

Application of sodium conducting membranes in direct methanol alkaline fuel cells

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Abstract

A study of a direct methanol alkaline fuel cell (DMAFC) operating with sodium conducting membranes is reported. Evaluation of the fuel cell was performed using membrane electrode assemblies incorporating carbon supported platinum catalysts and Nafion[®] 117 and 112 membranes. A membrane electrode assembly was also prepared by the direct chemical deposition of platinum into the surface region of the membrane. Evaluation of the chemically deposited assembly showed it to be less active than those based on carbon supported catalysts. SEM & TEM analysis indicate that this behaviour is due to the low surface area of the chemically deposited catalyst layer. The fuel cell performance with Nafion membranes is reported and is not as good as achieved with hydroxide ion conducting membranes suggesting that Nafion may not be suitable for DMAFC operation.

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 has not been realised due to its relatively low power density, compared to hydrogen polymer electrolyte fuel cells.

A major contribution to the overall polarisation of the DMFC is from kinetic constraints in the methanol oxidation reaction. It has been suggested that improved methanol oxidation kinetics can be facilitated using basic media. 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). To examine the feasibility of a DMAFC system, a system was designed to operate using cationic membranes, for which Nafion[®] is highly applicable. A Na⁺ ion form of Nafion was used as it offers much greater stability than currently available OH⁻ ion (anion) conducting membranes [1]. A disadvantage of the Na⁺ ion form of Nafion is that the ionic conductivity is lower than that

of the H⁺ ion form of Nafion. Thus there will be a compromise between ionic conductivity and electrocatalyst activity at both anode and cathode. These factors affect both the membrane, membrane-catalyst layer interface and the bounded electrocatalyst layers. A schematic diagram of the electrochemical reactions and transport processes in such a system is shown in Figure 1. The electrolytic conduction process in this system is by the transport of Na⁺ ions in the direction of the cathode. A practical consequence of DMAFCs operating in such a manner is that hydroxide ions produced by oxygen reduction react rapidly with Na⁺ ions leading to the formation of sodium hydroxide in the cathode side of the cell. In addition, water is transported across the cell to the cathode. This being the case, it is necessary to recycle this component to the anode to maintain an overall sodium ion balance in the system.

Chemical deposition of platinum directly onto Nafion membranes was first developed by Takenaka et al. [2] for water electrolysis. Further investigations on the electrodes prepared by this method have been reported in various research areas, such as water electrolysis [3–5] and electrooxidation of alcohols [6, 7]. As platinum was deposited directly onto the membrane surface, an increase of adhesive strength of the catalyst to the membrane was achieved. Furthermore, a decrease of

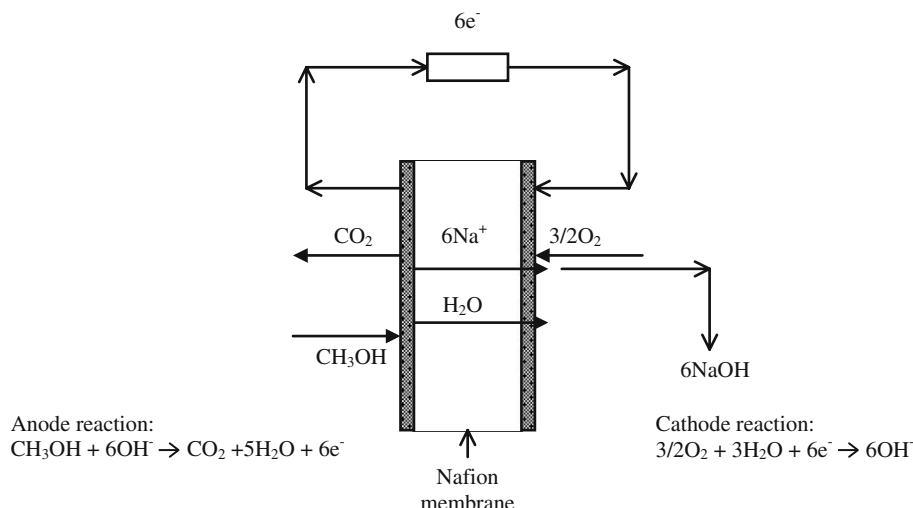


Fig. 1. Schematic of reactions and transport processes in a DMAFC incorporating a Na⁺ form Nafion[®] membrane.

contact resistance in the catalyst/membrane interface and a decrease of resistance within the catalyst layer were also obtained.

