Methanol-tolerant electrocatalysts for oxygen reduction in a polymer electrolyte membrane fuel cell

S. GUPTA, D. TRYK, S. K. ZECEVIC, W. ALDRED, D. GUO, R. F. SAVINELL

Department of Chemical Engineering and the Ernest B. Yeager Center for Electrochemical Sciences, Case Western Reserve University, Cleveland, OH 44106-7217, USA

Heat-treated μ-oxo-iron(III) tetramethoxy phenyl porphyrin (Fe-TMPP)$_2$O and iron(III) tetramethoxy phenyl porphyrin (FeTMPP-Cl) as well as iron(III) octaethyl porphyrin (FeOEP-Cl) adsorbed on high-area carbons such as deashed and un-deashed RB carbon (Calgon) and Black Pearls-2000 (Cabot) have been found to exhibit stable and very high oxygen reduction rates. Experiments done over a period of 24 h showed no performance degradation. Measured performances were very similar to supported platinum (E-Tek), when tested in 85% H$_3$PO$_4$-equilibrated Nafion® 117 membrane at 125 °C and hydrated-Nafion® membrane at 60 °C in a minifuel cell. The macrocycle cathodes are insensitive to the presence of methanol whereas the platinum cathodes are very sensitive and show degradation in the oxygen reduction performance.

Keywords: oxygen reduction, fuel cell, Nafion®, solid polymer electrolyte, macrocycles, porphyrins

1. Introduction

One of the serious problems with the direct methanol–air fuel cell is that the polarization of the air cathode, which typically contains a platinum-based electrocatalyst, is adversely affected by the presence of methanol, which can diffuse through the polymer electrolyte membrane from the anode. The main adverse effects are: (i) a mixed-potential effect, in which methanol is oxidized essentially at a mass transport-limited rate at the cathode, and the methanol oxidation current simply opposes the oxygen reduction current and (ii) more severe poisoning effects. A possible approach is to use oxygen reduction electrocatalysts that are inactive with respect to methanol oxidation and whose activity for oxygen reduction is not adversely affected by the presence of methanol or its oxidation products. Heat-treated transition metal macrocycles adsorbed on high-area carbons have shown promise in this regard [1–3]. Two heat-treated iron macrocycles such as iron(III) tetramethoxy phenyl porphyrin and iron(III) octaethyl porphyrin adsorbed on high-area carbons have recently been found to exhibit very high oxygen reduction performance, being similar to the supported platinum electrocatalyst, when tested in phosphoric acid-equilibrated Nafion® 117 at 125 °C and hydrated-Nafion® 117 at 60 °C in a mini fuel cell. The results of these studies are given here.

2. Experimental details

The tetramethoxy phenyl porphyrin (H$_2$ TMPP) was prepared and purified following the procedure described by Adler *et al.* [4]. The μ-oxo form of the iron tetramethoxyphenyl porphyrin (FeTMPP)$_2$O was synthesized by the route described by Torrens *et al.* [5]. The unreacted H$_2$ TMPP was removed by column chromatography employing a benzene–chloroform mixture (1 : 1 v/v). The (Fe TMPP)$_2$O was then diluted using a benzene-methanol mixture (20 : 2 v/v) and subsequently filtered in a sintered glass funnel and evaporated to dryness. The crystals were finally dried under vacuum at 80 °C for 4 h.

Another sample of iron tetramethoxy phenyl porphyrin in the form of Fe(III)TMPP–Cl was obtained from Aldrich Chemical Company and was used without further purification. Iron octaethyl porphyrin Fe(III)OEP-Cl was also obtained from Aldrich Chemical Company and used as received. The macrocycles were adsorbed on various high-area carbons from their acetone solutions. The high-area carbons used in this study were as-received RB carbon (Calgon Corp., Pittsburgh, PA; BET area 1200 m^2 g^{-1}) and also de-ashed RB carbon (DRB), obtained from Electromedia Corp., Englewood, NJ, as well as Black Pearls 2000 (Cabot Corp., Billerica, MA, BET area 1675 m^2 g^{-1}). The catalysts were prepared by dissolving specified amounts of macrocycles in acetone, next mixing a specified amount of carbon black and agitating the mixture using a magnetic stirrer for 20 h and then filtering rapidly through a nuclepore polycarbonate membrane (1 μm pore size). The concentration of the macrocycle in the filtrate was measured spectrophotometrically and thus the amount of the macrocycle adsorbed on the high-area carbon was calculated. The catalyst loading is reported here as a weight percentage macrocycle of the total weight of carbon and macrocycle. The solid samples were then heat-treated in a horizontal tube furnace at 800 °C for

2 h under continuous flow of purified argon (Matheson, H.P. grade) and allowed to cool while still under flowing argon. The adsorption characteristics of these macrocycles on various carbons have been studied and will be reported in a separate paper [6].

Thin porous coating rotating disc electrodes were prepared by placing $\sim$10 mg of the catalyst/carbon mixture in a small beaker with distilled water ($\sim$20 ml) under ultrasonic agitation for about 5 min. Subsequently, a dilute suspension of a Teflon emulsion (du Pont T 30 B) was added to the dispersion to yield $\sim$10 wt % of Teflon in the final dry solid material. The mixture was filtered through a 1 μm Nucleopore membrane, kneaded with a spatula into a glass slide and about 1 mg, based on dry weight was applied into shallow disc cavity ($\sim$0.1 mm deep) of a pyrolytic graphite (PG) disc (area 0.28 cm^2) which was part of a rotating disc electrode (RDE) assembly [7]. The surface of this porous carbon coating was smoothed using a spatula so as to create a common plane with the front of the electrode assembly. Oxygen from the solution phase diffuses through the gas-filled channels within this layer to reach the wetted catalyst/carbon agglomerates. The electrolytes, 0.05 M H$_2$SO$_4$ (Ultrex) and 0.5 M HClO$_4$ (Optima) were saturated with purified argon or oxygen at 1 atm for cyclic voltammetry and oxygen reduction studies, respectively. Gold foil was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference with the potentials converted to reversible hydrogen electrode (RHE). The steady state disc currents were recorded from positive to negative potentials. The thin porous coating (TPC) RDE technique was used as a reliable method for quick prescreening of various high-area catalysts in dilute acid electrolytes. The catalysts were also examined with porous gas-diffusion electrode (GDE) technique using polymer electrolyte membrane minifuel cell.

