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Improvement of direct methanol fuel cell performance using a novel mordenite barrier layer

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The selective incorporation of a functionalised inorganic component at the interface between the Nafion membrane and the catalyst is demonstrated to increase the power density of a Direct Methanol Fuel Cell by 57% with no other change in operating conditions. The simple addition of 0.5wt% zeolite (mordenite) in the Nafion 'ink,' which is used as a glue to fix the precast Nafion membrane onto the catalyst/gas diffusion layer, provides an organophobic quality to the MEA which enhances performance and durability. The targeted addition of such small amounts of the 'organophobe' at the interface where the chemical effect is required is a novel approach to improving DMFC MEA's and means that the usual trade-off between methanol permeability and proton conductivity is not observed as proton conductivity is maintained while methanol crossover is reduced.

Introduction

Historically, the major development work for low temperature fuel cells has been carried out on systems using hydrogen as a reactant. From an emissions stand point, this is the most attractive system. However, the storage and infrastructure problems associated with hydrogen have led to greater interest in liquid fuels, and the Direct Methanol Fuel Cell (DMFC) is a potential solution to this problem, as a power source in portable applications such as mobile phones and laptop computers as well as passenger vehicles. In the past, DMFCs have been developed using technology and materials designed and developed for Proton Exchange Membrane (PEM) fuel cells with hydrogen as the fuel, and, consequently, the use of methanol creates a series of problems. Modern DMFCs use polymer membranes as the electrolyte. These are typically solid, hydrated sheets of sulfonated fluoropolymers, as used in conventional PEM fuel cells[1]. These membranes are typically 50-250µm thick and are capable of withstanding high-pressure differentials. Besides functioning as an electrolyte, the membrane also separates the fuel from the oxidant. In hydrogen fuel cells, perflorosulfonic acid membranes perform this role well, but methanol readily transports across these membranes. The permeability of methanol through the Nafion 117 membrane, regarded as the standard in DMFC research, has been measured as 4.9×10^{-6} cm^2/s at 60°C, and increases further with increasing temperature[2].

The power densities achieved by DMFCs are typically an order of magnitude or more lower than those obtained from hydrogen PEM fuel cells. This is partly due to methanol crossover, which leads to increased losses at the cathode; it is also associated with the relatively slow electrochemical kinetics at the anode. However, the anode fuel is typically diluted with water to give a methanol concentration of order 1 M, in order to mitigate the methanol crossover problem.

While the transfer of methanol is much slower than that of water, it is a serious problem in DMFCs. The oxidation of methanol can occur chemically or electrochemically at the cathode and is catalysed by the platinum electrode. In either case, the fuel efficiency of the cell is reduced, as no current is produced. Also the electrochemical oxidation of methanol at the cathode creates a mixed potential, which increases the activation overpotential required to drive the cathodic oxygen reduction reaction.

Strategies involving elevated gas pressure at the cathode have been used to inhibit crossover with some success[4], however, this solution adds complexity and additional balance of plant to the system.

That increased temperature increases the rate of methanol diffusion is not doubted[6], but even at higher methanol concentrations, cell performance is enhanced by increased temperature[7,8]. This is probably a result of reductions in activation overpotentials and lower ohmic losses, due to the increased conductivity of the membrane; these have a more significant effect on the performance than the increased rate of methanol crossover. However beyond 100°C, Nafion 117 has neither sufficient conductivity nor thermal stability to be a suitable DMFC membrane.

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Thin Nafion membranes have advantages due to their increased ionic conductivity. Initially it was thought that the increased methanol crossover would be unacceptable. However, despite decreased open circuit voltages, DMFC performance has been shown to be higher for thinner Nafion membranes[9]. It is postulated that, providing there is sufficient catalyst at the cathode, the methanol can be oxidized chemically, and therefore the total amount of methanol crossover is less significant in generating a mixed potential. The fuel utilisations for the thinner membranes are, however, much lower, due to the increased rate at which methanol is lost through the membrane. A similar effect occurs with membranes of lower equivalent weight, whereby, despite the increased methanol crossover, performance is enhanced at higher current densities, due to the higher conductivity of the membrane.