In this work, DMAFCs operating with Nafion[®] 117 and Nafion[®] 112 membranes were investigated. Membrane electrode assemblies (MEAs) were produced using both conventional carbon supported platinum electrocatalysts and by chemical deposition of platinum into the membrane surface.

2. Experimental

2.1. Membrane pre-treatment

Prior to MEA fabrication Nafion[®] 117 and 112 membranes were converted to the Na⁺ form by boiling first in deionised water for 30 min and then in 1 M NaOH for 1 h. Excess NaOH was then removed by rinsing and boiling in deionised water.

2.2. MEA preparation

2.2.1. Carbon supported catalysts

Electrodes incorporating carbon supported catalysts were prepared by brushing catalyst inks onto carbon substrates. The carbon substrates consisted of carbon paper (Toray TGHP-090, 20 w/o wet proofed) to which a gas diffusion layer was applied. The gas diffusion layer was applied by painting an ultrasonically mixed ink comprising of carbon black (Ketjen black 300), cyclohexane, and PTFE suspension. Catalyst layers were then applied to the substrates by painting an ultrasonically mixed ink containing the electrocatalyst (60 w/o Pt on Vulcan XC-72, ETEK Inc), Nafion solution (Aldrich), and isopropanol. MEAs were prepared by hot pressing the electrodes together with Nafion[®] membranes (Na⁺ form) for 3 min at 150 °C and 120 kg cm⁻².

2.2.2. Catalysed membranes prepared by chemical deposition

Chemical deposition of platinum into the surface region of the polymer membranes was performed according to the Takenaka method [2] and is shown schematically in Figure 2. A platinum salt solution (e.g., 0.25 mM to 2.0 mM Pt(NH₃)₄Cl₂·H₂O, Alfa Aesar) and reducing agent (5 mM NaBH₄, Aldrich) were circulated to opposing sides of the polymer membrane for between 90 and 150 min. During this period, the platinum solution permeated the membrane and was reduced when it came into contact with the reducing agent. A low concentration of reducing agent was used, since this favoured the production of a platinum deposit in the surface region of the membrane (reducing agent side), as opposed to its interior [7, 8]. The temperature of the deposition process was controlled at 45 °C by circulating the platinum salt and reducing agent solutions from containers held within a thermostatically controlled water bath.

The platinum loadings of the catalysed membranes were determined from the difference in the concentration of the platinum solution before and after deposi-

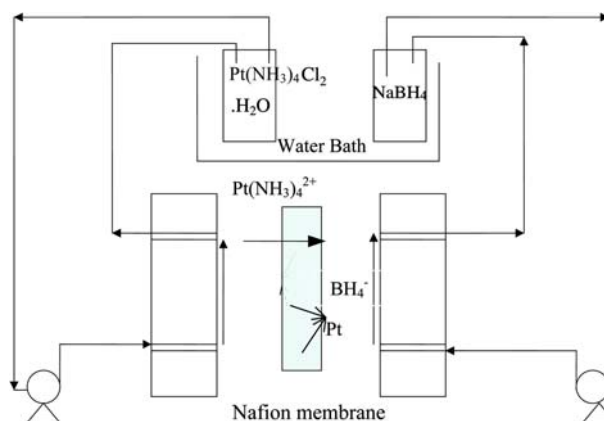


Fig. 2. Schematic diagram of the platinum deposition process.

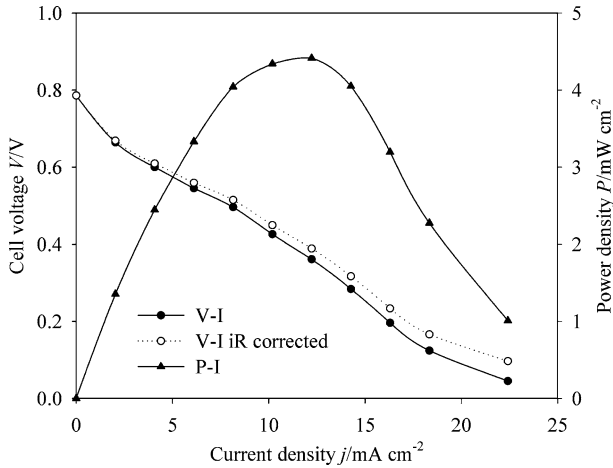


Fig. 3. Polarisation characteristics of a DMAFC incorporating a Nafion® 117 membrane. Pt loading 2 mg cm^{-2} . Cell tested at 60°C with 2M methanol and 1M NaOH. Air pressure: 2 bar.

tion using Atomic Adsorption Spectroscopy (AAS, Unicam 929) and Inductive Coupled Plasma spectroscopy (ICP).