The gas diffusion electrodes (GDE) were prepared as follows: A specified amount of the catalyst/C material (50 mg) was mixed in a glass beaker with $\sim$25 ml of distilled water and ultrasonically agitated until the catalyst particles dispersed in water. Subsequently, a dilute suspension of PTFE (ICI Americas, Fluon AD704, 2 mg ml^{-1}) was added to the slurry so that the Fluon content in the dry electrode was $\sim$20 wt % and agitated ultrasonically again for 5 min. This mixture was then filtered through a polycarbonate filter membrane (1 μm pore size). The resulting paste was shaped into a disc of 1.75 cm o.d. in a circular stainless steel die, first using hand pressure and subsequently employing a commercial unit at $\sim$712 × 10^4 Pa. The disc was then attached to a porous carbon layer (Spectrocarb 2050 carbon paper, 0.25 mm thick) by pressing at $\sim$222 × 10^4 Pa at room temperature, and then dried in flowing argon at 80 °C for 1 h. The electrode surface was treated with a Nafion® solution (5 wt % in alcohol–water mixture, Aldrich chemical Co.) so that the Nafion® content was 2–3 mg cm^{-2}. The electrodes were finally dried in flowing argon at 60 °C for 1 h in order to remove the alcoholic solvent from the electrode structure. The membrane electrode assembly was formed by hot-pressing a hydrogen anode (E-Tek Pt supported on Vulcan XC-72 carbon, 2 mg cm^{-2} loading) on one side of the H$_3$PO$_4$[8] or H$_2$O-equilibrated Nafion® 117 membrane, with the oxygen cathode on the other side, at 145 °C, first at a pressure of 44.5 × 10^4 Pa for 3 min and then at 890 × 10^4 Pa for 2 min.

Minifuel cell steady-state measurements were carried out using a PTFE assembly which included hydrogen-fed counter and reference electrodes (E-Tek Pt on XC-72 carbon). The single cell was incorporated in a test station with temperature controllers, gas humidification bubblers and flow meters. The polarization measurements were carried out galvanostatically, using the current interruption method to correct for ohmic drop [9]. The oxygen was pre-equilibrated with either distilled water or a 1 : 1 (v/v) water–methanol mixture.

3. Results

3.1. *Oxygen reduction on TPC electrodes*

Several heat-treated iron macrocycle catalysts were prepared in high-area form and examined for oxygen reduction performance both with and without methanol in dilute acid electrolyte. Heat-treated (FeTMPP)$_2$O, FeTMPP–Cl and FeOEP–Cl adsorbed on high-area carbons such as RB and Black Pearls were found to exhibit excellent electrocatalytic activity. Figures 1 and 2 show the oxygen reduction performance for the heat-treated (800 °C) samples of (FeTMPP)$_2$O/DRB (10 wt % of C) and FeOEP/DRB (14.6 wt %) in 0.05 M H$_2$SO$_4$ with and without methanol in the solution. It can be seen that methanol does not have any effect on the oxygen reduction performance with macrocycle catalysts, whereas the oxygen reduction is adversely effected by the presence of methanol with Pt as the electrocatalyst (Fig. 3).

To increase the amount of FeTMPP–Cl on the carbon in the heat-treated material, and thus possibly improve the oxygen reduction kinetics, further amounts of FeTMPP–Cl were reabsorbed on the already once heat-treated catalyst/carbon material. The resulting material was then reheat-treated at 800 °C for 2 h in an Ar atmosphere. The reabsorbed and reheat-treated catalyst material (24.2% w/w) showed better oxygen reduction performance as compared to the initially adsorbed and heat-treated material (12.3% w/w) (Fig. 4). However, further reloading and heat-treating of the macrocycle on carbon did not produce significant changes in the activity for oxygen reduction. Better oxygen reduction performance was also obtained with once-only maximally-loaded (19.75% w/w), heat-treated sample of FeTMPP–Cl on RB carbon as compared to the once-only lower-loaded, heat-treated sample (12.3% w/w). The increase in activity with more highly
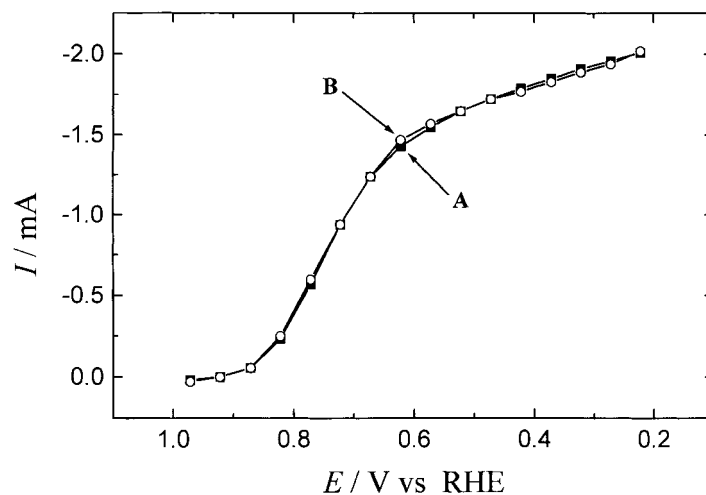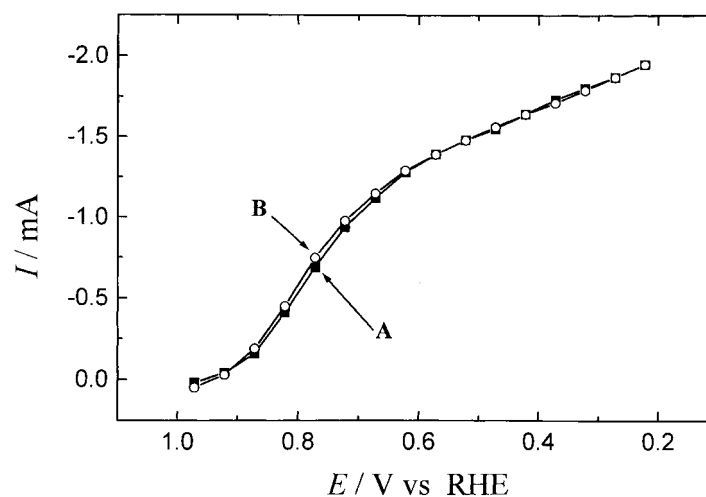
Fig. 1. Steady-state rotating disc currents for oxygen reduction (1 atm) on thin porous coating (TPC) electrodes in O_2-saturated 0.05 M H_2SO_4 at 25 °C; disc area (geometric) 0.28 cm^2; 2500 rpm; Teflon content 10%. Curve A(■): 10 wt% $(FeTMPP)_2O/DRB$ (800 °C H.T) with 1 M methanol in electrolyte gas sparging solution. Curve B(○): 10 wt % $(FeTMPP)_2O/DRB$ (800 °C H.T.) with no methanol in electrolyte gas sparging solution.

