Short communication

# Performance of a direct methanol alkaline membrane fuel cell

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## Abstract

A study of a direct methanol fuel cell (DMFC) operating with hydroxide ion conducting membranes is reported. Evaluation of the fuel cell was performed using membrane electrode assemblies incorporating carbon-supported platinum/ruthenium anode and platinum cathode catalysts and ADP alkaline membranes. Catalyst loadings used were $1 \, mg \, cm^{-2}$ Pt for both anode and cathode. The effect of temperature, oxidant (air or oxygen) and methanol concentration on cell performance is reported. The cell achieved a power density of $16 \, mW \, cm^{-2}$, at $60 \, °C$ using oxygen. The performance under near ambient conditions with air gave a peak power density of approximately $6 \, mW \, cm^{-2}$.
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*Keywords:* Methanol fuel cell; Alkaline media; Hydroxide ion conducting membrane

## 1. Introduction

The direct methanol fuel cell (DMFC) is currently under development as an alternative power source for applications ranging from portable power to medium scale power generation. One of the main advantages of the DMFC is the high energy content of methanol, which provides scope for the development of systems that are capable of extended electrical discharge compared to existing electrochemical power sources. To date, the full potential of the DMFC, based on proton conducting membranes, has not been realised due to its relatively low power density, compared to hydrogen fuelled polymer electrolyte fuel cells. A major contribution to the relatively low DMFC performance is from kinetic constraints in the methanol oxidation reaction [1]. It has been suggested that improved methanol oxidation kinetics can be facilitated using basic media [2]. Accordingly, the approach taken in this study was to develop an alkali analogue of the DMFC, i.e. a direct methanol alkali fuel cell (DMAFC). A potential problem with the use of an alkaline electrolyte is its reaction with carbon dioxide to produce carbonates. However with an anion conducting membrane there is no hydroxide ion in free solution and problems associated with carbonation are less likely to occur. In addition to the advantage of improved anodic oxida-

tion kinetics and reduced polarisation, a fuel cell that operates using conduction of $OH^-$ offer a number of features:

- For oxygen reduction low cost, non-platinum catalysts, e.g. Ag or Co, perform favourably in this environment.
- Many materials show superior corrosion resistance in alkaline than in acid environments.
- Electro-osmotic drag transports water away from the cathode preventing flooding on the cathode.
- Hydroxide ion transport from cathode to anode should reduce the 'crossover' problem of methanol in the fuel cell.

One of the major challenges with the development of the DMAFC is the availability of suitable anion-exchange membranes which offer suitable ionic conductivity and that are stable under fuel cell operating conditions. Recent work on the development of anion-exchange membranes for application in fuel cells include, the fabrication of radiation-grafted anion-exchange membranes [3–5].

A disadvantage of the anion membrane is that the ionic conductivity can be lower than that of the $H^+$ ion conducting membranes. This factor affects the membrane, membrane–catalyst layer interface and the bounded electrocatalyst layers. In the latter case this occurs if the anion-exchange material is used as the ionomer to improve the ionic conductivity in both the anode and cathode. Thus there will be a compromise

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Anode reaction:
$$CH_3OH + 8OH^- \Longrightarrow CO_3^{2-} + 6H_2O + 6e^-$$

Cathode reaction:
$$3/2O_2 + 3H_2O + 6e^- \Longrightarrow 6OH^-$$

Overall cell reaction:
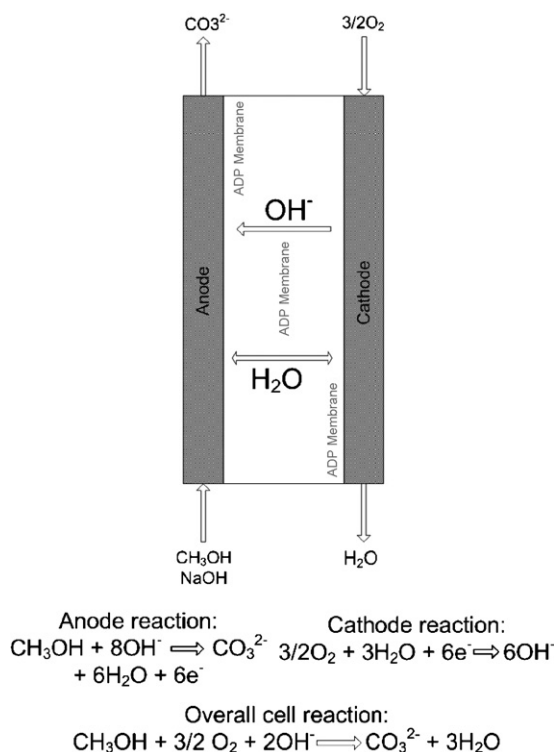$$CH_3OH + 3/2\,O_2 + 2OH^- \Longrightarrow CO_3^{2-} + 3H_2O$$