To summarise, methanol crossover is increased by increasing cell temperature and feed concentration and reduced by increasing cathode pressure, current density, and membrane thickness. However, cell performance at operational current densities is favoured by increased cell temperature, cathode pressure and methanol concentration and by reduced membrane thickness and equivalent weights.

If membranes or Membrane Electrode Assemblies (MEA) structures can be developed which inhibit methanol crossover, the methanol concentration can be increased and losses reduced.

The key to any improved membrane is that it must have low methanol permeability, while simultaneously possessing high proton conductivity. As has been shown for Nafion, most measures that improve the ionic conductivity of perflorosulfonic acid membranes cause a consequent increase in the methanol permeability, and vice versa. Therefore significant progress is only likely to be made by targeted modifications to the membrane electrode assembly rather than simply adding inorganic, organophobic, structures to the Nafion membrane itself.

Some alternative polymer membranes which have been examined include: sulphonated poly (ether ketone) and poly (ether sulfone), polyvinlidene fluorides, styrene grafted and sulphonated membranes. Inclusion of numerous inorganic structures into polymer membranes has been attempted with varying results, usually trading off reduced methanol crossover with reduced ionic conductivity. For example, the zeolite membranes, designed as pervaporation membranes, were examined as possible DMFC membranes[6]. While the material exhibited no permeation to methanol, the cell performance was very poor due to the low conductivity of the membrane. In addition, a range of ceramic materials (clays, etc.) have been used to try to produce an organophobic quality to polymer membranes; this has met with some success, but again at the cost of proton conductivity, since the incorporation of these materials effectively reduces the concentration of the ion conducting polymer thereby inhibiting proton transport.

In all cases of inclusion of inorganic species, the method of incorporation involves the physical mixing of the inorganic with the polymer precursor prior to casting, usually on a glass slide to produce a composite membrane with a random distribution of the inorganic material throughout the membrane. In this study, a novel approach to the incorporation of an organophobic component has been taken which has been shown to significantly improve DMFC performance. This paper reports the targeted addition of very small amounts of an inorganic material in the position in the cell where it can be the most effective. Earlier work involved the incorporation of a zeolite directly into the Nafion membrane by casting a composite[11-13]. This led to a reduction in methanol crossover but at the cost of reduced proton conductivity. This work demonstrated mordenite to be the most effective zeolite for preventing methanol crossover but was not as effective as a pure Nafion membrane in a DMFC.

Here we describe a method developed to introduce a very small quantity of mordenite, to the place where it can be most effective, close to the catalyst layer. By adding mordenite to the binder which is used to bind the catalyst layer to the membrane the addition is in exactly the desired place and shows significant improvement on the standard Membrane Electrode Assembly.

The effect of functionalising the surface of the zeolite using silanisation to provide a better bond with the Nafion polymer as already been demonstrated and hence the concentration of the material in the Membrane Electrode Assembly structure is investigated.

Experimental

Refinement of the inorganic component

Commercially available Na^+-mordenite powder (Na-MOR) was obtained from Zeolyst International (CBV10A). The average particle size is 3.5µm and it is has a Si/Al ratio of 5 which means it is hydrophilic and hence organphobic.

Several samples of mordenite were prepared using a process of ball-milling, protonation, and silanation to aid adhesion to the Nafion. This allowed examination of the effect of this pre-treatment on the efficacy of the barrier layer.

The Zeolyst CBV10A (NaMOR-UG) with an average particle size of 3.5 µm was placed within a ball mill and wet ground for 24 hours, 125 ml of zeolite was added to 125 ml of water and 250 ml of 3 mm diameter stainless steel ball bearings. This was then milled in a 500 ml 7 cm diameter ball mill at 160 rpm. SEM analysis and dynamic light scattering gave an average particle size of the ground mordenite of ~300 nm. XRD analysis showed no generation of amorphous phase during grinding.

The protonation[14, 15] was achieved by mixing 1 g of sodium mordenite with 100 ml of 1M H_2SO_4 for 24 hours, this was then filtered and washed with deionised water followed by drying at 40°C for 24 hours. XRD analysis was used to ensure no loss of crystallinity.

