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Direct methanol alkaline fuel cells with catalysed anion exchange membrane electrodes

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Abstract

Membrane electrodes prepared by chemical deposition of platinum directly onto the anion exchange membrane electrolyte were tested in direct methanol alkaline fuel cells. Data on the cell voltage against current density performance and anode potentials are reported. The relatively low fuel cell performance was probably due to the low active surface area of Pt deposits on the membrane comparing to other membrane electrode assembly (MEA) fabrication methods. However, the catalysed membrane electrode showed good performance for oxygen reduction. A reduction in cell internal resistance was also obtained for the catalysed membrane electrode. By combining the catalysed membrane electrodes with a catalysed mesh, maximum current density of 98 mA cm^{-2} and peak power density of 18 mW cm^{-2} were achieved.

1. Introduction

The direct methanol fuel cell (DMFC) is one of the most promising alternative power sources due to ease of use of a liquid fuel, which is more convenient to store and refuel. Proton conducting polymer membranes are normally used as polymer electrolyte in DMFCs. However, poisoning of the anode during methanol oxidation and the methanol crossover limit the performance of DMFCs. Using an alkaline environment offers a potential solution to these problems [1]. Studies on developing alkaline anion exchange membranes for applications in low temperature portable DMFCs [2, 3] have been carried out. Ogumi et al. [4] investigated the feasibility of using OH form anion exchange membrane on fuel cells using ethylene glycol as the fuel. The results suggested the potential application of anion exchange membranes in direct alcohol fuel cells. Anion-exchange membranes for hydrazine fuel cell electrolyte were studied by Yamada et al. [5]. Fuel cells using borohydrides as the fuel have also been investigated in alkaline systems with anion exchange membranes [6, 7]. The high hydrogen content in borohydrides, for example, 10.6 wt % hydrogen in $NaBH_4$, makes borohydrides very attractive fuels [8].

Chemical deposition of platinum onto solid polymer electrolyte (SPE) membrane (Nafion®) was first developed by Takenaka et al. [9]. Applications of the electrodes prepared by this method have been reported for water electrolysis [10–12] and electrooxidation of methanol [13] and ethanol [14]. The advantages of using this method include an increase of adhesive strength of the catalyst to the membrane, a decrease of contact resistance in the catalyst–membrane interface and a decrease of resistance within the catalyst layer. Kita et al. [13] studied SPE membrane electrodes, prepared by chemical deposition, for electrocatalysis on methanol oxidation using both cation-exchange (Nafion®) and anion-exchange membranes (Asahi Kasei A201). They found that the electrochemically active zone was located around the Pt–SPE interface just inside membrane. Compared to a platinized Pt electrode, the Pt–SPE electrode retained a high activity over a long time of operation. From these studies, it appears that the metal-bonded SPE electrode, obtained by chemical deposition, has a high catalytic active area and thus, could be promising for the use in fuel cells.

In addition, the compact configuration of catalysed membrane electrodes could benefit fuel cell applications for microelectronics which require a miniaturized design and high efficiency.

In this study, electrochemical and fuel cell tests were conducted to examine the activity of the catalysed membranes. Results were compared with those obtained with other membrane electrode assembly (MEA) fabrication methods.

2. Experimental details

An anion exchange membrane (Morgane®-ADP, Solvay SA) was used for fuel cell applications. However, a limitation with this approach is that using an anion exchange polymer there is no ionmer solution such as Nafion® available for binding catalyst. Hence, a PTFE suspension was used as a binder in the catalyst layer, for example, the carbon supported catalyst. Although PTFE is a good adhesive, it is also an insulator and hence the presence of PTFE in the catalyst layer could reduce the active area of the catalyst and increase the electric resistance of the catalyst layer. Eliminating PTFE from the catalyst layer could be a way of improving the fuel cell performance.

