

The setup of online Fourier transform infrared spectroscopy (FTIRS) in conjunction with the prototype DMFC is shown in Fig. 2. A Bomem MB100 FTIR single-beam apparatus equipped with a high intensity SiC source, a liquid nitrogen cooled mid-band MCT detector and an Arid-Zone™ sample compartment was used. The stainless steel gas cell body included KBr windows, two captive stopcocks for gas inlet and outlet and rectangular cell mount for positioning on a standard sample holder. The volume of the gas cell was small, and with 20 mm path length. Temperature of the gas cell was controlled by a Hoval temperature controller (Hartmann & Braun). The instrument was purged throughout the experiment with high purity nitrogen gas. For each spectrum 100 interferograms were collected at 4 cm^{-1} resolution, which took about 125 s.

The experiments using the FTIRS/DMFC combination were performed as follows: the cathode gas

outlet was connected to the inlet of the FTIR gas cell. During the measurements, the prototype DMFC was placed in an oven, and the temperature was kept constant at 150°C . The cathode was purged with 24.7 ml min^{-1} of humidified air (medical grade). The anode feed rate was always adjusted to $2.7\text{ liquid ml h}^{-1}$ methanol or water/methanol mixture using a syringe pump.

2.6. Online MS analysis

The details of the experimental setup and the procedure to analyse cathode products by using online mass spectrometry (MS) have already been reported elsewhere [16]. The cathode exhaust gas outlet was directly connected to the MS instead of the gas cell of FTIR as shown in Fig. 2, so that the products emanating from the cathode can be analysed conveniently. The procedure of online MS/DMFC experiment was similar to that of on-line FTIRS/DMFC experiment. The mass signals for methanol ($m/e = 31$) and carbon dioxide ($m/e = 44$) were monitored.

3. Results and discussion

3.1. Electrode structure optimization

Many efforts were made to optimize the FeTMPP electrode structure and to examine the effect of the methanol permeation across the membrane on the cathode performance for direct methanol PBI fuel cells. The FeTMPP cathode structures were optimized in terms of the composition of FeTMPP catalyst, PTFE and PBI polymer electrolyte in gas diffusion layers.

The effect of the PTFE content on the FeTMPP cathode performance is shown in Fig. 3. All of these electrodes were impregnated with $21\ \mu\text{l}$ of H_3PO_4 . It

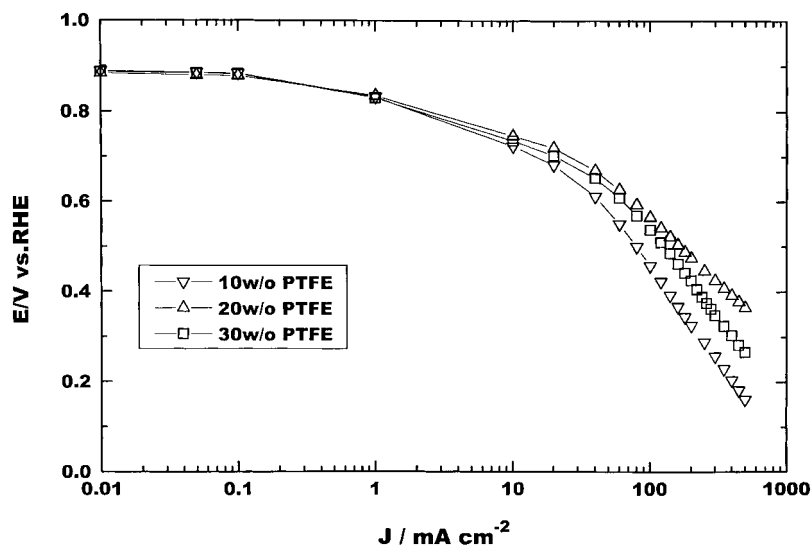


Fig. 3. Polarization curves of the FeTMPP cathodes. Cathode: 1.0 mg cm^{-2} FeTMPP (17.6 w/o FeTMPP on RB carbon) and different amount of PTFE. All the electrodes impregnated with $18\ \mu\text{l}$ $5\text{M H}_3\text{PO}_4$ solution. 1 atm O_2 humidified at room temperature. Anode was fed with 1 atm hydrogen humidified at room temperature. Cell operating temperature 150°C .

shows that the electrode with PTFE content of 20 w/o demonstrates the best electrode performance. The function of the PTFE in the electrode structure is believed as a binder for catalyst particles and a pore structure former. The gas transport resistance probably limited the electrode performance with the PTFE content of 10 w/o. In addition, a high PTFE content probably causes a higher catalytic layer resistance, which results in loss of the electrode performance.