Because of the low Si/Al ratio (5) the surface of the mordenite is organophobic in nature which could produce interfacial incompatibilities with the Nafion matrix (i.e. pinhole formation), which would allow methanol to pass through the

composite material unhindered. This problem can be overcome by functionalising the surface of the mordenite with a silane coupling agent such as (3-mercaptopropyl)trimethoxysilane (MPTS), which is a method that has been used to functionalise several zeolites previously including mordenite[11,12,16,17]. Silanes can form durable bonds between organic and inorganic compounds even when one is siliceous (e.g. zeolites) and are used to modify the inorganic surface to generate heterogeneous environments or to incorporate bulk properties of different phases into a uniform composite structure.

Previous work[11,12,16-19] has proved that the silane functionalising of zeolites increases surface adhesion between the (inorganic) zeolite and the (organic) Nafion, resulting in improved fuel cell performance. Xiao Li et al[11] demonstrated that using the silane coupling agent (3-aminopropyl)triethoxysilane (APTS) reduced the methanol permeability (20%) and proton conductivity (13%) of a zeolite-A/Nafion composite membrane resulting in improved fuel cell performance compared to unmodified zeolite-A. Work by Yoonoo et al[12,17] highlighted the importance of choosing the correct silane. APTS is basic (pH11) due to the amino (R) group, meaning it is not conducive to good proton mobility. Using a silane that is acidic should therefore offer a path which is less resistant to proton transfer[12, 16, 17] and therefore MPTS (pH4) was chosen for use for this study. The method of incorporating the silane is decribed in the work by Yoonoo[12].

Silanation of protonated (H+) Mordenite was mixed with 2ml of silane agent (MPTS) in dichloromethane solution. The mixture was then dried at 40°C overnight, then used in preparing the barrier layer ink.

Synthesis of 'barrier layer'

The Nafion/mordenite composite ink was prepared with a range of weight percent mordenite in the composite layer. The weight of mordenite used in the mordenite ink was only a few micrograms and to ensure the correct mass fraction of mordenite was present, a tenfold dilution was used. The amount of Nafion used in the composition is enough to form a 1 mg cm^{-2} layer on the electrode surface. The ink was prepared using an ink composing 1 ml of acetone/mordenite slurry, 0.1215 g of 20% Nafion (Ion Power, DE2021) and 4 ml of acetone.

The ink was sprayed in 3 ml aliquots onto the anode surface. Each aliquot then underwent heat treatment at 100°C to form a discreet layer. The compositions of the composite layers for each of the finished electrodes are shown in Table 1.

Table 1. the composition of the barrier layer for the novel MEA's examined.

%wt mordenite relative to the dry Nafion 117 membrane	0.25%	0.50%	0.75%	1.00%
mass of mordenite (mg/cm^2) in composite layer	0.09	0.18	0.27	0.36
mass of dry Nafion (mg/cm^2) in composite layer	1.20	1.20	1.20	1.20
%wt mordenite in composite layer	7.04%	13.15%	18.51%	23.25%

Membrane Electrode Assembly preparation

The Membrane Electrode Assemblies (MEA's) were fabricated in house employing (single cell) by spraying carbon ink (Ketjen Black) on a carbon paper (ETEK carbon Toray paper; PTFE treated, 20% wet proof) as a gas diffusion layer giving a loading of $1mg/cm^2$. This was followed by a catalyst layer (platinum loading of $1mg/cm^2$ at the cathode and $1mg/cm^2$ of platinum and $1mg/cm^2$ of ruthenium at the anode) supported on Vulcan XC-72.

A Nafion 117 (DuPont) membrane was pre-treated with hydrogen peroxide and sulfuric acid solutions for activation purposes.

Four MEAs were fabricated which featured anodes with mordenite loading of 0.25%, 0.5%, 0.75% and 1%, expressed as a percentage of the dry weight of the Nafion 117 membrane.

The binder ink was sprayed using a Badger LG100 modellers airbrush at a distance of 2-3 cm, using nitrogen as a propellant, onto the electrode over a surface area of 3 x 3 cm for each electrode. The mordenite ink was agitated with a magnetic stirrer at all times during the spraying process to ensure that the mordenite did not settle out of solution and that the correct ink composition was maintained. Nafion 117 membrane was then sandwiched between the two electrodes and went through hot press at 135°C for 30 minutes. Finally, the composite membrane MEA was placed in the fuel cell and kept overnight under hydration in deionised water.