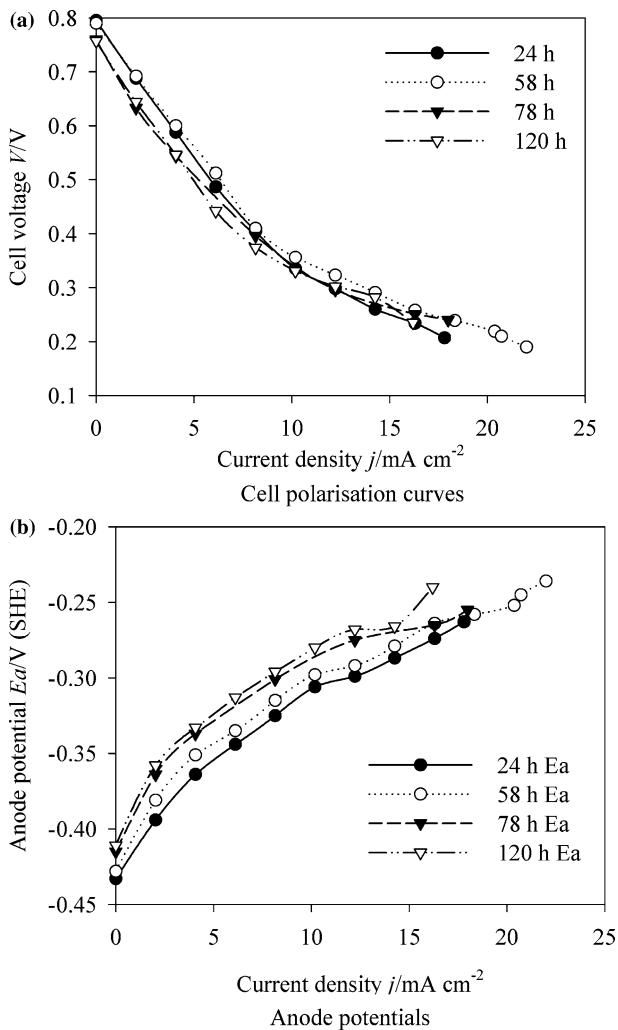


Fig. 4. Fuel cell stability tests of Nafion MEAs Cell tested at 60°C in 2 M methanol and 1 M NaOH, air pressure: 2 bar.

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.

2.4. Fuel cell testing

The fuel cell was machined from stainless steel and contained parallel channels for both fuel and oxidant flow fields. The detailed fuel cell set-up was described previously [9]. The active area of the cell was 4.9 cm^2 . The fuel solution (2 M methanol in 1 M NaOH) was fed to the cell using a peristaltic pump (Watson Marlow). Air was supplied from gas cylinder. Both the fuel solution and the cell were thermostated at 60°C .

Cell polarisation data was obtained using a Kenwood PE-151 electronic load. In order to examine the individual electrode polarisation characteristics, the anode potential was also measured against a mercury/mercury oxide (MMO) reference electrode. From this the cathode potential was obtained by subtracted the anode potential

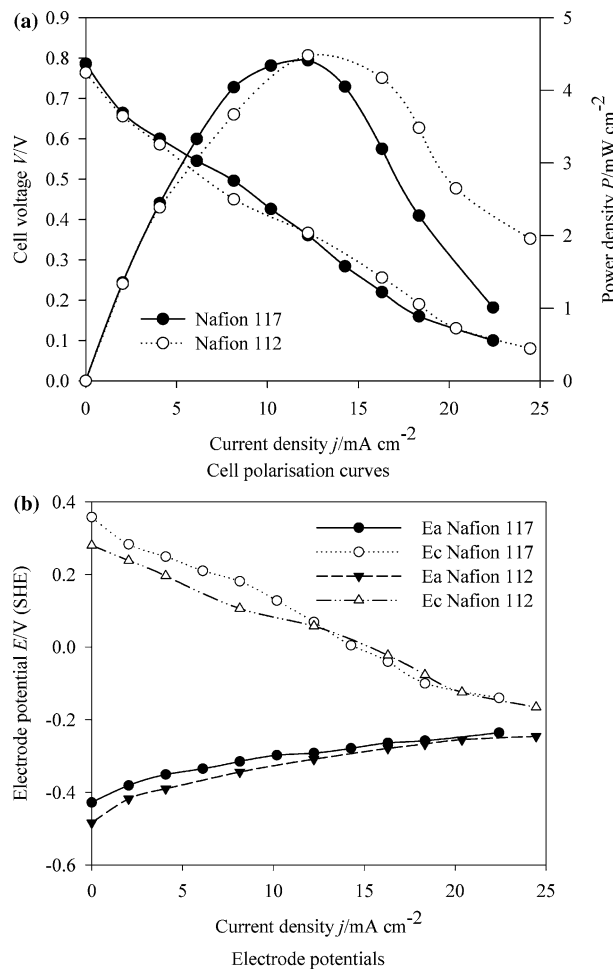


Fig. 5. Polarisation characteristics of DMAFCs incorporating Nafion® 112 and 117 membranes.