Figure 4 shows a comparison of the performance of the cathodes with different FeTMPP catalyst loadings. It can be seen that the electrodes with 1.5 and 2.0 mg cm⁻² FeTMPP catalyst loading in the electrodes show good performances as compared to the electrode with 1.0 mg cm⁻² catalyst loading, especially at high current density. For the electrodes with 2.5 and 3.0 mg cm⁻² FeTMPP catalyst loadings, the cathode performance was almost the same as the others at low current density. However, the performance decreased significantly at high current density. The most probable reason for this is that the electrodes with high catalyst loading have a relatively thick catalytic layer, which results in increasing the ionic charge and gas transport resistances in the layer. Therefore, only the catalyst particles located near the interface between membrane and catalytic layer in the electrode contribute to the catalysis, whereas, those catalytic sites far from the interface do not contribute to reaction enhancement.

The effects of polymer impregnated into the structure of electrodes on cathode performance are shown in Fig. 5. It clearly shows that in cases of both impregnating PBI and Nafion polymer in the structure of the electrodes the cathode performances were improved significantly at high current density as compared to the electrode without impregnating polymer in the electrode. The function of impregnating polymer into the structure of the electrode im-

proves ion conductivity in the catalytic layer and reduces interfacial resistance between membrane and the catalytic layer. Note that for the electrode impregnated with Nafion[®] polymer did not perform as well as did the electrode impregnated with PBI polymer.

The molecular weight of FeTMPP is heavier than the atomic weight of Pt, hence if assuming that each FeTMPP generates one catalytic active site, the number of catalytic active sites in FeTMPP catalyst are much less compared to that of platinum black catalyst at the same weight loading. To increase the FeTMPP loading without increasing the electrode thickness too much (causing a large mass transport resistance), high loadings of FeTMPP catalyst on RB carbon were prepared. A higher FeTMPP loading on RB carbon was achieved by repeating the adsorption and heat treatment process. The highest FeTMPP loading catalyst was 36.9% FeTMPP on RB carbon which was obtained by repeating four times the adsorption and heat treatment process. Figure 6 shows a comparison of the cathode performance with different FeTMPP catalyst loading on RB carbon. The total FeTMPP loading for each electrode was the same. The results show that the catalysts with low FeTMPP loading, for example 18.4% FeTMPP chelate on RB carbon, had a better activity than those with a high FeTMPP loading catalysts, although the latter has a thinner electrode structure. This result indicates that the high FeTMPP chelate loading catalyst does not show the same specific catalytic activity as the low loading catalysts. The reason for this observation is not very clear now. According to a preliminary experiment [17], repeatedly treating the FeTMPP catalyst at high temperature may cause the molecular structure change, resulting in the deactivation of the catalyst.

The best cathode performance in H₂/O₂ and CH₃OH/O₂ PBI fuel cells gave a potential over 0.6 V