2.1. *MEA preparation*

A flow cell, shown in Figure 1, was used to deposit Pt on the ADP membrane. 250 ml each of H_2PtCl_6 and $NaBH_4$ solutions were circulated, on opposite sides of the membrane, simultaneously using two peristaltic pumps (Watson Marlow, UK). In this procedure, platinum was deposited on the side of the membrane where platinum salt was circulated. After deposition of Pt on the first side, the membrane was removed, rinsed and turned to expose the other side of the membrane to the Pt salt to deposit platinum on the second side. H_2PtCl_6 solution concentrations used were as low as 0.2 mM and 5–10 mM $NaBH_4$ solutions were the reducing agents. The temperature for deposition was 45–48 °C.

MEAs, made with catalysed ADP membranes were prepared by hot pressing the catalysed membrane and cathode gas diffusion layer together at 100 °C, 120 kg cm^{-2} for 3 min. The properties of ADP membrane are listed in Table 1.

A non-teflonized Toray 90 carbon paper was applied as the anode current collector. The cathode gas diffusion layer consisted of a layer of 10 wt % teflonized Ketjen black 300 carbon powder (Akzo Nobel, UK) painted on top of 20 wt % teflonized Toray 90 carbon paper (thickness 0.26 mm) (Etek, USA). Cyclohexane was used as the solvent for preparing the ink for gas diffusion layer. The mixture of carbon black, PTFE suspension (33 wt %, ICI) and cyclohexane was agitated in ultrasonic bath for 3 h before painting.

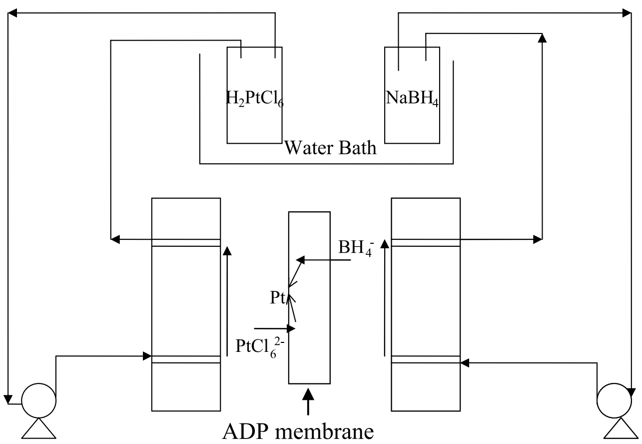

Fig. 1. Schematic diagram of chemical deposition of Pt on ADP membrane using a flow cell (Takenake method).

Table 1. Basic properties of the ADP membrane

Membrane	ADP
Material	Cross-linked fluorinated polymer
Exchange group	Quaternary ammonium
Thickness/μm (fully humidified)	150–160
Resistance (in 0.6 M NaCl)/Ω cm^2	1.5–4.5
Resistance (in 1 M NaOH)/Ω	0.5
Membrane operational temperature/°C	55
Working pH	0–10

2.2. *Fuel cell tests*

The fuel cell consisted of the MEA sandwiched between two stainless steel blocks with 2 mm parallel channels acting as flow fields for methanol and air. The cross section area of the cell was 4.9 cm^2. The fuel used in this study was 2 M methanol in 1 M NaOH, at an operating temperature of 60 °C unless otherwise specified. A peristaltic pump (Watson Marlow, UK) was used to supply methanol to the cell. A water bath (Cole Parmer, USA) and home-made temperature controller were used to maintain the temperature at 60 °C. Before each test, a short circuit current was loaded for few minutes to activate the cell. The anode potential was measured by a mercury/mercury oxide (MMO) reference electrode and the cathode potential was obtained by subtracted the anode potential from the cell voltage. Data were taken after 24 h of cell conditioning. A Kenwood PE-151 electronic load was used to collect cell polarization data. All electrode potentials are referenced to the standard hydrogen electrode (SHE).

The internal resistance (R_{cell}) was measured by high frequency a.c. impedance at open circuit. Pt loadings on the electrodes referred to the geometric area of the electrodes. To eliminate the influence of ohmic resistances on the cell voltage and the cathode potential and understand better the catalyst activity and reactant mass transport, cell polarisation curves were *iR* corrected.