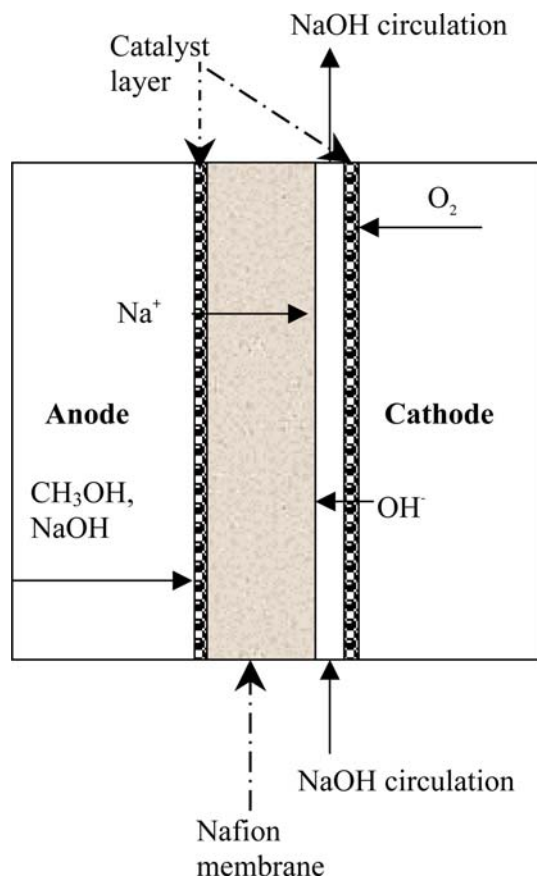


Fig. 6. Schematic diagram of DMAFC with Nafion membrane and incorporating an electrolyte circulating layer in the cathode compartment

from the overall cell voltage. In this case, the cathode potential includes the majority of the iR losses associated with the MEA. The internal resistance (R_{cell}) was measured by AC impedance at open circuit potential.

3. Results and discussion

3.1. MEAs incorporating carbon supported catalysts

Figure 3 shows the polarisation characteristics of a MEA incorporating a Nafion 117 membrane and electrodes prepared with carbon supported platinum catalysts. The potential-current (V - I) polarisation curve without iR loss is also presented. Although the open circuit voltage obtained was favourable (ca. 0.8 V), in comparison to DMFCs operating in acidic media, the polarisation of the DMAFC was greater [10]. This greater polarisation is due to the greater ionic resistance of the Na^+ conduction and kinetic factors associated with the electrochemical reactions. In the case of the latter, carbonate formation at the anode by reaction of CO_2 with the supporting electrolyte is likely to result in concentration polarisation, especially at high current densities. It is also possible that the surface coverage of OH species on the electrode is reduced by the specific adsorption of CO_3^{2-} and HCO_3^- ions, hindering the