Fig. 1. Transport processes and electrode reactions in DAMFC.

between ionic conductivity and electrocatalyst activity at both anode and cathode. A schematic diagram of the electrochemical reactions and transport processes in the DMAFC is shown in Fig. 1. The ionic conduction in this system is by the transport of $OH^-$ ions from the cathode to the anode.

There are limited reports of anion-exchange membranes in fuel cells. The use of alkaline ion-exchange membranes has been previously reported in fuel cells which use the direct oxidation of sodium borohydride under alkaline conditions [6]. The development of a Pt/Pd electrocatalysts for solid alkaline fuel cells using methanol has been investigated. Power densities of up to $20\,mW\,cm^{-2}$ were produced [7]. A novel, quaternary ammonium-functionalised radiation-grafted ethylenetetrafluoroethylene (ETFE) alkaline anion-exchange membrane (AAEM) has been developed for applications in fuel cells. A $H_2/O_2$ fuel cell peak power performance of $130\,mW\,cm^{-2}$ was obtained for an alkaline membrane electrode assembly and a maximum power density of $8.5\,mW\,cm^{-2}$ was obtained with a methanol/$O_2$ fuel cell [8].

Alkaline direct alcohol fuel cells using an $OH^-$ form anion-exchange membrane and polyhydric alcohols have been studied [9]. A high open circuit voltage of ca. 800 mV was obtained for a cell using Pt–Ru/C (anode) and Pt/C (cathode) at 323 K. The alkaline direct ethylene glycol fuel cells using silver as a cathode catalyst gave excellent performance because higher concentrations of fuel could be supplied to the anode [9]. A quaternised polyethersulphone anion-exchange membranes for direct, methanol alkaline fuel cells has been synthesised and characterised for conductivity and methanol permeability. The material however was not used in the DMFC [10].

In this research, DMAFCs operating with a Morgane®-ADP hydroxide ion conducting membrane were investigated. The study used low loadings of Pt-based anode and cathode electrocatalysts and investigated the influence of methanol concentration on the cell power performance.

## 2. Experimental

### 2.1. MEA preparation

Membrane electrode assemblies were prepared by bonding anode and cathode catalyst layers to opposite sides of a polymer electrolyte membrane and covering the catalyst layers with carbon paper-based current collectors (or gas distributors). This experimental work used an anionic-exchange polymer electrolyte (ADP-Morgane® membrane (Solvay S.A.). Table 1 gives the basic proprieties of the ADP-Morgane® membrane at 25 °C.

Before fabrication of the membrane electrode assembly (MEA), the membrane was rinsed with de-ionised water and dried. The catalyst electrodes were made from ink prepared by mixing isopropyl alcohol (IPA) with 10% Nafion® and carbon-supported catalyst. In the anode catalyst layer ink, carbon-supported Pt–Ru (60 wt.%, ETEK, USA) was used and for cathode catalyst layer carbon-supported Pt (60 wt.%, ETEK, USA) was used. Nafion® was used as the binder, as a solubilised form of the anion-exchange membrane was not available. Nafion® has a proven ability to act as a binder in PEM fuel cells, especially when low pressing temperatures are required, as in this work. In this context it is preferable to PTFE. In electrode preparation the catalyst layer was sprayed on top of one gas diffusion electrode. An alternative may be to use a polyacrylate–polyalcohol or similar commercialised anionic ionomer. However these materials may present issues in electrode fabrication and performance and were thus not considered at this stage of the research programme.