3. Results and discussion

3.1. *Comparison of methanol oxidation on the platinized mesh, carbon supported Pt catalyst and catalysed membrane electrodes*

The specific surface active areas of three different types of catalysts: platinized Ti mesh, carbon supported Pt catalyst and catalysed ADP membrane were obtained by determining the charge associated with hydrogen desorption on the electrode surface, from cyclic voltammograms in 0.5 M NaOH solution. The estimated active areas are based on 210 μC cm^{-2} for hydrogen adsorbed, and are listed in Table 2.

Table 2. Estimated active surface area of the Pt catalyst on various materials in 1 M NaOH at 60 °C

Materials	Active surface area/ $cm^2\ mg^{-1}$
Platinized Ti mesh with Pt 0.5 mg cm^{-2}	464.8
Carbon supported Pt with Pt 1.0 mg cm^{-2}	286.5
Chemical deposition of Pt on ADP, 1.2 mg cm^{-2}	102.1

It is clear that the platinized mesh had the highest active surface area, and the chemically deposited Pt on the ADP membrane showed the lowest active surface area, probably due to the compact structure of Pt particles on and within the membrane.

Figure 2 compares the voltammograms of methanol oxidation for the three catalytic materials. The methanol oxidation current densities on the platinized mesh was significantly higher than those for the other two catalytic materials. At a potential about 2 mV vs SHE, the current densities, from the linear sweeps were 38.70, 140.85 and 392.90 mA cm^{-2} for the Pt deposited ADP, carbon supported Pt and platinized mesh, respectively. This shows that catalytic activity is highest on the platinized Ti mesh, and lowest on the Pt deposit on the membrane.

3.2. *Fuel cell tests on the MEA using catalysed ADP membranes*

The cell was tested with the catalysed ADP membrane with Pt loadings of 0.93 mg cm^{-2} on the anode and 0.55 mg cm^{-2} on the cathode. The cell polarization curves are shown in Figure 3. A peak power density of 5.54 mW cm^{-2} was achieved at 60 °C. At the peak power density, the current density was 32.6 mA cm^{-2} and the cell voltage was 0.17 V. The open circuit potentials for the anode and cathode were 0.43 and 0.22 V. The standard electrode potentials for the anode and cathode are −0.81 and 0.402 V, respectively. The reasons for the difference between experiment and thermodynamic values are the potential losses due to activation potential. As shown in Figure 3(b) the anode contributed the major part to the cell polarization. The test was repeated after 22 h to exam the stability of the electrodes.

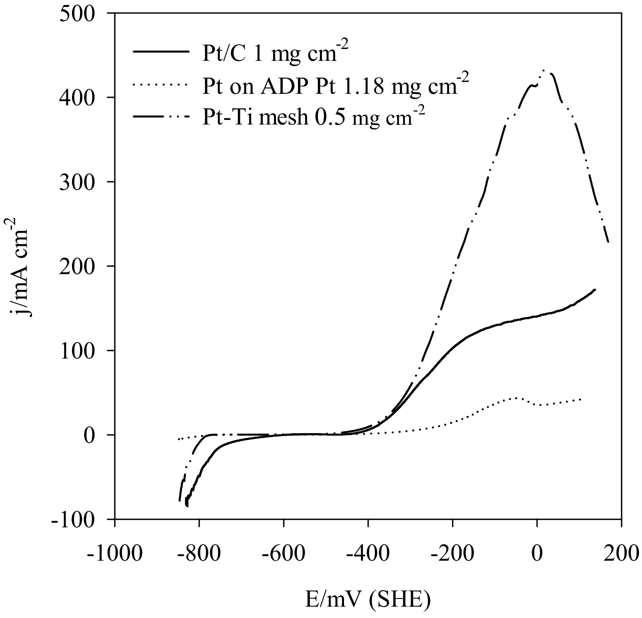

Fig. 2. Linear sweeps for methanol oxidation on carbon supported Pt catalyst and catalysed ADP membrane. Solution: 2 M methanol in 0.5 M NaOH, $T = 60$ °C.