Electrochemical testing

The DMFC system used to test the MEA's was an in-house designed single cell[13] with an active area of $9cm^2$. The temperature of the tests was varied between 40°C-70°C but the other conditions remained constant: methanol concentration = 1M, 2M and 4M, methanol flow rate = 5 ml/min, air flow rate = 1L/min (at 1 bar gauge), cathode Pt loading = 1 mg/cm^{-2}, anode Pt and Ru loading = 1 mg/cm^{-2}, constant load = 80 mA/cm^{-2}.

Electrochemical impedance spectroscopy (EIS) was carried out to determine the proton conductivity (σ) of the MEA under working cell conditions, i.e. with a methanol feed at the anode and an air feed at the cathode.

Previous work[11] found that the membrane resistance was unaffected by changes to the applied current. The AC impedance measurements were carried out at cell voltage of 0.4V for temperatures of 40°C, 50°C, 60°C and 70°C.

The methanol permeability of MEA's produced was determined using a method described by Ren et al[20]. By preventing the oxygen reaction occurring at the cathode using humidified nitrogen feed to that electrode, the only reaction that can occur at the cathode is the reduction of methanol. By measuring the reaction rate using linear sweep voltammetry, the methanol crossover current can be determined from which the diffusion coefficients can subsequently be calculated. Results obtained using this method has been performed for MEAs both with and without the composite layer.

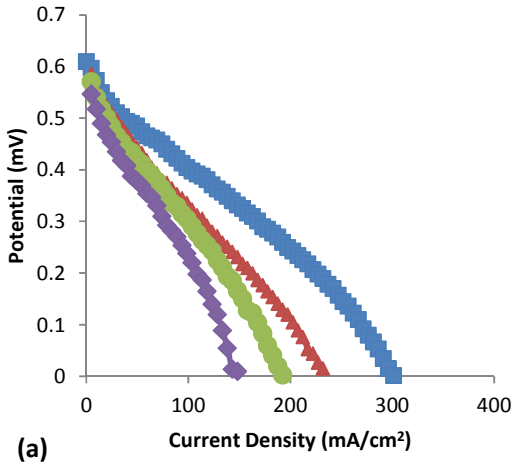
Results and Discussion

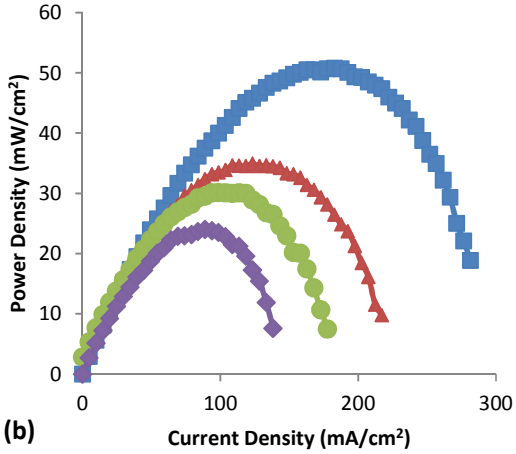
Effect of 'barrier layer' with temperature and methanol concentration

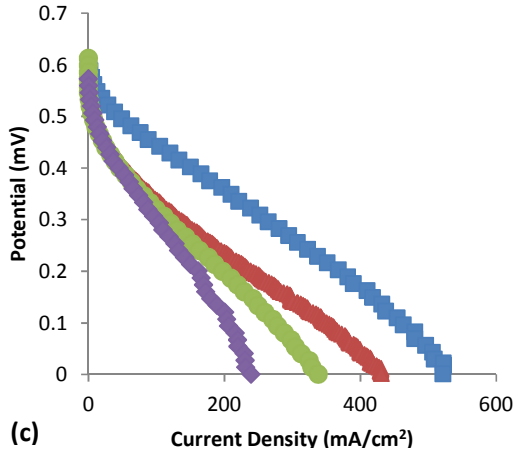
Previous work[12] highlighted that the best results obtained for a composite Nafion/mordenite membrane occurred when the mordenite was first ground, then protonated and functionalised. In this study, the mordenite loading in the composite layer was varied to determine the optimum loading for maximum fuel cell power density, but a constant average particle size of 300nm with MPTS functionalisation and protonation was maintained for all loadings.