For electrode preparation the catalyst layer was sprayed on top of one gas diffusive electrode. The platinum catalyst loading used was $1\,mg\,cm^{-2}$ for both electrodes. The gas diffusion electrode consisted of a micro-porous layer (Ketjen black carbon, with 10% polytetrafluoroethylene (PTFE)) sprayed on top of a carbon paper (Toray 90 carbon paper, ETEK, USA) which was wet-proofed with 20 wt.% PTFE. After the electrode preparation, the membrane was sandwiched between the anode and cathode and hot pressed together at $50\,kg\,cm^{-2}$ for 5 min at 80 °C. This temperature is slightly above the recommended long-term operating temperature of the membrane, but was used

Table 1
Basic properties of Morgane®-ADP membrane

| Membrane | Morgane®-ADP |
|---|---|
| Material | Cross-linked fluorinated polymer |
| Exchange group | Quaternary ammonium |
| Thickness fully humidified ($\mu$m) | 150–160 |
| Resistance (in 0.6 M NaCl) ($\Omega\,cm^2$) | 1.5–4.5 |
| Resistance (in 1 M NaOH) ($\Omega\,cm^2$) | 0.5 |
| Maximum operational temperature (°C) | 55 |
| Working pH | 0–10 |

to try to ensure good adhesion between the catalysts layers and membrane.

## 2.2. Fuel cell tests

In assembling the DAMFC the anode and cathode of the MEA were in contact with high-density graphite blocks (Ralph Coidan, Middlesbrough), impregnated with phenolic resin, into which were cut the gas/liquid flow channels. The ridges between the channels provided the electrical contact to the carbon electrodes. The active area of the cell on which current densities are based was the total machined surface area of $4 \, cm^2$, i.e. the MEA surface area. Copper sheets contacted the graphite blocks as current collectors. Electrical heaters were mounted at the rear of the Cu plates to maintain the desired cell temperature which was controlled through a temperature controller and monitored by thermocouples buried in the graphite blocks. Conditioning of the MEA, to ensure that the membrane was hydroxide ion conducting, was carried out by passing a $1.0 \, mol \, dm^{-3}$ (M) NaOH solution in the anode chamber for 5 h followed by de-ionised water through both cell chambers at $40 \, °C$ for 10 h. The cell was then fed with an aqueous solution of methanol for performance studies. Once the cell voltage had decayed to a steady value, polarisation curves were recorded in a galvanostatic mode, starting from the open circuit point and moving to higher current densities. Anode polarisation curves were measured with respect to the cathode fed with hydrogen; acting both as a reference electrode and as a counter electrode. Cathode polarisation data were derived by subtracting electrode polarisation values from the respective cell polarisation data at various current densities.

## 2.3. Physical analysis

Scanning electron microscopy (SEM, Jeol JSM 5300LV), transmission electron microscopy (TEM, Philips CM10) and X-ray diffraction (XRD) (Philips X'Pert) analysis were conducted to determine the morphology and distribution of the platinum deposited in the membrane.

## 3. Results and discussion

The study focused on investigating the influence of temperature, oxidant, methanol concentration and anode feed rate on fuel cell performance. All the anodic polarisation curves were obtained using the internal hydrogen reference electrode. A set of standard test conditions were adopted except when a particular variable was under study:

- $60 \, °C$ temperature;
- methanol flow rate $2.78 \, cm^3 \, min^{-1}$;
- methanol concentration $1.0 \, M$;
- air flow rate $0.4 \, dm^3 \, min^{-1}$;
- un-humidified air at 1 bar pressure.

Fig. 2 shows the cell polarisation curves and power density curves obtained for the DAMFC at temperature between 30 and $60 \, °C$. The data shows very clearly the improvement in cell performance when the temperature is increased. Open circuit
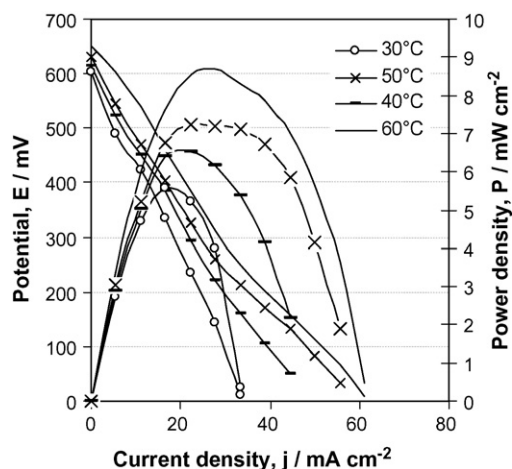


Fig. 2. Cell polarisation curves and power density curves for the DMAFC using air.

potentials are around 600 mV and the higher temperature gave a higher open circuit potential, of some 50 mV.