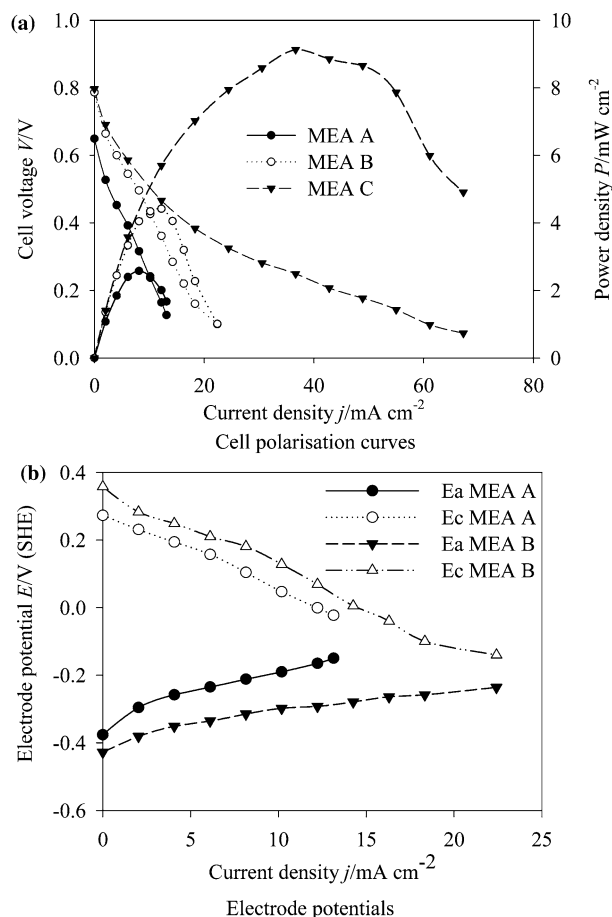


Fig. 7. Comparison of the polarisation characteristics of a DMAFC incorporating Nafion® 117 membrane and ADP membrane. (a) Overall cell polarisation, (b) individual electrode polarisation. MEA A Platinised Nafion membrane. Pt loading anode 2.43 mg cm^{-2} , cathode 2.61 mg cm^{-2} . MEA B Nafion with Pt/C catalysts. Pt loading anode 2.07 mg cm^{-2} , cathode 2.15 mg cm^{-2} . MEA C ADP membrane with Pt/C, anode and cathode Pt loading 2 mg cm^{-2} . Cell tested at 60°C in 2 M methanol and 1 M NaOH, air pressure: 2 bar.

methanol oxidation kinetics [11]. Further evidence of the latter can be seen in the data of Figure 4, concerning the stability study of the cell performance. Cell polarisation tests were carried out after 24 h of cell conditioning and conducted with 24 h interval, for up to 6–7 days. When the cell was not tested, it was left with circulating methanol solutions at the anode at 60°C , and without cathode air supply and without applying a load. The best cell performance was reached after 58 h, after which the cell performance deteriorated with time. It may be concluded that for Nafion MEAs, it is necessary to condition the cell for at least 24 h and better for 48 h. The anode potentials shown in Figure 4(b) shifted by approximately 20–30 mV to more positive values with time, suggesting that decreasing activity of the anode is responsible for the loss in cell performance. This factor can be explained by a combination of the continuous loss of Na^+ from the electrolyte and a slow carbonation process at the anode, from the formation of CO_2 from methanol oxidation.

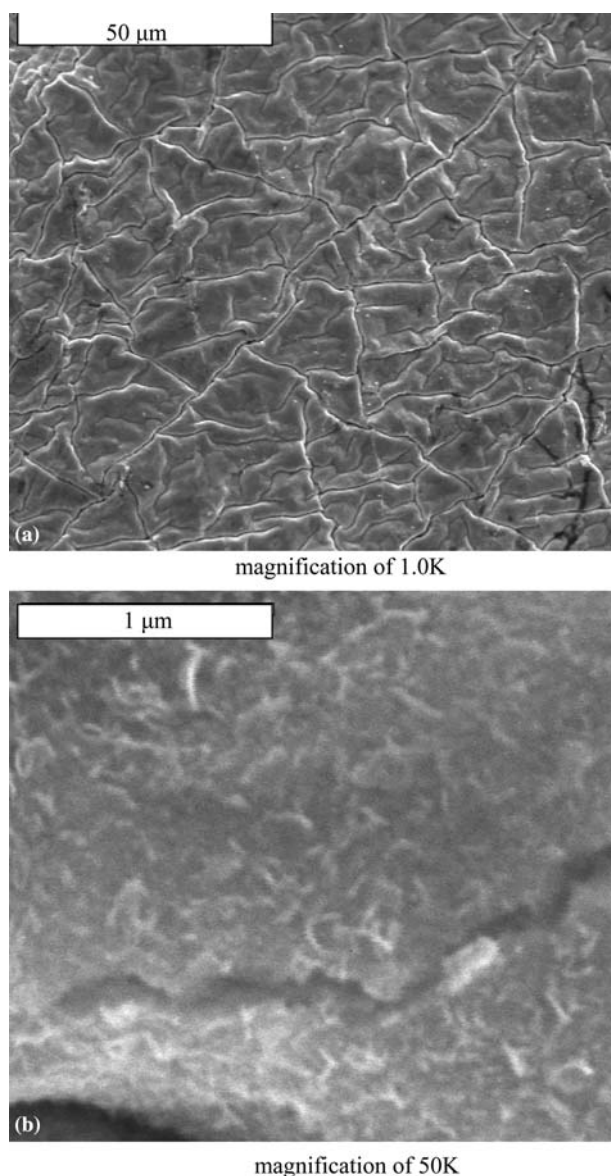


Fig. 8. SEM images of the platinum catalysed Nafion[®] 117 surface. Deposition conditions: 0.5 mM Pt(NH₃)₄Cl₂, 5 mM NaBH₄. (a) magnification 1.0 K, (b) magnification 50 K.