Fig. 2. Steady-state rotating disc currents for oxygen reduction (1 atm) on thin porous coating (TPC) electrodes in O_2-saturated 0.05 M H_2SO_4 at 25 °C; disc area (geometric) 0.28 cm^2; rotation rate 2500 rpm; Teflon content 10%. Curve A(■): 14.6 wt % FeOEP/DRB (800 °C H.T.) with 1 M methanol in electrolyte gas sparging solution. Curve B(○): 14.6 wt % FeOEP/DRB (800 °C H.T.) with no methanol in electrolyte gas sparging solution.
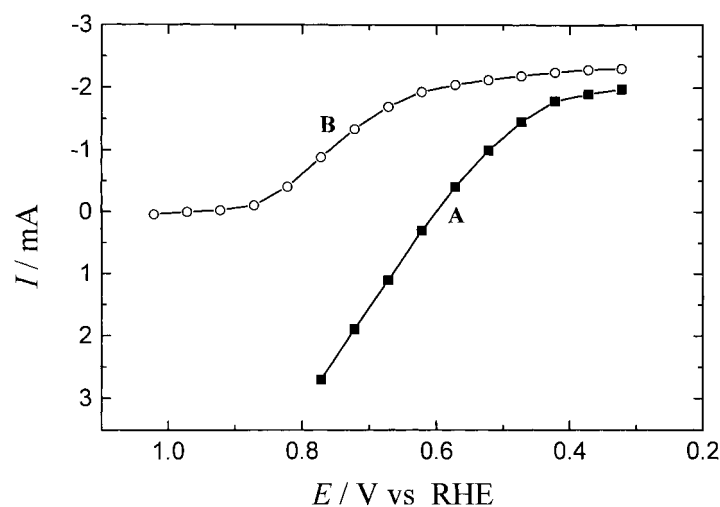

Fig. 3. Steady-state rotating disc currents for oxygen reduction (1 atm) on thin porous coating (TPC) electrodes in O_2-saturated 0.05 M H_2SO_4 at 25 °C; disc area (geometric) 0.28 cm^2; rotation rate 2500 rpm; Teflon content 10%. Curve A(■): 20 wt % Pt/XC-72 (E.S.C) with 1 M methanol in electrolyte gas sparging solution. Curve B(○): 20 wt % Pt/XC-72 (E.S.C.) with no methanol in electrolyte gas sparging solution.
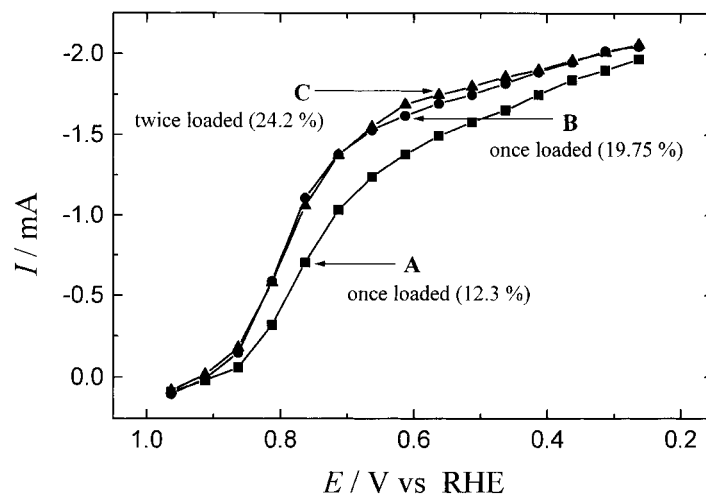
Fig. 4. Steady-state rotating disc currents for oxygen reduction (1 atm) on a thin porous coating (TPC) electrode containing FeTMPP–Cl on RB carbon (800 °C H.T.) at different loadings. Electrolyte 0.5 M HClO₄; disc area (geometric) 0.28 cm²; Teflon content 10%; rotation rate 2500 rpm.: (A) 12.3% FeTMPP adsorbed on RB (800 °C H.T.), (B) 19.75% FeTMPP adsorbed on RB (800 °C H.T.), and (C) 24.2% FeTMPP on RB, prepared using two sequential adsorption-heat treatment (800 °C) procedure.

loaded samples is probably due to the increased density of FeTMPP–Cl active sites on the carbon.