The improvement of cell performance with increasing temperature is due to the improvement in methanol oxidation at higher temperature, as confirmed in the study of methanol oxidation in alkaline media [11]. The maximum current density that can be drawn from the cell (at 0.0 V) was around $60 \, mA \, cm^{-2}$. The performance of the cell is much lower than that achieved with equivalent direct methanol fuel cells that use proton-exchange membranes. For example previous work with Nafion® membranes in cells with similar catalyst loadings has given current densities of $100 \, mA \, cm^{-2}$ at a cell voltage of 0.4 V [12], compared to approximately $30 \, mA \, cm^{-2}$ with the DMAFC in this work.

The shapes of the cell polarisation curves are approximately linear which would indicate that a significant factor in controlling the available power is the ionic resistance. If we assume that the cell polarisation curve is dominated by ionic resistance the estimated value of conductivity from the curve is approximately $5 \times 10^{-3} \, S \, cm^{-1}$. The conductivity is much lower than that expected for the anion-exchange membrane which indicates that other internal resistances as well as anode and cathode polarisation contribute the relatively low cell performance. These resistances can be contact resistances and ionic resistances in the electrocatalysts layers. In the latter case this will arise from the use of Nafion® as binder in the layers: a solubilised form of the ionomer was not available for electrode fabrication. Nafion® was used mainly because it provided better characteristics than alternatives such as PTFE; i.e. better oxygen solubility and methanol diffusion. If a solubilised form of the ionomer becomes available then this should enable better electrode performance to be obtained with its use in the electrocatalyst layers. Alternatively it may be possible to produce the membrane material as a powder to be used as ionic conductor in the electrocatalyst layers.

Fig. 3 shows the cell polarisation curves and power density curves obtained for the DAMFC at temperature between 30 and $60 \, °C$, using oxygen not air as oxidant. The higher temperature again gave the better performance. From a comparison of the data with air and oxygen (Fig. 4), we can see that the
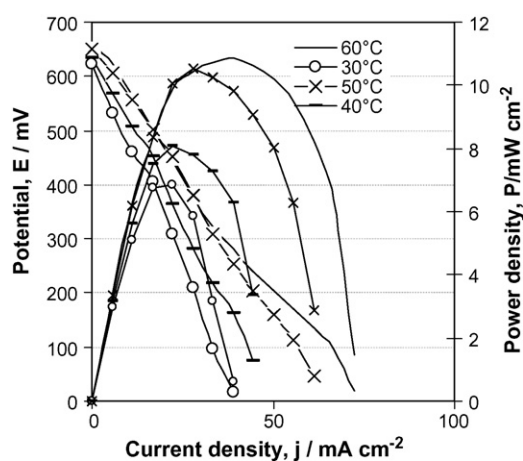
Fig. 3. Cell polarisation curves and power density curves for methanol/O$_2$ cell.



Fig. 5. Peak power densities as a function of temperature using air and oxygen in the DMAFC.

system using oxygen gave the better performance. The open circuit potentials is typically around 10 mV higher with oxygen than with air and the maximum current densities are around 15 mA cm$^{-2}$ higher.

The overall effect of oxidant can be explained by the different partial pressures of oxygen reaching the cathode catalyst layer in these two cases. Fig. 4 indicates that the difference (improvement) in cell voltage of the DAMFC when operated oxygen rather than air is due to better cathode kinetics. The difference between the current densities using oxygen and air increases with decreasing cell voltage or increasing cathode overpotential.

Fig. 5 compares the influence of temperature on the DAMFC peak power density using air and oxygen and clearly shows how temperature increases the power density. For air, over the range of temperatures of 30–60 °C, the range of peak power density is between approximately 6–9 mW cm$^{-2}$ while for oxygen it is between 7 and 11 mW cm$^{-2}$.