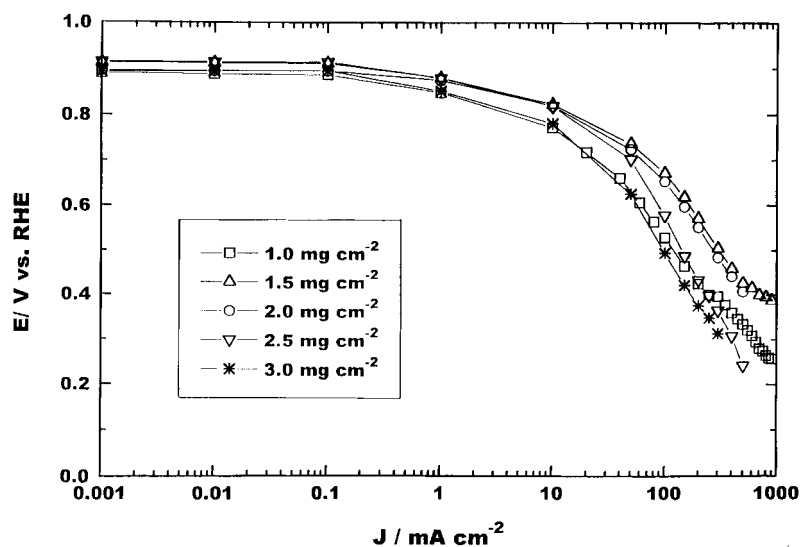


Fig. 4. Comparison of cathode performance with different FeTMPP loading (17.6 w/o FeTMPP on RB carbon) cathodes. Cathodes: various amount of the catalyst with 20 w/o PTFE and 15 w/o PBI (with 10 mol H₃PO₄ per PBI repeat unit). 1 atm O₂ humidified at room temperature. Anode fed with 1 atm H₂ humidified at room temperature. Cell operating temperature 150 °C.

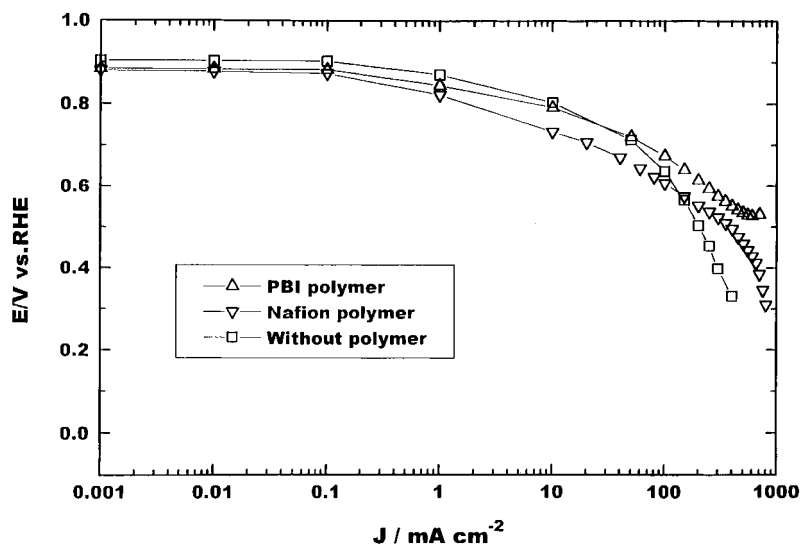


Fig. 5. The effect of impregnating polymer electrolyte into electrode structure on the FeTMPP cathode performance. Cathode: 1.5 mg cm^{-2} FeTMPP (17.6 w/o FeTMPP on RB carbon). 25 w/o PBI (with 1000% H_3PO_4) or 25 w/o Nafion[®] (5%) were impregnated in the surface of the electrodes. 1 atm O_2 humidified at room temperature. Anode fed with 1 atm H_2 , humidified at room temperature. Cell operating temperature 150°C .

vs RHE at the current density of 900 mA cm^{-2} , as shown in Fig. 7. The catalyst used was 17.6 wt % FeTMPP supported on RB carbon which was heat treated at 800°C in argon. The cathode performance was not affected adversely by switching hydrogen to methanol at the anode, thus a methanol tolerant behavior for the catalyst was demonstrated clearly.

3.2. Online FTIR

To investigate the effect of methanol permeation from the anode to the cathode on FeTMPP cathode performance, an online FTIRS/FC experiment was carried out. Figure 8 shows the FTIR spectra of the cathode exhaust gases at open circuit condition. When the anode was fed with pure methanol, the FTIR spectrum of the cathode exhaust gases clearly

shows the methanol signals centered at $\sim 2900 \text{ cm}^{-1}$ (ν_{CH_3}) and 1027 cm^{-1} ($\nu_{\text{C-O}}$) (see Fig. 8(a)). The downward peaks between $1750\text{--}1250 \text{ cm}^{-1}$ indicate the partial pressure of water decreases because of the dilute effect due to the methanol reaching the cathode. When the anode was fed with a mixture of methanol and water, the FTIR spectrum is similar to that of pure methanol (see Fig. 8(b)), but the peaks between $1750\text{--}1250 \text{ cm}^{-1}$ are upward, indicating that water is also reaching the cathode. However, in both cases, no visible peaks associated with CO_2 (2350 cm^{-1}) was observed. This FTIR experiment shows that the carbon supported FeTMPP catalyst does not have catalytic activity to the oxidation of methanol. Otherwise, the oxidation products of methanol, such as CO_2 , should be observed. This result agrees well with that of the elec-