Consequently, the methanol oxidation activity decreased due to the decrease in OH coverage on the anode surface [12, 13].

From Figure 5, the combined loss of voltage was 400 mV over 20 mA cm⁻², from internal resistance and cathode polarisation, i.e. of the order of 20 Ω cm². The internal resistance of the cell as measured by high frequency AC impedance was 0.47 Ω. This value is much higher than that with H⁺ form Nafion, c.a. lower than 0.05 Ω [14].

In order to investigate the contribution of the membrane resistance to the overall polarisation behaviour, the fuel cell activity was compared to that obtained using a thinner (51 μm), lower resistance membrane i.e., Nafion[®] 112. The polarisation characteristics obtained with Nafion 117 and 112 are shown in Figure 5, from which there appears to be very little difference in the

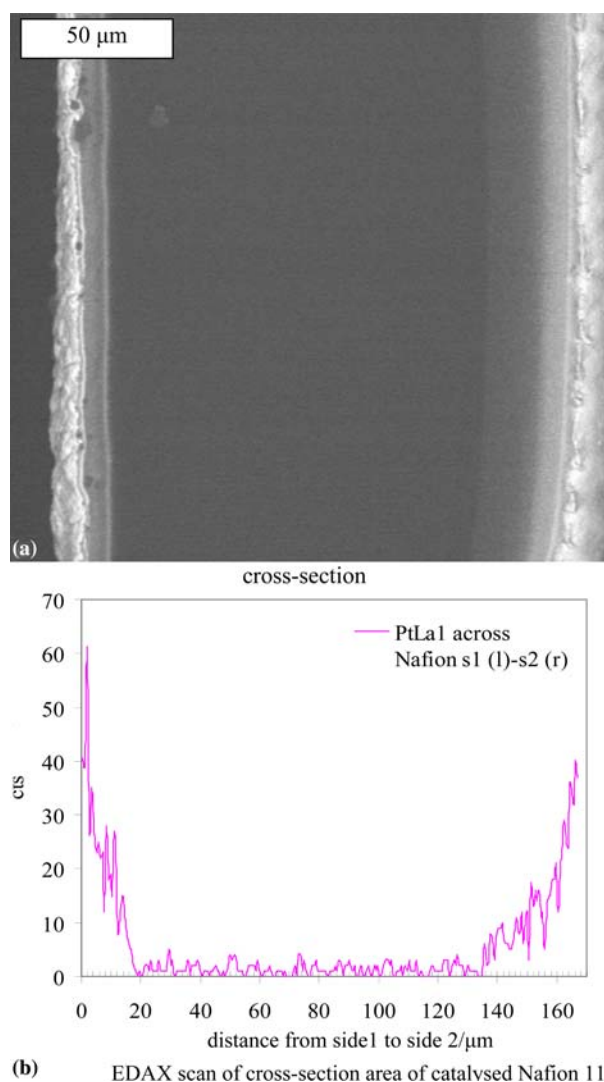


Fig. 9. SEM and EDAX analysis of the platinum distribution across the platinum catalysed Nafion[®] 117 cross-section. (a) SEM, (b) EDAX.

overall performance, despite the reported higher conductivity of the thinner membrane. Although the anode polarisation characteristics obtained with Nafion[®] 112 showed a minor improvement, this was countered by a reduction in the activity of the cathode. It has been reported previously that the membrane thickness has a significant impact on water and methanol crossover rates [12, 13]. Accordingly, the increased cathode polarisation obtained with Nafion[®] 112 may reflect more severe polarisation associated with methanol crossover.

However, it should be noted that the extent of carbonation of the electrolyte was not large because the carbonation of the electrolyte was not a rapid process, with copious CO₂ gas evolution observed during operation. Thus a practical DMAFC would operate with replacement of hydroxide electrolyte after many days of operation.