### 3.1. Influence of methanol concentration

Fig. 6 shows the anode polarisation curves obtained, in situ in the DMAFC, for different methanol concentrations. The data
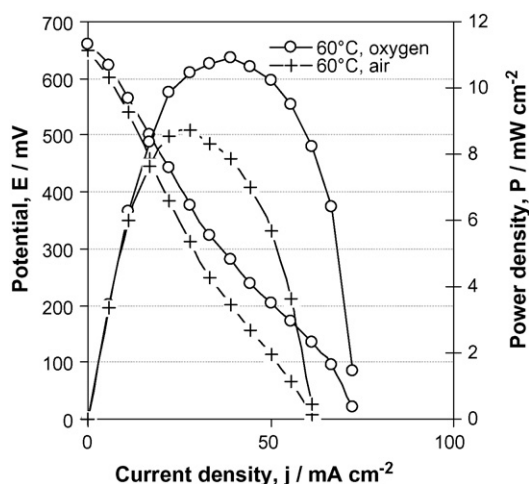
exhibit only a mall variation with methanol concentration with a slight increase in the anode performance, of approximately 40 mV, at a fixed current density, when the methanol concentration is increased from 1.0 to 4.0 M. It should however be noted that the in situ measurement of anode potential using a hydrogen anode gives only approximate values of anode potential.

Fig. 7 shows the cell polarisation curves and the corresponding power density curves obtained for different methanol concentrations. There is an increase in the cell performance when the methanol concentration is increased from 1.0 to 2.0 M. With a methanol concentration of 4.0 M the lowest cell performance is achieved. This data would suggest that crossover of methanol affects the DMAFC performance. The anticipated benefit of hydroxide ion membrane stopping methanol crossover due to electro-osmotic drag occurring from cathode to anode is not been fully realised. This factor is partly influenced by the relatively low current densities experienced in the cell which are probably not sufficient to eliminate methanol crossover by diffusion. However with the anion-exchange membrane the problem of crossover is not as severe as reported with proton conducting membrane such as Nafion®, which exhibit a large fall in performance at methanol concentrations of 4.0 M and greater. For example with Nafion®, power densities fall from approximately



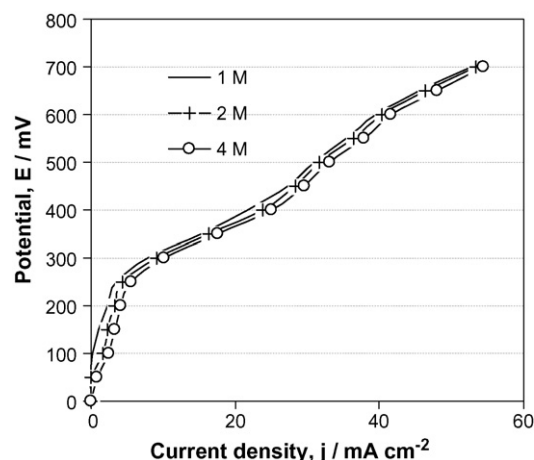Fig. 4. Difference between cell operating with air and oxygen.
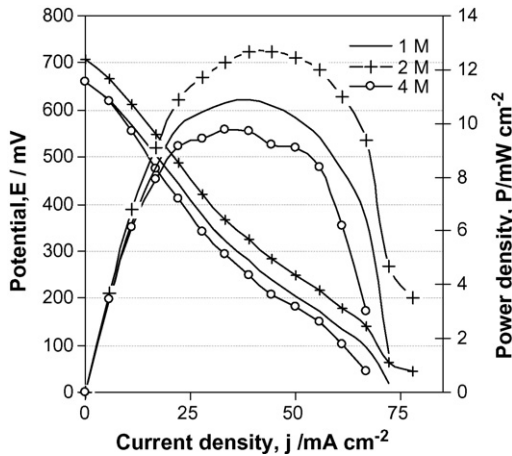


Fig. 6. Anode polarisation curves obtained for different methanol concentrations.

Fig. 7. Cell polarisation and power density curves obtained for different methanol concentrations. Oxygen fed cathode.



Fig. 9. Cell polarisation and power density curves obtained for different anode feed rate. Oxygen cathode.

$60\,\text{mW}\,\text{cm}^{-2}$ to around $20\,\text{mW}\,\text{cm}^{-2}$ as methanol concentration increases to 4.0 M, as a result of the reduction in cathode potential due to methanol crossover which, is of the order of 100–200 mV [12]. The reduced extent of crossover could apparently enable the cell to partly benefit from improved methanol oxidation kinetics at a higher concentration—explaining why the highest potentials are observed with a 2.0 M methanol solution.