3.2. *Oxygen reduction on GDE electrodes*

3.2.1. *Evaluation of catalysts in 85% H_3PO_4-equilibrated Nafion® membrane electrode assembly.*
Figure 5 gives the oxygen reduction polarization behaviour for the heat-treated (800 °C) FeOEP on DRB carbon (3.0 mg cm⁻²) with and without RuO_2 in the electrode structure. Hydrated RuO_2 (18 mg) powder was mixed with the macrocycle/C (50 mg) for the fabrication of the GDE with RuO_2. Data for the E-Tek platinum electrode (0.75 mg Pt cm⁻² on XC-72 carbon) is also included for comparison. The performance of heat-treated FeOEP on de-ashed RB carbon, without the addition of RuO_2 was equal to that of supported Pt (E-Tek commercial electrode, 0.75 mg cm⁻² Pt). With the addition of RuO_2, the performance was superior

to that of supported Pt, particularly at higher current densities. For instance, at 250 mA cm⁻², the potential was ~800 mV compared to ~730 mV vs RHE for the E-Tek electrode. The increase in performance with RuO_2 may be due to the fact that RuO_2 is found to be a highly active catalyst for peroxide elimination [3]. Because of the absence of a clearly defined Tafel-linear region in the polarization curves, little can be said mechanistically about the oxygen reduction reaction. Studies with rotating ring disc electrodes with thin coatings of high-area heat-treated macrocycles on carbon blacks have shown that FeTMPP operates to a larger extent through a series pathway, in which oxygen is reduced first to peroxide and then the peroxide is partially eliminated either through decomposition or through further electrochemical reduction [10]. The limiting current for a four-electron reduction of O_2 to water in 0.05 M H_2SO_4 using an electrode with geometrical area of 0.28 cm² and
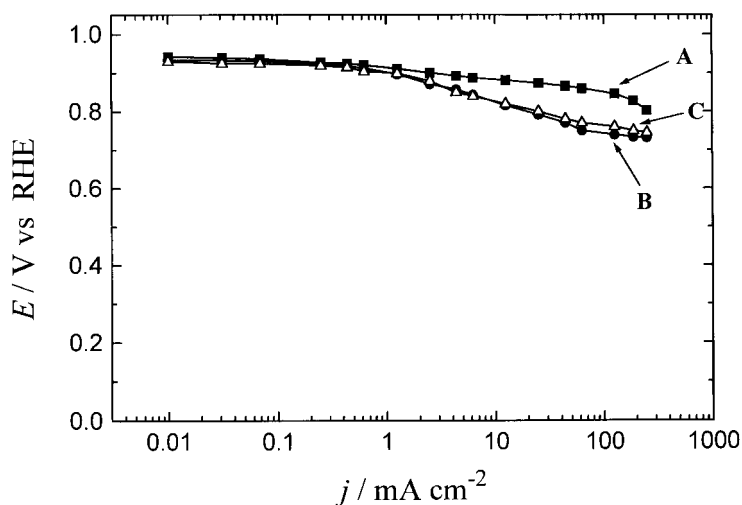

Fig. 5. Steady-state polarization curves for oxygen reduction (1 atm, H₂O-saturated) in a H₂/O₂ minifuel cell with H₃PO₄-equilibrated Nafion® 117 at 125 °C. The oxygen cathodes were catalysed with (A, ■) FeOEP/DRB (14.6 wt %, 800 °C H.T.) + RuO₂, (B, ●) Pt/XC-72 (E-Tek, 0.75 mg Pt cm⁻²) and (C, △) FeOEP/DRB (14.6 wt %, 800 H.T.).

available data for oxygen solubility and diffusion coefficient etc. [11] at 2500 rpm is calculated to be ~2.03 mA (see Figs 1–4). However, no limiting current plateau was obtained with TPC–RDE electrodes in acid electrolytes, which may be due to complications arising from the porous nature of the carbon.

Excellent oxygen reduction performance has been obtained with macrocycles on other carbon supports as well. Oxygen reduction performance in 85% H_3PO_4-equilibrated Nafion® at 125 °C obtained with heat-treated FeTMPP–Cl or FeOEP–Cl on high-area RB and Black Pearls exceeded that for supported Pt (E-Tek, 0.75 mg Pt cm^{-2}) by ~100 mV at 500 mA cm^{-2}, even without RuO_2 in the electrode structure. A typical polarization curve is shown in Fig. 6, which gives oxygen reduction polarization behaviour for heat-treated FeOEP–Cl on Black Pearls (5 mg cm^{-2}). This is the highest performance achieved for a macrocycle electrocatalyst without RuO_2 at CWRU. At 100 mA cm^{-2}, the potential was ~0.82 V vs RHE, which is a very good potential at this current density.

Figures 7 and 8 show the effect of methanol on the oxygen reduction behaviour in Nafion®/H_3PO_4 electrolyte at 125 °C with the heat-treated macrocycle catalyst (FeOEP on DRB carbon, ~3 mg cm^{-2}) and with the E-Tek platinum (0.75 mg Pt cm^{-2}) electrode, respectively. The macrocycle electrode showed good performance with oxygen (bubbled through H_2O at room temperature), which changed little when the oxygen was bubbled through pure methanol at room temperature. This small change is attributed to a decrease in the oxygen partial pressure when it is bubbled through methanol. The E-Tek platinum electrode showed good performance with room temperature hydrated oxygen but significantly poorer potentials at low and medium current densities when the oxygen was bubbled through a 10% methanol–water mixture, as expected for a mixed potential effect of methanol on oxygen reduction [3]. Increasing the methanol partial pressure further is expected to have a much more serious adverse effect on the

cathode potential, although this experiment was not carried out. However, the detrimental effect on performance with methanol is less with high platinum loadings (e.g. 3 mg cm^{-2}).

3.2.2. Evaluation of catalysts in hydrated Nafion® membrane electrode assembly. Initial polarization scans for oxygen reduction with E-Tek platinum electrodes and CWRU-fabricated FeTMPP–Cl/RB electrodes with hydrated Nafion membrane at 60 °C were poor and not reproducible. Considerable efforts were devoted to obtain better and reproducible oxygen reduction polarization behaviour with hydrated-Nafion® at 60 °C. Improvements resulted from several modifications in the experimental procedure and in the structure for the GDE. These include larger amounts of Nafion® in the electrode structure, higher temperature for electrode-to-membrane pressing, slow hydration of the membrane at low current densities and improvements in gas flow control as well as gas hydration.