In addition, in the system used, Na⁺ ions cross from the anode and combine with OH⁻ ions produced at the cathode and the resulting NaOH is removed in the cathode condensate. An alternative method of operation

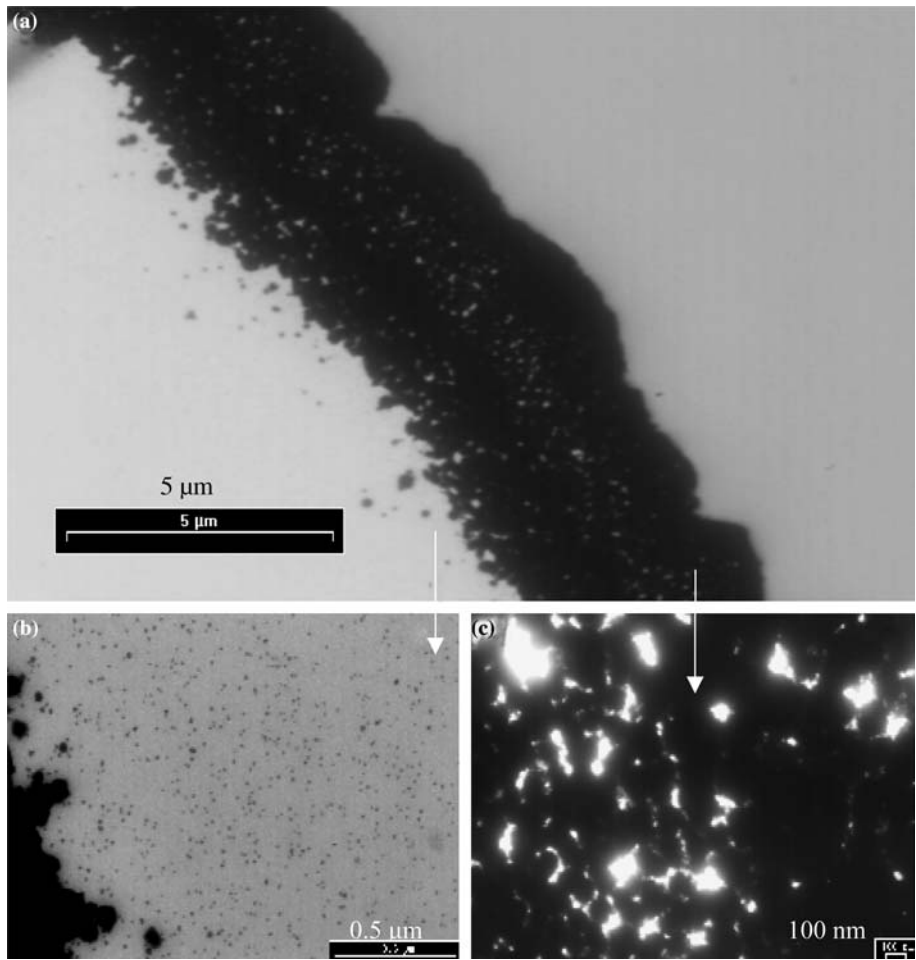


Fig. 10. TEM images of the platinum catalysed Nafion® 117 membrane.

would be to have a third layer of circulating electrolyte between the membrane and the cathode gas diffusion electrode, in which Na^+ ions and OH^- ions combine to

form NaOH , shown schematically in Figure 6. Such a concept of electrolyte circulation has been used in the acid form of the DMFC.

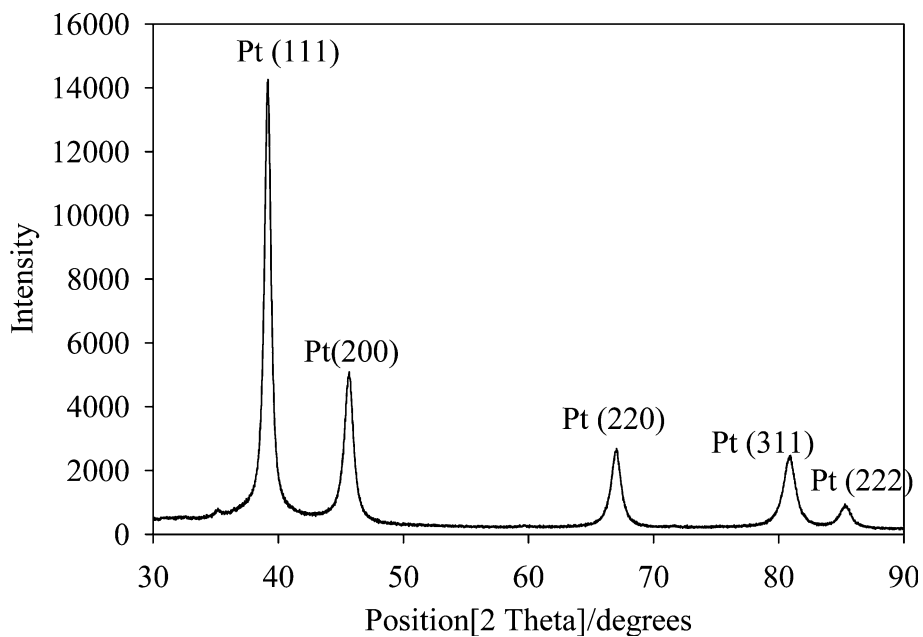


Fig. 11. XRD scan of Platinum catalysed Nafion 117.