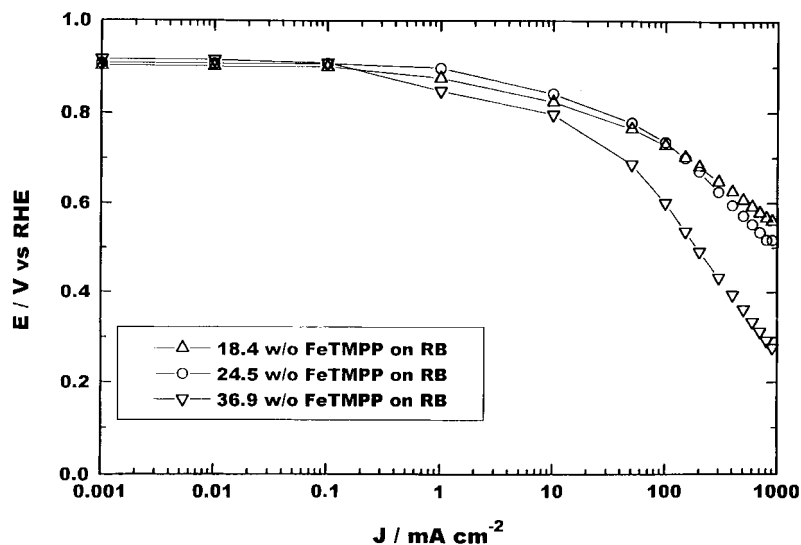


Fig. 6. Comparison of the catalysts with different FeTMPP loading on RB carbon. Cathodes: 2.0 mg cm^{-2} FeTMPP catalysts and 25 w/o PBI (with 1000% H_3PO_4), 1 atm O_2 humidified at room temperature. Anode fed with 1 atm H_2 humidified at room temperature. Cell operating temperature 150°C .

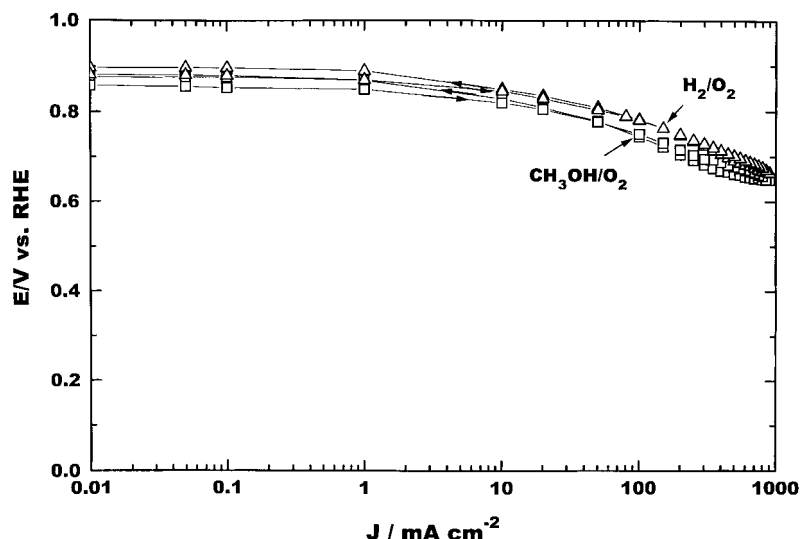


Fig. 7. Comparison of cathode performance with and without methanol crossover. Cathodes: 1.5 mg cm^{-2} FeTMPP (18.4 w/o FeTMPP on RB carbon and 25 w/o PBI (with 10 mol H_3PO_4 per PBI repeat unit), 1 atm O_2 humidified at room temperature. The anode fed with 1 atm H_2 humidified at room temperature or a mixture of water and methanol in a molar ratio of 2, respectively.

trochemical polarization measurement as described in Fig. 7.