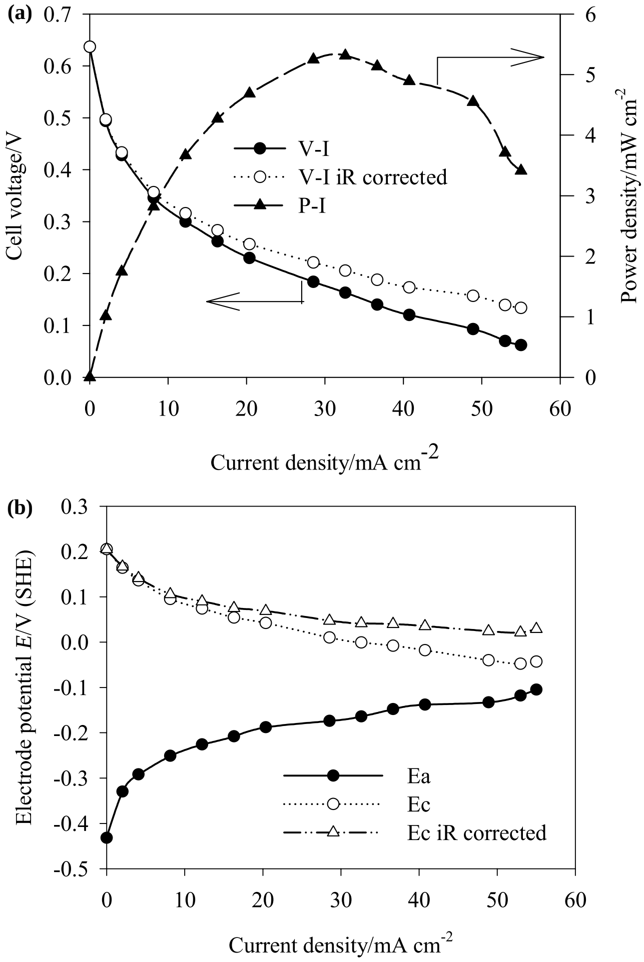

Fig. 3. Fuel cell tests on catalysed ADP membranes. Anode: Pt 0.933 mg cm^{-2} chemical deposition with non teflonised Toray 90. Cathode: 0.526 mg cm^{-2} chemical deposition, gas diffusion layer: 2 mg cm^{-2} Ketjen Black with 10 wt % PTFE on 20% teflonized Toray 90. Cell tests at 60 °C, air pressure 1 bar, 2 M MeOH, 1 M NaOH with methanol flow rate of 60.6 ml min^{-1}.

Figure 4 shows the cell and anode polarisation curves produced at increased times of cell operation. Both the cell and anode performance decreased with time. The cell voltage was 40 mV lower for the test at 42 h compared to that at 20 h at a current density of about 40 mA cm^{-2}. Meanwhile, the anode potential, at 42 h, shifted to a value 34 mV more positive to that after 20 h, indicating that the deterioration in the cell performance was mainly due to the deterioration in