The effect of methanol concentration on fuel cell performance with an air cathode is similar to that with an oxygen cathode. The performance of the cell improves when the methanol concentration is increased from 1.0 to 2.0 M, followed by a decrease in performance with a methanol concentration of 4.0 M. Fig. 8 shows the variation in peak power densities with methanol concentration for the DAMFC, where we can see the increase in cell performance when oxygen is used in place of air. For example when the methanol concentration is 2.0 M, the power corresponding to peak power is increased by 27% when the oxidant is oxygen.

## 3.2. The influence of methanol flow rate

Fig. 9 shows the cell polarisation and the corresponding power density curves obtained for different anode feed rates. The data exhibits somewhat unusual behaviour in that a significant rise in voltage is achieved at the higher flow rates. The largest increase in power is obtained on increasing flow rate
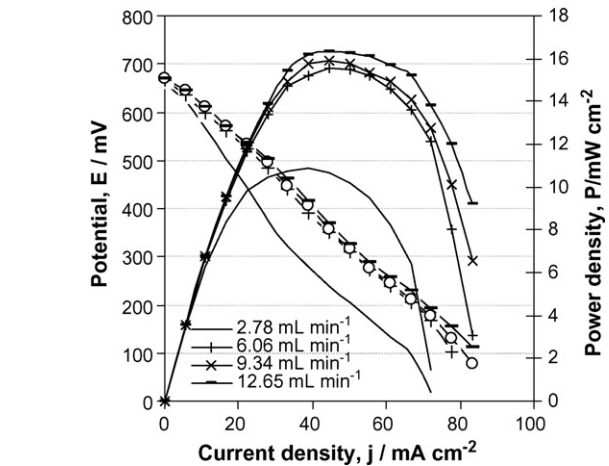
to $6\,\text{cm}^3\,\text{min}^{-1}$, when thereafter further increases in flow rate have only a marginal effect, within the experimental error of the measurements. Notably however peak power densities of around $16\,\text{mW}\,\text{cm}^{-2}$ are achieved, which represents a significant performance using an un-optimised membrane not specifically designed for an alkaline methanol fuel cell.

Fig. 10 shows the anode polarisation curves obtained for different methanol flow rates. From this data we can see almost the same trend in anode polarisation as obtained in the cell polarisation. When the feed rate is increased from 2.78 to 6.06 mL min a large improvement (increase in current at a fixed potential) in anode performance is obtained. With subsequent increases in flow rate we can see a negligible increase in anode performance. This behaviour cannot be fully explained but may be in part due to an improvement in mass transport behaviour and carbon dioxide gas release from the electrode surface and improvement in gas flow from the anode side of the cell at the higher flow rate; the latter two may have been poor at the lower flow rate.

### 3.2.1. Durability

Long-term durability of MEAs is always a question for any fuel cell and in particular when a potential cause of degradation is identifiable. In the case of the alkaline conducting membrane one possible cause is the interaction of hydroxide ions with carbon dioxide; either in the air stream or formed as part of fuel oxidation. In the case of the MEA, based on the ADP membrane,
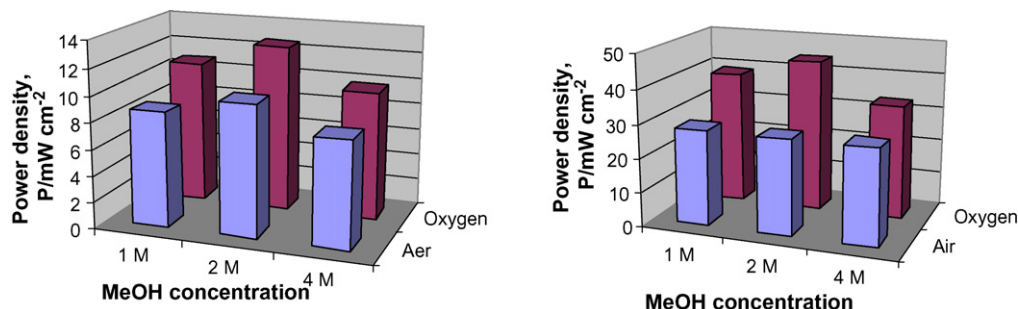