MEA's were fabricated using the procedure described and these were tested and compared to an MEA using a standard Nafion 117 membrane (N117) which was prepared using the same procedure without mordenite loading at the anode. Concentrations of 1M, 2M, and 4M methanol were used to conduct the fuel cell tests and all of the MEAs were tested using a temperature range of 40°C – 70°C.

The experimental results showing DMFC performance for an MEA incorporating a functionalised mordenite composite layer with 0.5% loading are shown in Figure 1. for a 1M methanol solution. The summarised results for the other loadings (0.25%, 0.75% and 1% are shown in Figure 2, and indicate that the 0.5% loading is the optimum for maximum fuel cell power density.







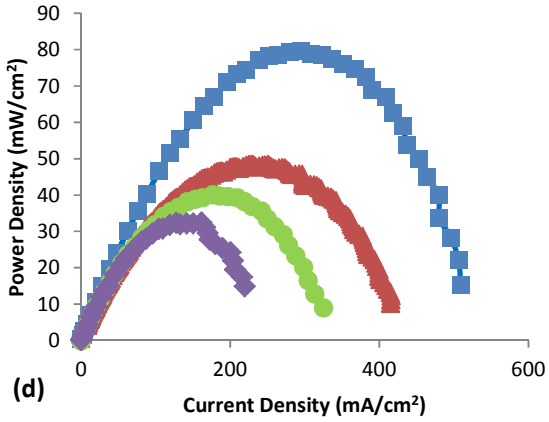


Figure 1. Experimental results showing DMFC performance for a standard Nafion 117 MEA. ■ 70°C, ▲ 60°C, ● 50°C, ◆ 40°C. (a,b) compared with an MEA incorporating a functionalised mordenite composite layer with a loading of 0.5% mordenite (c,d). A 1M methanol feed and operating temperatures between 40°C and 70°C were used. (a and c) Polarization curves (b and d) Power Density curves.

Similar results were obtained at 2M and 4M methanol (the polarization curves and power density curves for these concentrations are displayed in the supplementary data, Figure S1 and S2), and the peak power densities are summarised in Figures 3 and 4.

It is clear from Figures 2, 3 and 4 that at all temperatures and methanol concentrations studied, the MEA featuring the composite layer with 0.5% functionalised mordenite loading out-performed the other MEA's incorporating the mordenite composite layer and the Nafion 117 MEA. When an operating temperature of 70°C was employed the 0.5% mordenite loading MEA had a maximum power density of 80mW/cm^2 which was an improvement of ~60% over the standard Nafion MEA (50mW/cm^2), as shown in Figure 1.

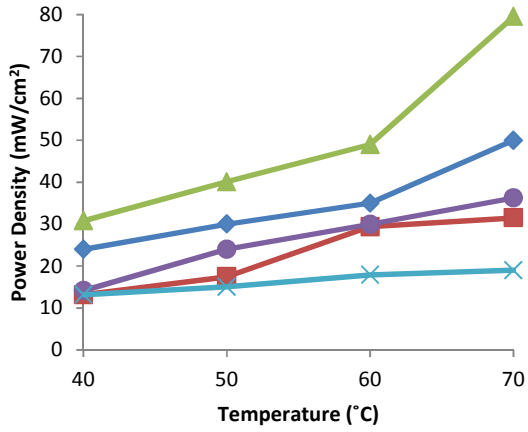


Figure 2. Experimental results showing peak power densities for a DMFC with a 1 M methanol feed. ◆ Nafion 117, ■ 0.25% loading, ▲ 0.5% loading, ● 0.75% loading, ✱ 1% loading, using a standard MEA and MEAs featuring a mordenite composite layer with a range of mordenite loadings (0.25 % to 1.0 %).