Figure 9 shows a comparison of the oxygen reduction polarization measurements with an E-Tek platinum electrode (2 mg cm^{-2}) and heat-treated FeTMPP–Cl/RB electrodes with two different loadings (2.5 and 5 mg cm^{-2}). IR-free oxygen cathode potentials (vs RHE) were 0.76 V for the FeTMPP–Cl/RB electrode (2.5 mg FeTMPP–Cl cm^{-2}, 12.3%) and 0.79 V for the E-Tek Pt electrode (2 mg Pt cm^{-2}) at a current density of 250 mA cm^{-2}. However, the higher-loaded FeTMPP–Cl/RB sample (5 mg cm^{-2}, 24.2%) exhibited 0.82 V at 250 mA cm^{-2}, which is 30 mV more positive than the E-Tek electrode. The effect of methanol on the oxygen reduction performance at the cathode in a mini-fuel cell of hydrated Nafion® 117 at 60 °C for FeTMPP–Cl/RB (34.4 wt %, 800 °C HT) and Pt/XC-72 (E-Tek, 2 mg cm^{-2}) as the electrocatalysts is given in Figs 10 and 11, respectively. Again, the macrocycle cathodes are insensitive to the presence of methanol, whereas the Pt cathodes are sensitive and show degradation in the oxygen
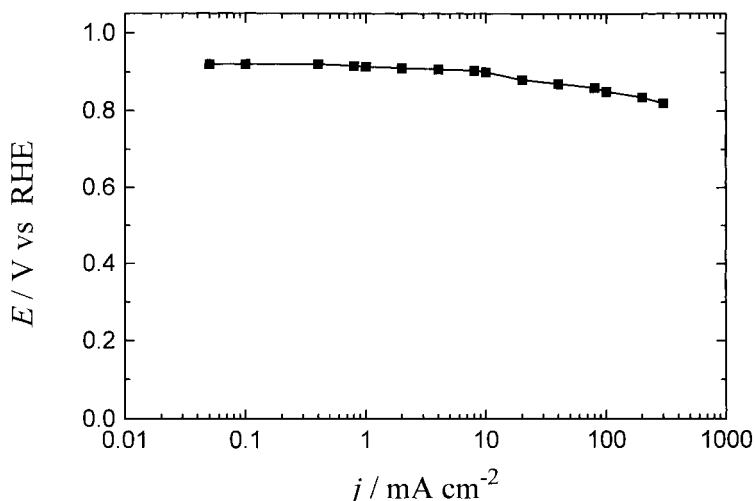

Fig. 6. Steady-state polarization curve for oxygen reduction with a GDE prepared from FeOEP on BP carbon (24.98 wt %, 800 °C H.T.) in a Nafion® 117/H_3PO_4 minifuel cell at 125 °C, using humidified oxygen at 1 atm.
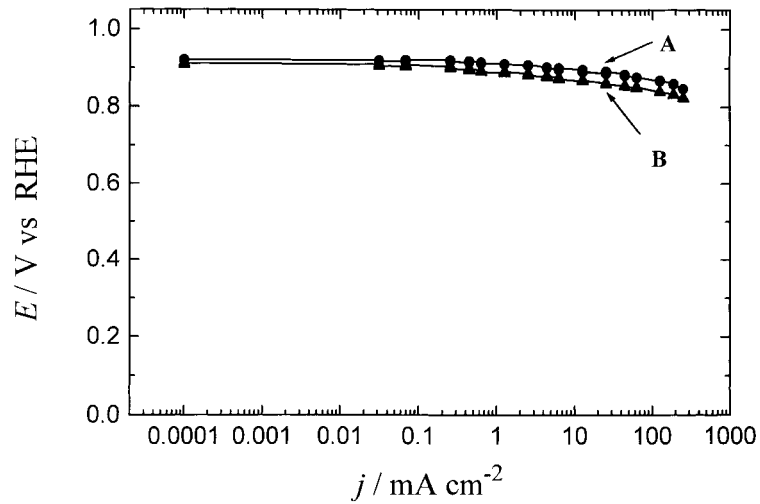
Fig. 7. Steady-state polarization curves for oxygen reduction with a GDE prepared from FeOEP on de-ashed RB carbon (14.6 wt %, 800 °C H.T.) in an H_2/O_2 minifuel cell with a H_3PO_4-equilibrated Nafion® 117 membrane at 125 °C, with the oxygen bubbled through (A, ●) H_2O and (B, ▲) through pure methanol.
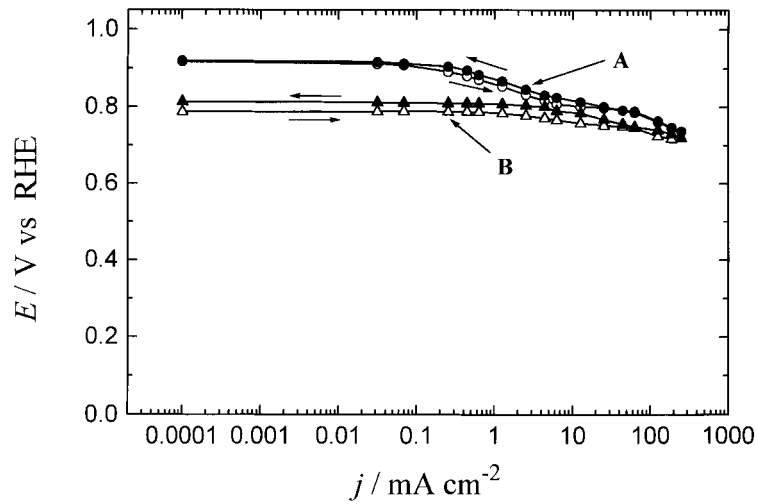

Fig. 8. Steady-state polarization curves for oxygen reduction with an E-Tek (platinum on XC-72 carbon, 0.75 mg cm^{-2}) electrode in an H_2/O_2 minifuel cell with a H_3PO_4-equilibrated Nafion® 117 membrane, at 125 °C with the oxygen bubbled through (A, ○, ●) H_2O and (B, △, ▲) through a 10% (v/v) mixture of CH_3OH with H_2O.
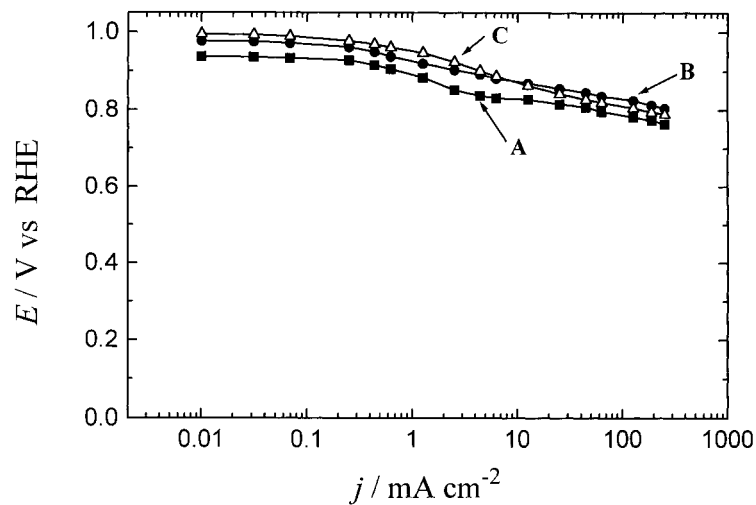