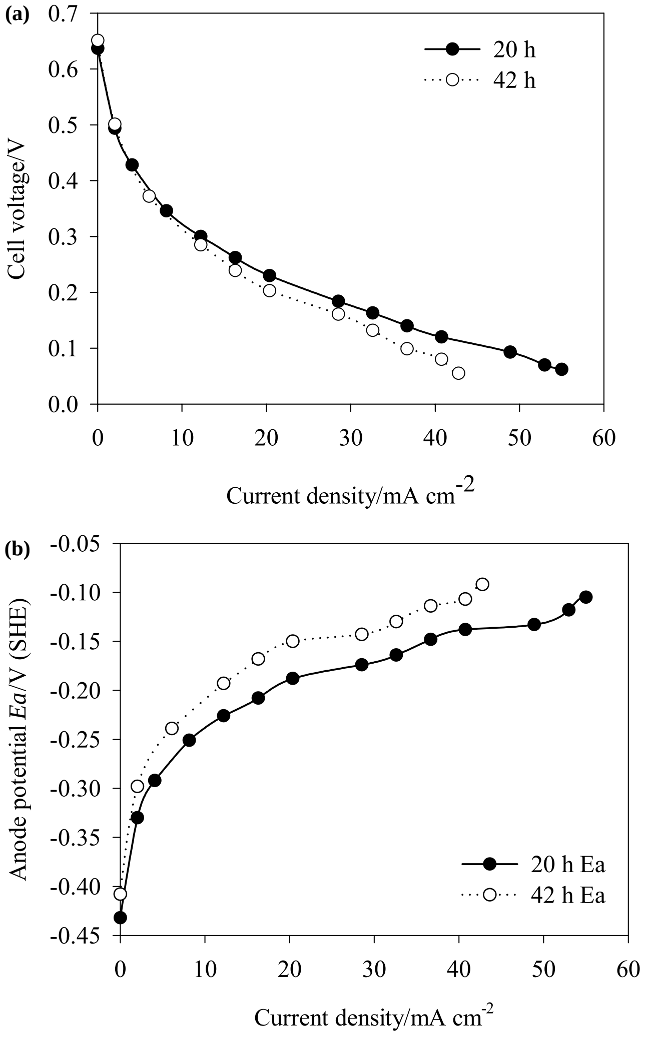

Fig. 4. Fuel cell tests on the catalysed ADP membrane at 20 and 42 h Anode: Pt 0.933 mg cm^{-2} chemical deposition with non teflonised Toray 90. Cathode: 0.526 mg cm^{-2} chemical deposition, gas diffusion layer: 2 mg cm^{-2} Ketjen Black with 10 wt % PTFE on 20% teflonized Toray 90. Cell tests at 60 °C, air pressure 1 bar, 2 M MeOH, 1 M NaOH with methanol flow rate of 60.6 ml min^{-1}.

the anode performance. This lack of stability of the anode is probably due to poisoning of the anode and carbonation of the electrolyte. In the oxidation of methanol, CO_2 gas was released, which being vigorously liberated from the liquid phase contributes to a slow carbonation of the electrolyte. Our previous studies have shown the deteriorated effect of carbonate and bicarbonate on methanol oxidation activity [15].

3.3. *Comparison of fuel cell performances using MEAs fabricated with the platinized mesh, carbon supported Pt catalyst and catalysed membrane*

3.3.1. *Fuel cell resistance and electrode potentials*

Fuel cell resistances were determined by high frequency impedance spectroscopy at open circuit, and listed in Table 3. As shown in Table 3, the cell resistance was lower with MEAs prepared using Pt catalysed ADP membranes. This was probably due to a lower contact resistance because of the improved electric contact between the conducting platinum layer on and within the membrane. Hence, the entire cell resistance was lower for MEAs containing catalysed membranes.

Table 3. Fuel cell resistances with various MEA fabrications

Cell fabrication	Cell resistance/Ω
Hot-pressed carbon supported Pt gas-diffusion electrodes	0.36–0.52
Platinized mesh as anode and normal gas-diffusion cathode	0.42
Catalysed membranes	0.27
Platinized mesh and catalysed membranes	0.21
Hot-pressed carbon supported Pt gas diffusion electrodes with H^+ form Nafion® membranes	0.05

3.3.2. *Fuel cell performances*

Fuel cell performances for the cell with various MEA configurations are compared in Figure 5. With similar Pt loading, on the anode about 1 mg cm^{-2}, the