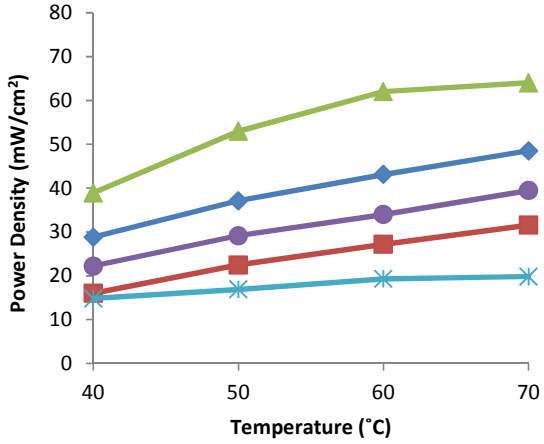


Figure 3. DMFC peak power densities with a 2 M methanol feed. ◆ Nafion 117, ■ 0.25% loading, ▲ 0.5% loading, ● 0.75% loading, ✱ 1% loading using a standard MEA and MEAs featuring a mordenite composite layer with a range of mordenite loadings (from 0.25 % to 1.0 %).

If we assume that the mordenite is acting as an organophobic barrier and plays no part in the conduction of protons through the membrane as it has a proton conductivity 1% of that of Nafion 117, then it is clear that an MEA with 0.5 % wt mordenite using the composite binding layer is the optimum loading to achieve repulsion of methanol while having negligible effect on proton conductivity.

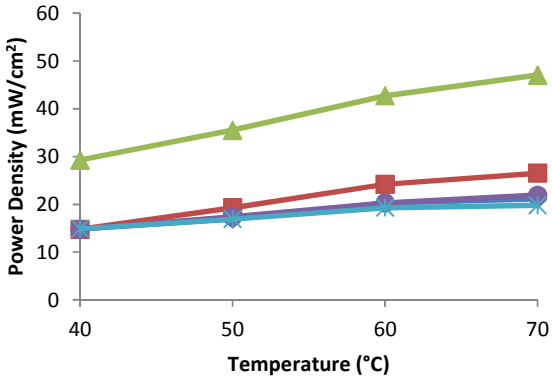


Figure 4. DMFC peak power densities with a 4 M methanol feed. ◆ Nafion 117, ■ 0.25% loading, ▲ 0.5% loading, ● 0.75% loading, ✱ 1% loading using a standard MEA and MEAs featuring a mordenite composite layer with a range of mordenite loadings (from 0.25 % to 1.0 %).

The effect of different concentrations of the zeolite, in terms of peak power density, is summarised in Figure 5 at 1, 2 and 4M methanol concentrations, reinforcing that 0.5wt% of the ground zeolite which was protonated and functionalised gave the best performance as inorganic filler.

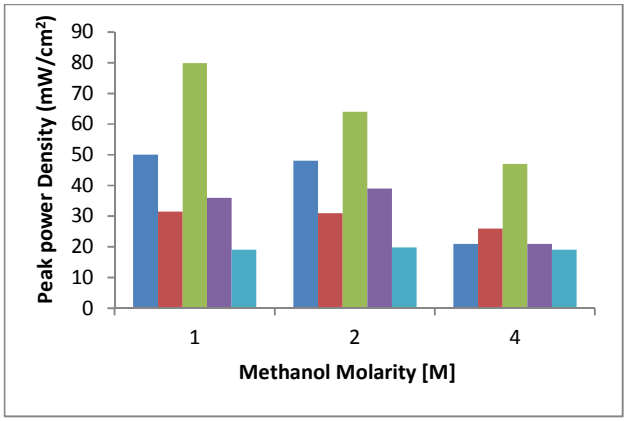


Figure 5. . ■ Nafion 117, ■ 0.25% loading, ■ 0.5% loading, ■ 0.7% loading. and ■ 1% loading. Peak power densities for DMFCs using a range of different MEAs, operating at 70°C with 1M, 2M and 4M methanol feed.

Durability data

The durability of the MEAs was tested over 72 hours and the results are displayed in Figure 6. There was no performance loss in the case of the 0.5% mordenite MEA over 72 hours but

in terms of both potential and power density, the Nafion MEA performance decreased by 4%.