Fig. 9. Steady-state polarization curves for oxygen reduction (1 atm) on FeTMPP-Cl/RB electrode of different loadings, with a Pt/C (E-Tek) electrode for comparison in an H_2/O_2 minifuel cell with hydrated Nafion® 117 at 60 °C (A, ■) 12.3% FeTMPP–Cl on RB (800 °C H.T.); (B, ●) 24.2% FeTMPP–Cl on RB (800 °C H.T.); and (C, △) Pt/XC-72 (E-Tek, 2.0 mg Pt cm^{-2}).

reduction performance at current densities lower than $20 \, mA \, cm^{-2}$. The reproducibility of the oxygen reduction performance in hydrated Nafion® at 60 °C, however, needs further examination.

The short-term life testing of the FeTMPP-based porous oxygen cathodes was done over a period of 24 h in a minifuel cell with H_3PO_4-equilibrated Nafion® 117 membrane as the electrolyte at 125 °C. About eight polarization scans were recorded with current densities ranging from 0.05 to $400 \, mA \, cm^{-2}$. The cell was left at open circuit in between the recording of the polarization curves. The potentials that were recorded at a current density of $100 \, mA \, cm^{-2}$ (increasing current density) during each polarization scan showed no significant variation. The effect of an overnight cool-down followed by warm-up for the potential at $100 \, mA \, cm^{-2}$ was also studied. The measurement showed a decrease in the potential at this current density for the first scan following the warm up, but the subsequent measurements then reproduced the previous level. The first few scans also showed the effect of electrode break-in, as the electrolyte (85% H_3PO_4) slowly penetrated into the porous electrode structure.

Thus, stable, high oxygen reduction performance has been achieved for the heat-treated iron porphyrins adsorbed on high-area carbons in H_3PO_4-equilibrated Nafion® 117 at 125 °C and hydrated-Nafion® at 60 °C in a minifuel cell. The macrocycles were also found to be methanol-tolerant electrocatalysts.

4. Discussion

A thin porous Teflon-bonded layer (TPC) deposited onto a RDE represents a simulation of a gas diffusion electrode (GDE). The electrochemical performance of a GDE depends on the active surface area inside the pores, which in turn depends on the specific surface area of the carbon as well as the pore volume size and their distribution. Thus, it is not possible to distinguish the intrinsic catalytic activity of a catalyst adsorbed on high area carbon from the structural effects of the GDE. On the other hand, a TPC is very suitable for quick prescreening of various high-area catalysts, but on a qualitative basis only. Despite this limitation in use of TPC electrodes, the results obtained by this technique (Figs 1–3) clearly show that heat-treated $(FeTMPP)_2O/C$ and FeOEP/C are quite inactive with respect to methanol oxidation. Besides, they are methanol-tolerant catalysts for oxygen reduction in dilute sulfuric acid solutions, whereas Pt/C catalyst is not under the same experimental conditions. In addition, the Pt/C catalyst is so active with respect to methanol oxidation that the oxygen reduction is completely depressed at potentials more positive than 0.55 V vs RHE.

The TPC technique was also successfully used in determining the catalyst loading effects on their activity for oxygen reduction in dilute perchloric acid (0.5 M) solution. This technique, although qualitative in nature, has shown that the catalytic activities of pyrolyzed porphyrins were higher at higher catalyst loadings, irrespective of how the higher loading was accomplished, that is, in a single step or in two successive steps. The two-step reloading and reheat treatment technique was used to increase the catalyst surface coverage. Results shown in Fig. 4 indicate that a maximum coverage of the surface active sites was obtained after heat treatment of the sample containing ~20 wt% of FeTMPP–Cl on RB, because further reloading and heat-treating of the catalyst did not produce significant changes in the activity for oxygen reduction. These results are in agreement with those of Lalande et al. [12] who investigated loading effects of heat-treated Co-phthalocyanines (CoPc) on Vulcan XC-72 on oxygen reduction. At loadings larger than used in this work, Lalande et al. [12] observed a decrease in activity. The authors proposed this behaviour to be due to a multilayer adsorption of the macrocycle where the maximum activity corresponds to a full monolayer coverage of the CoPc on the carbon support.
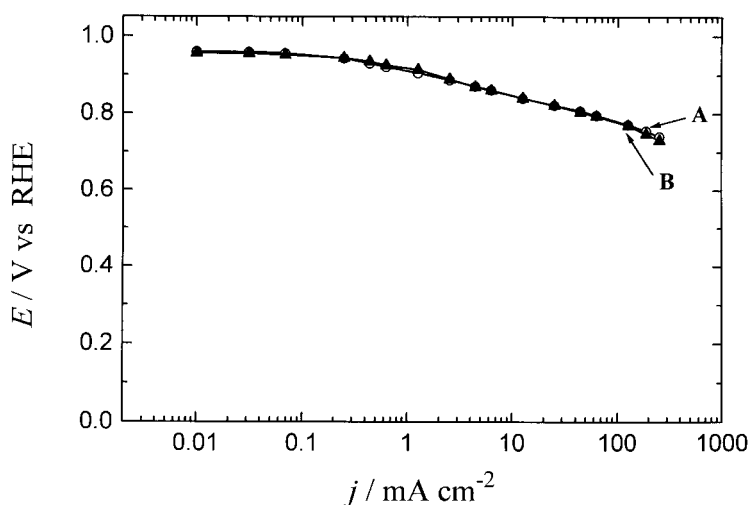