3.3. Online MS

The experiment of combining multipurpose electrochemical mass spectrometry (MPEMS) and the prototype DMFC is also aimed to investigate the effect

of methanol permeation from the anode to the FeTMPP cathode. Figures 9 and 10 show the mass spectra of cathode gas from cathodes with Pt black and FeTMPP catalysts, respectively, at open circuit condition. The ion current for methanol ($m/e = 31$) and carbon dioxide ($m/e = 44$) were monitored before and after the anode was fed with a mixture of methanol and water. Figure 9(a) shows that when the

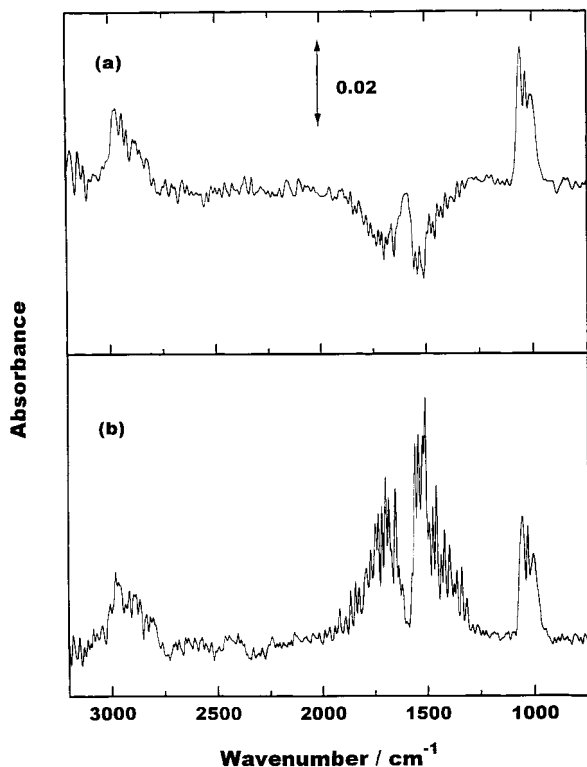


Fig. 8. Online FTIR spectra of the cathode gas outlet measured during the introduction of methanol at the anode, (a) pure methanol, (b) water/methanol molar ratio of 2. Electrolyte: PBI/TFA membrane doped with 6 mol H_3PO_4 /PBI repeat. Anode: fed with pure methanol or water/methanol mixture at 1 ml h^{-1} . Cathode: 2.2 mg cm^{-2} FeTMPP (18.4 w/o FeTMPP on RB carbon, 10 ml min^{-1} air. Cell temperature: 150°C .

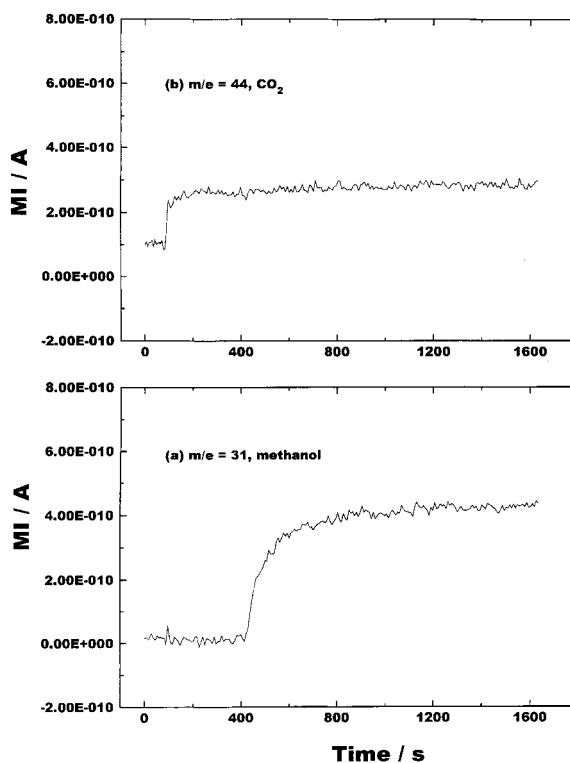


Fig. 9. Mass signals against time detected at Pt-black (4.0 mg cm^{-2} loading) cathode gas outlet. The anode was fed with 1:2 molar ratio of methanol to water. Operating temperature: 150°C ; anode feed: $2.7 \text{ liquid ml h}^{-1}$ methanol; cathode feed: 24.7 ml min^{-1} air; PEM: PBI doped with 5 mol H_3PO_4 per PBI repeat unit, 0.011 cm thick. (a) $m/e = 31$, methanol; (b) $m/e = 44$, CO_2 at cathode open circuit potential.