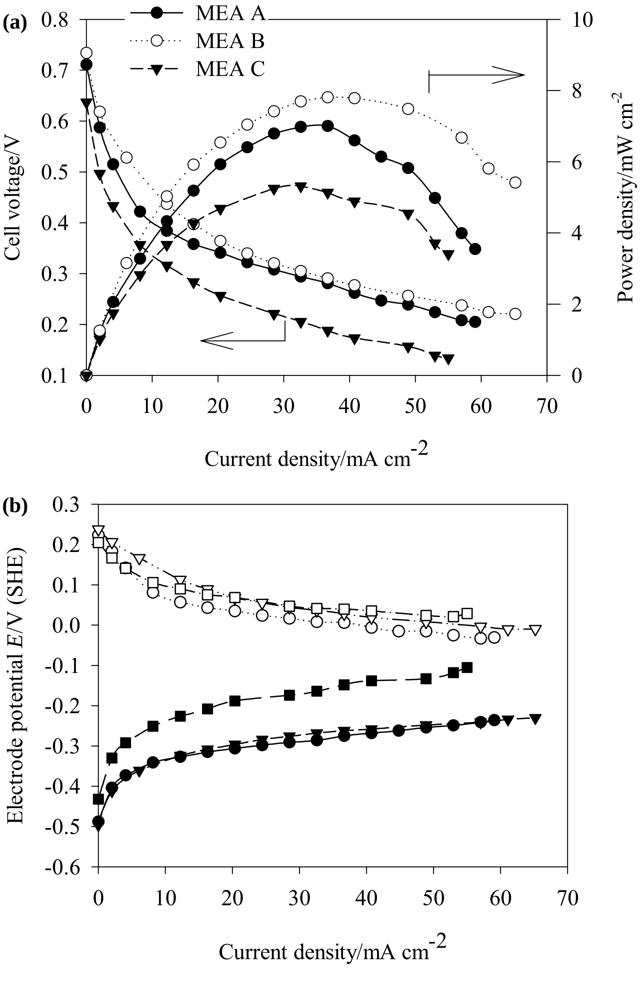

Fig. 5. Comparison between MEA A, MEA B and MEA C at 60 °C, air pressure 1 bar, 2 M methanol in 1 M NaOH with the flow rate of 60.6 ml min^{-1}. Key: (●) Ea MEA A, ○ Ec MEA A;(▼) Ea MEA B, (▽) Ec MEA B; (■) Ea MEA C, (□) Ec MEA C. The Cell voltages and cathode potentials are *iR* compensated.

platinized mesh showed higher performance and the catalysed membrane gave the lowest performance. This is consistent with the voltammetry data for methanol oxidation, and could be explained by the higher active surface area on the platinised mesh. Interestingly, despite the low methanol oxidation activity on the catalysed membrane, the best cathode performance for oxygen reduction was achieved with the catalysed membrane even though the Pt loading was only 0.53 mg cm^{-2}, compared to 2 mg cm^{-2} on the carbon supported Pt catalyst. Pt loadings and electrode configurations of these MEAs are summarized in Table 4.

At open circuit, and in the low current density region, the carbon supported Pt showed better performance than the catalysed membrane for oxygen reduction (i.e., a higher open circuit potential and lower potential loss). This behaviour is possibly due to the low Pt loading on the catalysed membrane. However, the change in cathode potential with the catalysed membrane was small in the higher current density region, and could be explained by the reaction occurring mainly at the interface of the membrane and the catalyst. In the carbon supported Pt catalyst, PTFE was used as the binder which made the catalyst layer hydrophobic and possibly reduced the contact between the Pt particles, membrane and reactants. Whereas on the catalysed membrane, Pt particles were deposited directly onto and inside the membrane, entirely exposed to the reactants: oxygen and water from the anode side. A superior reaction interface for oxygen reduction on the catalysed membrane, could contribute to a better cathode performance. This interface structure can be observed form the TEM image in Figure 6.

3.4. *Fuel cell performance with combination of the catalysed membrane and platinized mesh*

From the studies discussed above, the best performances for methanol oxidation and oxygen reduction were accomplished with the platinized mesh and catalysed membrane, respectively. Hence, a MEA was prepared, which combined the platinised mesh and the catalysed membrane. The anode was composed of non-teflonized Toray 90 carbon paper and a platinized mesh prepared by thermal decomposition of H_2PtCl_6 on a Ti mesh [16], with a Pt loading of 1.24 mg cm^{-2}, as well as chemical deposition of Pt on the ADP membrane, with a Pt loading of 0.55 mg cm^{-2}. The total Pt loading on the anode was 1.79 mg cm^{-2}. The cathode was a chemical deposit of 0.77 mg cm^{-2} Pt on the membrane covered with a gas diffusion layer. The cell test was performed at 60 °C, 1-bar air pressure and with 2 M methanol in 1 M NaOH (Figure 7). The cell performance improved dramatically with this MEA configuration. A maximum current density of 97.8 mA cm^{-2} and peak power density of 17.8 mW cm^{-2} at 0.23 V was achieved after 24 h of cell conditioning.