Fig. 10. Steady-state polarization curves for O_2 reduction (1 atm) with a FeTMPP-Cl/RB (34.4 wt %, 800 °C H.T.) electrode in an H_2/O_2 minifuel cell with hydrated Nafion® 117 at 60 °C, with the oxygen bubbled through (A, ○) H_2O and (B, ▲) through a mixture of 10% (v/v) CH_3OH with H_2O.
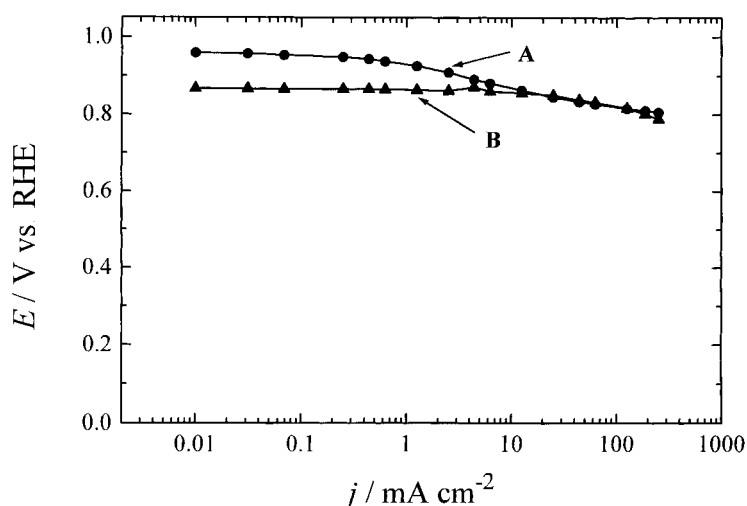
Fig. 11. Steady-state polarization curves for oxygen reduction (1 atm) with an E-Tek (Pt/XC-72, 2.0 mg Pt cm^{-2}) electrode in an H_2/O_2 minifuel cell with hydrated Nafion® 117 membrane at 60 °C, with the oxygen bubbled through (A, ●) H_2O and (B, ▲) through a mixture of 10% (v/v) CH_3OH with H_2O.

Although transition metal macrocycles are very interesting as catalysts for oxygen reduction, there are only a few papers dealing with GDE type electrodes for oxygen reduction catalysed with these complexes in acidic media. Many more papers in the literature are devoted to oxygen reduction on GDEs in alkaline solutions and to studies of the nature of the active sites in the heat-treated catalysts. For this latter purpose, various forms of the thin porous coating electrode immersed in electrolyte solutions were used. The operating conditions of these electrodes are different from those in fuel cells with solid polymer electrolytes, and therefore the results obtained may be different from those obtained under fuel cell operating conditions, as recently shown by Gouerec et al. [13, 14]. At any rate, the performance for oxygen reduction achieved in our work greatly exceeds that in previously published reports. Thus, typical potentials at a current density of 100 mA cm^{-2} reported in the literature fall in the range 0.6–0.7 V vs RHE for various heat-treated macrocycle catalysts: CoTMPP [13, 15], CoTAA [13], CoPC [16] and FeTMPP [15]. Our electrodes yielded approximately 100 mV more positive performance at the same current density. Particularly good performance was achieved with heat-treated FeOEP/BP in an 85% H_3PO_4-equilibrated Nafion® fuel cell (Fig.6).

In general, oxygen reduction performance obtained in the 85% H_3PO_4-equilibrated Nafion® fuel cell was better than that in the hydrated-Nafion® fuel cell. Furthermore, the reproducibility of the results was significantly better with the H_3PO_4-equilibrated membrane than with hydrated-Nafion®. One of the possible reasons for the better performance of the oxygen cathode in a fuel cell containing H_3PO_4-equilibrated Nafion® is the higher operating temperature (125 °C in H_3PO_4-equilibrated Nafion® fuel cell against 60 °C in hydrated-Nafion® fuel cell). Another possible reason for the better oxygen reduction performance in the cell with H_3PO_4-equilibrated Nafion®

is high ionic conductivity throughout the 0.1 mm thick electrode structure. High ionic conductivity within the electrode structure facilitates catalyst utilization. The conductivity of a proton-conductive polymer electrolyte such as Nafion® depends not only on the proton concentration in the polymer but also on the water content, that is, the humidity. In the case of a hydrated Nafion® membrane, which does not contain additional acid, water content is of even higher importance for the conductivity of the membrane. Moreover, a well-hydrated ionomer is a prerequisite not only for high electrolytic conductivity but also for fast interfacial oxygen reduction kinetics in polymer electrolyte fuel cells, as recently reported by Uribe et al. [17]. This high sensitivity of the membrane ionic conductivity on the water content may be responsible for the rather poor reproducibility of the results obtained in the case of hydrated Nafion® fuel cell cathodes. However, at present, it is difficult to identify all factors responsible for the poor reproducibility of the oxygen performance because of the rather complex structure of the GDE (determined by a number of parameters) and its fabrication procedure. Thus, the overall performance of a fuel cell oxygen cathode depends on the quality/type of high area carbon (surface area, porosity, particle size and shape, hydrophobicity), loading of the catalyst, PTFE binder and solid polymer, hot-pressing parameters (pressure, temperature, time), backing material, polymer electrolyte hydration, gas feed temperature, humidity, flow rates, etc. Although significant progress has been made thus far, further work on the electrode structure is needed in order to improve the reproducibility of oxygen cathode performance to a satisfactory level.