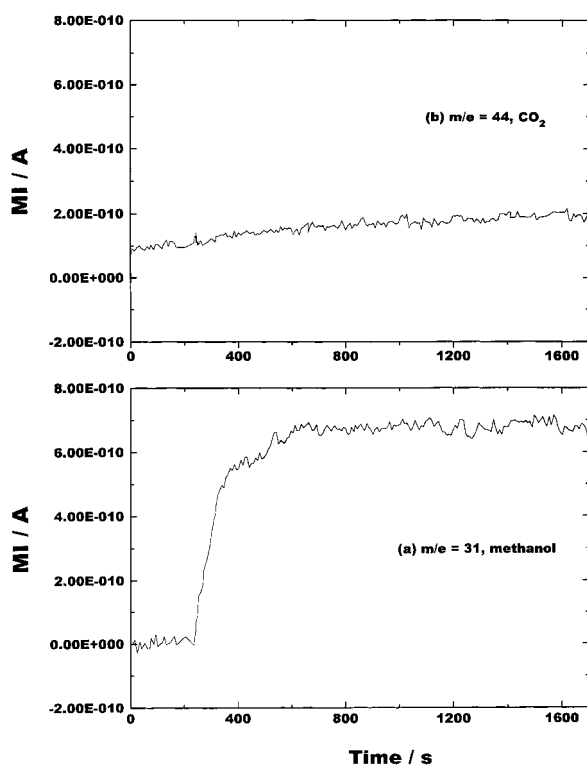


Fig. 10. Mass signals vs. time detected at carbon supported FeTMPP (1.5 mg cm^{-2} loading) cathode gas outlet. The anode was fed with 1:2 molar ratio of methanol to water. Operating temperature: 150°C ; anode feed: $2.7 \text{ liquid ml h}^{-1}$ methanol; cathode feed: 24.7 ml min^{-1} air; PEM: PBI doped with $5 \text{ mol H}_3\text{PO}_4/\text{PBI}$ repeat, 0.011 cm thick. (a) $m/e = 31$, methanol; (b) $m/e = 44$, CO_2 at cathode open circuit potential.

mixture of methanol and water with molar ratio of 1:2 was fed in the anode, methanol was oxidized completely into carbon dioxide at first. After a delay about 5 min, the concentration of methanol in the exhaust gases increased significantly, and then reached an equilibrium value that depended on the flow rate. However, the concentration of carbon dioxide in the exhaust gases increased significantly and it remained almost constant as shown in Fig. 9(b). This indicates that the amount of methanol oxidation catalysed by platinum is determined by the amount of active sites in catalyst and not on the amount of methanol present.

In contrast, when the mixture of methanol and water with molar ratio of 1:2 was fed to the anode, the concentration of methanol in the FeTMPP cathode exhaust gases increased significantly, and then reached an equilibrium values as shown in Fig. 10(a). Whereas, the concentration of carbon dioxide in the exhaust gases remained a constant low value as shown in Fig. 10(b). The $m/e = 44$ curve has a slope that is similar to that found in the case where the anode was not fed a mixture of methanol and water. This result demonstrates that the carbon supported FeTMPP catalyst is inactive to the oxidation of methanol, and is in excellent agreement with those in electrochemical polarization measurement and FTIR analysis.

4. Summary

A carbon-supported FeTMPP chelate heat treated at 800°C under argon atmosphere was used as catalysts of oxygen reduction in direct methanol PBI polymer electrolyte fuel cells. The best cathode performance reached over 0.6 V vs RHE at a current density of 900 mA cm^{-2} . The effects of methanol permeation from the anode to cathode on the performance of the cathode were examined using spectroscopic techniques, such as on line X-ray photoelectron spectroscopy (XPS), on line Fourier transform infrared (FTIR) spectroscopy and conventional polarization curve measurements under fuel cell operating condition. The results demonstrate that carbon supported FeTMPP chelate heat-treated at 800°C is a methanol tolerant and active catalyst for the oxygen reduction.

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