Table 4. Pt loading and electrode configurations of various MEAs

MEAs	Anode	Cathode
MEA A	Non-teflonized Toray 90 with Pt/C (60 wt %) Pt 1.46 mg cm^{-2}	Pt/C (60 wt %) with a gas diffusion layer Pt 2.05 mg cm^{-2}
MEA B	Thermal deposition of Pt on Ti mesh Pt 1.24 mg cm^{-2}	GDE with Pt/C (60 wt %) with a gas diffusion layer Pt 2.05 mg cm^{-2}
MEA C	Chemical deposition of Pt, Pt 0.933 mg cm^{-2}	Chemical deposition of Pt with a gas diffusion layer Pt 0.526 mg cm^{-2}
MEA D	Thermal deposition of Pt on Ti mesh (1.24 mg cm^{-2}) + chemical deposition of Pt (0.55 mg cm^{-2}) Pt in total: 1.79 mg cm^{-2}	Chemical deposition of Pt with a gas diffusion layer Pt 0.77 mg cm^{-2}

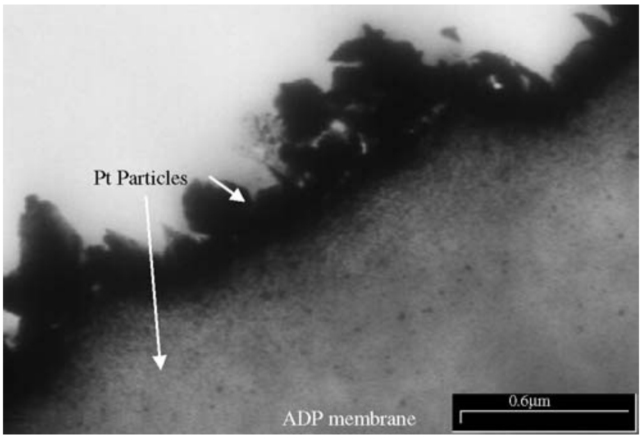

Fig. 6. TEM of the cross section of the catalysed ADP membrane: Pt deposit on the surface and inside the membrane.

A stability study of the cell performance was also carried out. It is shown, in Figure 8, that the cell performance decreased with time mainly due to

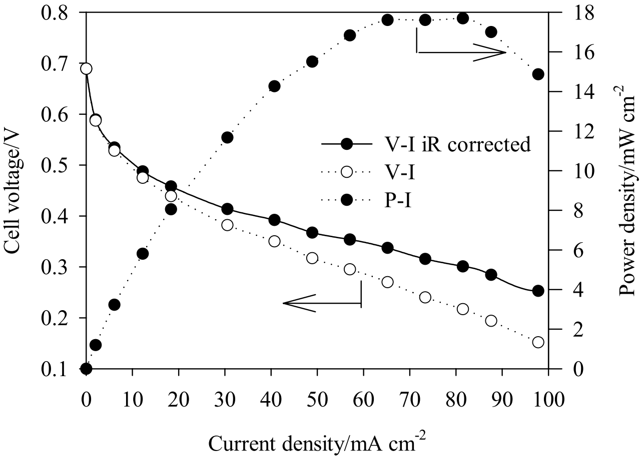

Fig. 7. Fuel cell performances on the MEA D with both catalysed Ti mesh and ADP membrane. Anode: Pt 0.55 mg cm^{-2} chemical deposition plus thermal decomposition of Pt on Ti mesh Pt 1.24 mg cm^{-2} with non teflonized Toray 90. Cathode: 0.77 mg cm^{-2} chemical deposition, gas diffusion layer: 2 mg cm^{-2} Ketjen Black with 10 wt % PTFE on 20% teflonized Toray 90. Cell tests at 60 °C, air pressure 1 bar, 2 M MeOH, 1 M NaOH with flow rate of 60.6 ml min^{-1}.