3.2. Catalysed Nafion[®] 117 membranes

Figure 7 compares the polarisation characteristics of a platinised Nafion[®] 117 membrane assembly to that obtained with a conventional MEA incorporating carbon supported catalysts. This graph, also shows data from a DMAFC operated with an OH⁻ ion conducting membrane. It is clear that the performance with this membrane is far better than that achieved with the Na⁺ ion conducting membranes. The overall activity of the chemically deposited membrane is clearly lower than that of the conventional system, indicating that further optimisation is required in the deposition procedure in order to provide a higher activity material.

3.3. Characterisation of catalysed membranes prepared by chemical deposition

3.3.1. SEM analysis

SEM analysis was performed to investigate the surface morphology of the deposited platinum. Figure 8 shows a SEM of the surface of a platinum layer that was chemically deposited onto Nafion[®] 117. Despite the appearance of numerous cracks the layer appears as a smooth, low surface area deposit. A cross-section image of the catalysed membrane is shown in Figure 9 from which three distinct platinum layers can be identified. The outer layer appears highly dense, whereas, the inner layers appear more diffuse. Further information on the catalyst layers may be deduced from the platinum distribution across the membrane obtained using energy disperse analysis of X-rays (EDAX) (Figure 9(b)). It was observed that the majority of the platinum was deposited on both surfaces of the membrane and that the amount of platinum decreased towards the centre of the membrane. The low surface area of the deposit, in conjunction with possible blocking of the surface to mass transport, may explain the relatively poor polarisation characteristics shown in Figure 7.

3.3.2. TEM analysis

Further examination of the platinum deposit across the membrane was conducted by TEM and again a solid and compact platinum layer was observed on the membrane surface (Figure 10). The average thickness of this layer was approximately 4 μm , consistent with that observed by SEM. Closer examination of the solid outer layer (Figure 10(c)) showed it to consist of an agglomeration of particles in the range of 90–120 nm.

Inspection of the interior of the membrane showed the presence of a highly dispersed layer of platinum particles (Figure 10(b)), with a total platinum penetration depth of 11 μm . The number of platinum particles within this layer decreased with increasing distance from the membrane surface. The average diameter of the dispersed platinum particles in this region was 11 nm.

3.3.3. X-ray diffraction (XRD) analysis

Further characterisation of the catalysed Nafion was conducted using X-ray diffraction (XRD). The XRD scan (Figure 11) shows typical peaks with Pt features. These Pt peaks suggest that the platinum orientation is random, but that Pt (111) is in a higher proportion than other orientations. The Pt crystallite size was approximately 10 nm, determined by the Scherrer equation calculated from the peak at 2θ of 67° . This is in agreement with the TEM observation.

In view of the above analysis, it is clear that in this particular experiment, the morphology and distribution of the platinum deposit was not optimised for fuel cell operation. Nevertheless, it appears that highly dispersed particles were deposited in the surface region of the membrane and, therefore, scope exists for the production of actively catalysed membranes through further optimisation of the deposition process.

4. Conclusions

A direct methanol alkali fuel cell operating with Na⁺ form Nafion[®] membranes has been demonstrated. In general, the electrochemical activity of the cell was low, reflecting the high ionic resistance of the conduction process and possibly kinetic factors associated with the formation of carbonate species.

A membrane assembly was prepared by chemical deposition of platinum into the surface region of a Nafion 117 membrane. The activity of the catalysed membrane in a DMAFC was lower than that obtained with a more conventional assembly utilising carbon supported catalysts. SEM and TEM analysis showed this to be a consequence of a highly agglomerated and dense surface deposit. Evidence for the production of a highly dispersed platinum deposit was observed, however, this was located within the interior of the membrane. Further optimisation of the deposition process is suggested as a means of improving the fuel cell performance.

The fuel cell performance with Nafion membranes was not satisfactory suggesting that Nafion may not be suitable for DMAFC operation.

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