The reproducibility problem, as already mentioned, was considerably less pronounced when the Nafion® membrane contained phosphoric acid, but such a membrane cannot be used in a fuel cell for long term application because of the very poor performance of the hydrogen gas anode with this electrolyte. The

reasons for this are not quite clear at present. However, regardless of the poor reproducibility of the results for the oxygen gas cathode in fuel cells with hydrated Nafion®, the present work has clearly shown that heat-treated FeTMPP/C and FeOEP/C are highly active catalysts for oxygen reduction. Their catalytic activities are comparable to that of pure platinum, which at present is considered to be the best catalyst for oxygen reduction. In some cases, the catalytic activity of these macrocycles exceed that for supported Pt, especially in the presence of RuO_2 in the electrode structure, which was found to be a highly active catalyst for peroxide decomposition [3]. The performance of an oxygen cathode containing heat-treated FeTMPP/C can also be improved by incorporating TiO_2 in the electrode structure, as recently reported by Wijnoltz [18], who observed that the TiO_2 reduces the amount of peroxide formed during oxygen reduction by a factor of ten. Fast elimination of the peroxide from the electrode structure is very important, not only for good E/j polarization characteristics but also for long-term operation performance. The catalytic activity of heat-treated macrocycles was generally found to decrease with time of operation at a rate which depends on several parameters such as, for example, heat-treatment temperature, type and loading of macrocycle, type of supporting carbon etc. This problem, however, has not been systematically investigated, most probably because of the rather time-consuming character of the experiments, but there is a general belief that the instability of the macrocycle catalysts is caused by aggressive attack of H_2O_2 as well as leaching out of the metal from the electrode. To stabilize the catalyst, H_2O_2 should be rapidly eliminated from the electrode structure, and this is the reason why RuO_2 and TiO_2 were used as co-catalysts in our work and in that of [18]. The polymer electrolyte may also impede the loss of metal from the electrode.

In addition to the high catalytic activity for oxygen reduction, it has been shown in this work that heat-treated FeTMPP/C and FeOEP/C are essentially completely methanol-tolerant. This was shown by using both TPC and GDE types of electrodes. In contrast to this, oxygen reduction catalysed with Pt was found to be highly sensitive to the presence of methanol. This is partially because of the high catalytic activity of the Pt catalyst for methanol oxidation. It is interesting, however, that this adverse effect of methanol on the oxygen reduction performance for Pt was smaller in GDE-type electrode than in TPC electrodes. In particular, at current densities larger than $10 \, mA \, cm^{-2}$, the effect of methanol on the GDE oxygen reduction polarization curve is insignificant. Possible reasons for this apparent difference in methanol effects on oxygen reduction catalysed with Pt on TPC and GDE electrodes could be in different operating temperatures in the two experiments. Furthermore, this difference in methanol effects can also be due to different electrode environments. In the case of TPC electrode the reaction takes place at the Pt/aqueous electrolyte interface, whereas in a GDE

the reaction occurs at a Pt/Nafion® interface. It is very likely that the kinetics of methanol oxidation on Pt is different at these different interfaces. However, the most important reason for the observed difference in behaviour is probably that, in the GDE, oxygen mass transport is intrinsically highly efficient, occurring largely through the gas phase, whereas, in the TPC–RDE experiment, the oxygen transport is entirely via the liquid electrolyte phase. Thus, the oxygen reduction current density in the case of the GDE is much larger, and thus the relative importance of the anodic methanol oxidation current is much less.

5. Conclusions

The following conclusions may be drawn from the experimental results:

(i) The heat-treated porphyrins FeTMPP–Cl and FeOEP–Cl adsorbed on high area carbon have very high catalytic activities for oxygen reduction in a H_2–O_2 fuel cell with a Nafion® membrane. The catalytic activities are very similar to that of supported platinum.

(ii) The macrocycle cathodes are insensitive to the presence of methanol, in contrast to platinum cathodes, which are sensitive and show worse performance at current densities smaller than $10 \, mA \, cm^{-2}$.

(iii) The reproducibility of the results with the hydrated Nafion® fuel cell is relatively poor and this must be improved in future work.

References

[1] R. Holze, I. Vogel and W. Vielstich, *J. Electroanal. Chem.* **210** (1986) 277.
[2] B. Bittins-Cattaneo, S. Wasmus, B. Lopez-Mishima and W. Vielstich, *J. Appl. Electrochem.* **23** (1993) 625.
[3] D. A. Tryk, S. L. Gupta, W. H. Aldred and E. B. Yeager, Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage(III), The Electrochemical Society, Pennington, NJ (1994), p. 294.
[4] A. D. Adler, F. R. Longo and J. D. Finaselli, *J. Org. Chem.* **32** (1967) 476.
[5] M. A. Torrens, D. K. Straubanel and L. M. Epstein, *J. Amer. Chem. Soc.* **94** (1972) 4160.
[6] S. Gupta, D. Tryk, G. Zheng and R. F. Savinell, to be published.
[7] A. A. Tanaka, C. Fierro, D. Scherson and E. B. Yeager, *J. Phys. Chem.* **91** (1987) 3799.
[8] R. Savinell, E. Yeager, D. Tryk, U. Landau, J. Wainright, D. Weng, K. Lux, M. Litt and C. Rogers, *J. Electrochem. Soc.* **141** (1994) L46.
[9] S. Gupta, D. Tryk, I. Bae, W. Aldred and E. Yeager, *J. Appl. Electrochem.* **19** (1989) 19.
[10] A. A Tanaka, Ph.D. thesis, Case Western Reserve University, Cleveland, OH (1985).

[11] J. H. Zagal-Moya, Ph.D. thesis, Case Western Reserve University, Cleveland, OH (1978).
[12] G. Lalande, G. Tamizhmani, R. Cote, L. Dignard-Bailey, M.L. Trudeau, R. Schultz, D. Guay and J.P. Dodelet, *J. Electrochem. Soc.* **142** (1995) 1163.
[13] A. Biloul, P. Gouerec, M. Savy, G. Scarbeck, S. Besse, J. Riga, *J. Appl. Electrochem.* **26** (1996) 1139.
[14] P. Gouerec, A. Biloul, O. Contamin, G. Scarbeck, M. Savy, J.M. Barbe and R. Guilard, *J. Electroanal. Chem.* **398** (1995) 67.
[15] G. Faubert, G. Lalande, R. Cote, D. Guay, J. P. Dodolet, L.T. Weng, P. Bertrand and G. Denes, *Electrochim. Acta* **41** (1996) 1689.
[16] G. Tamizhmani, J. P. Dodelet, D. Guay, G. Lalande, and G. A. Capuano, *J. Electrochem. Soc.* **141** (1994) 41.
[17] F. A. Uribe, T. E. Springer and S. Gottesfeld, *ibid.* **139** (1992) 765.
[18] A. L. Wijnoltz, Ph.D. thesis, Thechnische Universiteit, Eindhoven (1995).