Electrochemical and electron microscopy characterisation

A cross sectional image of the composite layer (0.5% functionalised H-mordenite) sprayed onto the GDL is shown in

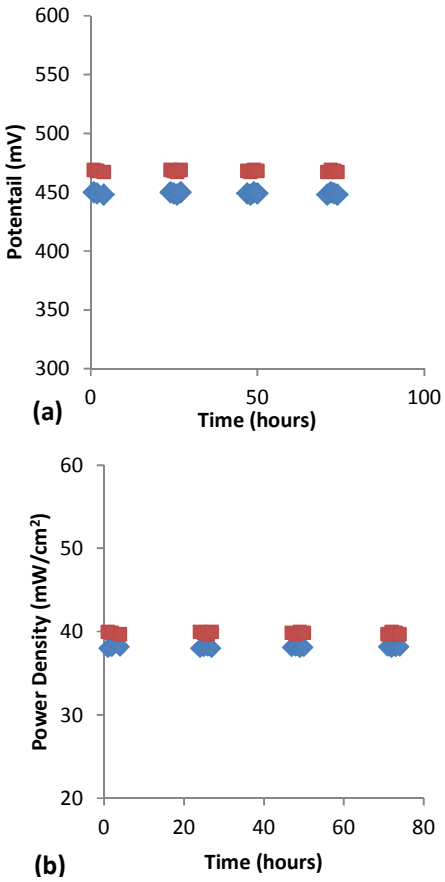


Figure 6. DMFC, ◆ Nafion 117, ■ 0.5% loading (a) potential and (b) power density variation during 100 hour operation using a single cell DMFC operating at 70°C, 1 M methanol feed, and at a current of 80 mA cm^{-2}.

Figure 7, however, the cryogenic fracturing of the system appears to have caused some damage to the layer, Figure 8 shows a cross section of a composite layer sprayed onto a glass slide which has then been cryogenically fractured.

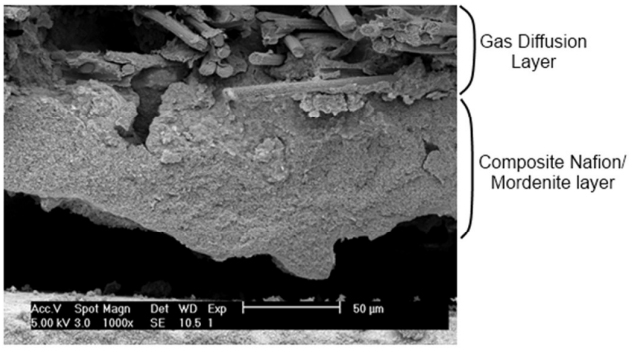


Figure 7. Cross sectional view of a composite layer (0.5% functionalised H-mordenite) on the surface of a gas diffusion layer obtained using scanning electron microscopy of a cryogenically fractured sample.

MEA's with the optimum loading of functionalised H-mordenite (0.5%) were fabricated and tested for proton conductivity within the DMFC using AC impedance spectroscopy. The MEA's were tested at open circuit voltage (OCV), with no external load connected. A methanol feed of 5 ml min^{-1} and an air feed of 1000 ml min^{-1} were used at operating temperatures of 40°C, 50°C, 60°C, and 70°C.

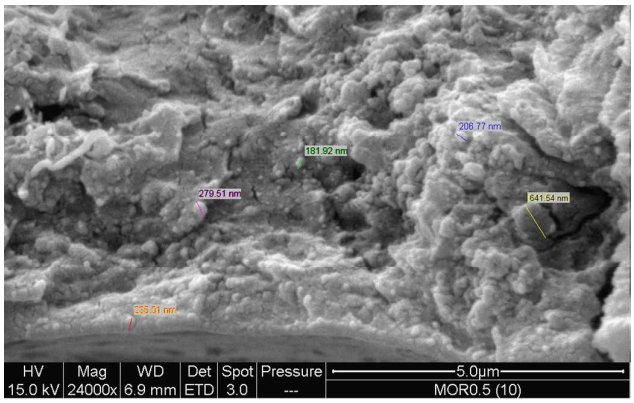


Figure 8. Cross sectional view of a 13.2% mordenite/Nafion composite layer sprayed onto glass, obtained using scanning electron microscopy of a cryogenically fractured sample. (NB This composition would give 0.5% functionalised H-mordenite if part of a complete MEA)

Impedance measurements for an MEA incorporating a standard Nafion 117 membrane indicated a proton conductivity of ~0.10 S cm^{-1} which are comparable to the value obtained by Yoonoo[17]. The proton conductivities measured at 1M, 2M and 4M are shown in figures 9, 10 and 11.