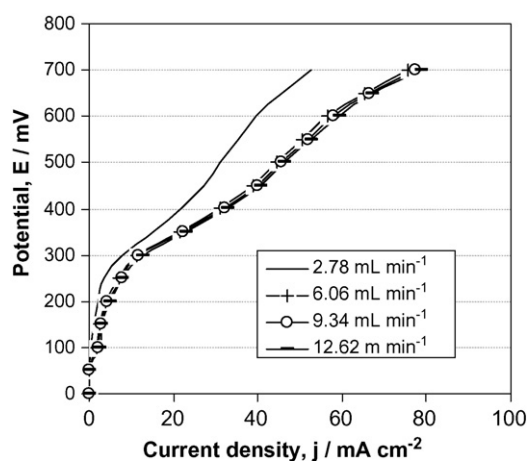Fig. 8. Power density and current density corresponding to power peak.

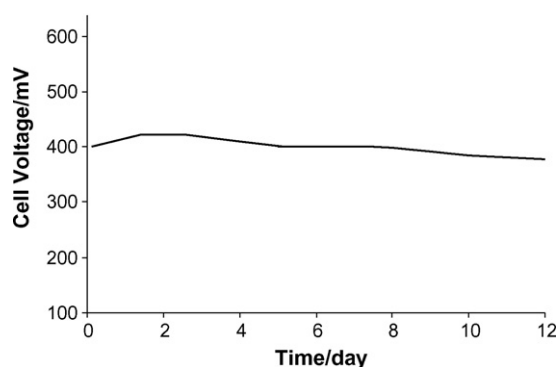Fig. 10. Anode polarisation curves obtained for different methanol flow rates.



Fig. 11. Cell voltage variation during cell testing: $20\,mA\,cm^{-2}$; air at 1 bar pressure $60\,°C$.
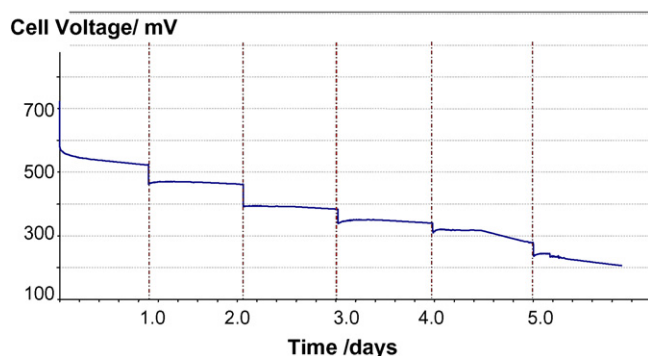


Fig. 12. Cell durability tests at different cell loads. Air at 1 bar pressure $60\,°C$. Each period represents an increment increase in current density.

this has undergone extended periods of operation with air without any significant loss in performance, as shown in Fig. 11. The MEA was tested for 6 days under variable operating conditions using air as the oxidant. The cell was started at open circuit and then operated at a fixed current density for periods of 24 h, followed by successive increases in current density for periods of 24 h. The tests were performed with one cell continuously operated without any change in fuel. For the first three periods; the cell voltage, shown in Fig. 12, remained approximately constant

over each test interval. In the last three periods the cell potential fell in the latter stages of each test period. At the highest current density the cell potential fell from 250 to 195 mV in the last 15 h. One cause of the reduction in potential may have been due to a gradual use of the fuel and a change in the fuel composition. On retesting the MEA polarisation behaviour, with fresh methanol solution, no discernable difference in performance was seen in comparison to previous polarisations. The tests demonstrated that a reasonably stable potential can be achieved with the alkaline conducting MEA.

## 4. Conclusions

A study of the effect of temperature, methanol concentration and flow rate, and oxidant on the performance of a direct methanol alkaline membrane fuel cell has demonstrated the viability of the concept. The performance of the DMAFC is good with modest loadings of $1\,mg\,cm^{-2}$ of anode and cathode catalysts. The cell performance improved when the temperature was increased due to the improvement in methanol oxidation. Methanol concentration has some influence on the cell performance. Although increasing the methanol concentration does not have a major influence on the methanol oxidation kinetics it does influence cell performance through an increase in crossover. The observed decrease in performance is not as great as that typically experienced with acidic methanol fuel cells and indicates a potential benefit for alkaline membrane methanol fuel cells especially when membranes with better conductivity become available and also a solubilised form of ionomer to bind electrocatalyst layers. Stable performance of the fuel cell MEA has been demonstrated over many days of continuous and intermittent operation.

## Acknowledgements

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