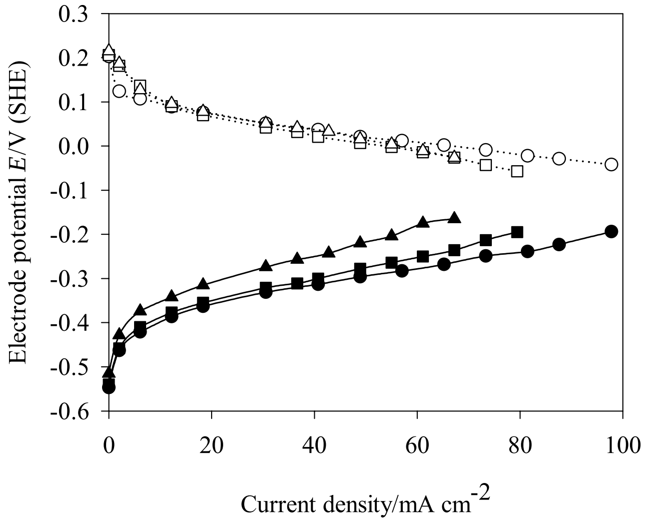

Fig. 8. Fuel cell stability study on the MEA D with catalysed Ti mesh and ADP membrane. Anode: Pt 0.55 mg cm^{-2} chemical deposition plus thermal decomposition of Pt on Ti mesh Pt 1.24 mg cm^{-2} with non-teflonized Toray 90. Cathode: 0.77 mg cm^{-2} chemical deposition, gas diffusion layer: 2 mg cm^{-2} Ketjen Black with 10 wt % PTFE on 20% teflonized Toray 90. Cell tests at 60 °C, air pressure 1 bar, 2 M MeOH, 1 M NaOH with flow rate of 60.6 ml min^{-1}. Key: (●) Ea 24 h, (○) Ec 24 h; (■) Ea 55 h, (□) Ec 55 h, (▲) Ea 98 h, (△) Ec 98 h.

deterioration in the anode performance. This behaviour is similar to that described in Section 3.2.

At similar cell operating conditions, the DMFC with proton conducting membranes using a platinized mesh anode gave a peak power density of 42 mW cm^{-2} at 0.28 V [17]. This performance is significantly higher than that achieved by a DMAFC, mainly due to the much lower conductivity of the OH$^-$ ion conducting membrane compared to Nafion® (e. g., 0.05 Ω). Thus, at 30–50 mA cm^{-2} we would expect a lower performance of 66–110 mV with the OH$^-$ ion conducting membrane.

With the DMAFC, the anticipated advantage of reduced cross-over of methanol does not appear to have materialized to a significant effect. This is likely due to the low current densities achieved where the electroosmotic transfer of methanol with OH$^-$ ions is small in comparison to the diffusion of methanol from anode to cathode [18].

4. Conclusions

Based on this preliminary study of fuel cell tests with the Pt catalysed Morgane®-ADP membrane, the following conclusions can be drawn. Compared to other MEAs, the active surface area of the Pt catalysed membrane is relatively small and, in turn, its catalytic activity towards methanol oxidation is relatively low. The platinized mesh had the highest active area compared to the carbon supported Pt catalyst and the catalysed ADP membrane. As a result, the highest methanol oxidation activity was achieved on the platinized mesh, and the lowest on the catalysed ADP membrane. Nevertheless, the catalysed ADP membrane gave the best performance for oxygen reduction.

By combining the platinised mesh and catalysed membrane into one MEA, the best fuel cell performance was accomplished using an anion exchange membrane in the DMFC. However, the cell performance declined with time because of a 'poisoning effect' on the catalysed membrane. Further optimisation is required to increase the roughness or active area of the catalysed membrane.

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