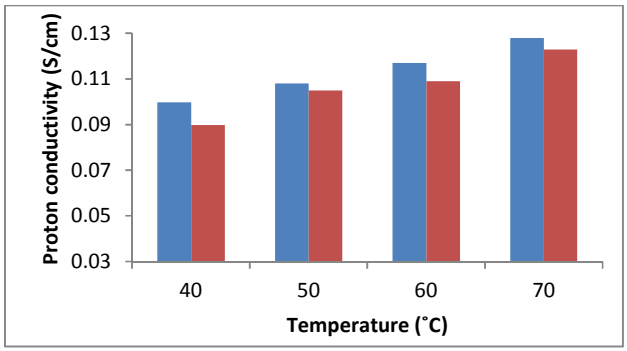


Figure 9. Nafion 117, 0.5% loading. Proton conductivity of MEAs determined using impedance spectroscopy at OCV with a 1M methanol feed at a range of operating temperatures and mordenite loading in the barrier layer.

The proton conductivity of the MEA falls with the addition of the mordenite across all temperatures and methanol concentrations. However, the drop in conductivity at 0.5wt% loading is low (~10%) for all conditions.

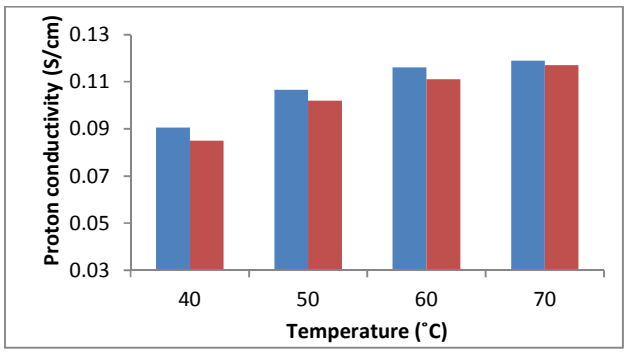


Figure 10. Nafion 117, 0.5% loading. Proton conductivity of MEAs determined using impedance spectroscopy at OCV with a 2M methanol feed at a range of operating temperatures and mordenite loading in the barrier layer.

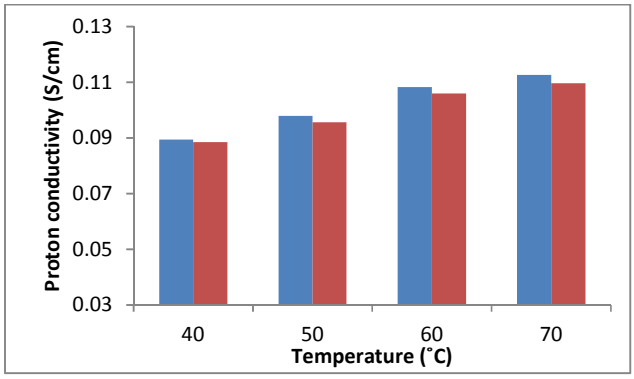


Figure 11. Nafion 117, 0.5% loading. Proton conductivity of MEAs determined using impedance spectroscopy at OCV with a 4M methanol feed at a range of operating temperatures and mordenite loading in the composite layer.

The methanol permeability of the standard N117 membrane and the membrane incorporating the 0.5% functionalised mordenite were determined using linear sweep voltammetry.

The 0.5% functionalised mordenite was selected for this test as it displayed the best DMFC performance in relation to peak power density and the corresponding current density. The crossover current density (j_{lim}) and methanol permeability (ρ) obtained for a fuel cell using a standard Nafion 117 MEA and an MEA with a 0.5% mordenite composite layer at a range of operating temperatures are shown in Figure 12 and 13. The values obtained for both MEAs, under 1M methanol, show that the methanol permeability increased with temperature, but the rate of increase was higher for the standard Nafion 117 MEA in comparison to the MEA using a 0.5% mordenite composite layer. The mordenite/Nafion MEA has methanol permeabilities that are lower than the MEA using Nafion 117 only. The difference becomes more significant (40°C= -3%, 50°C= -2.9%, 60°C= -7.4%, 70°C= -15.8%) as the temperature rises and the driving force for methanol diffusion is increased. This has a significant effect on improving the performance of the DMFC.

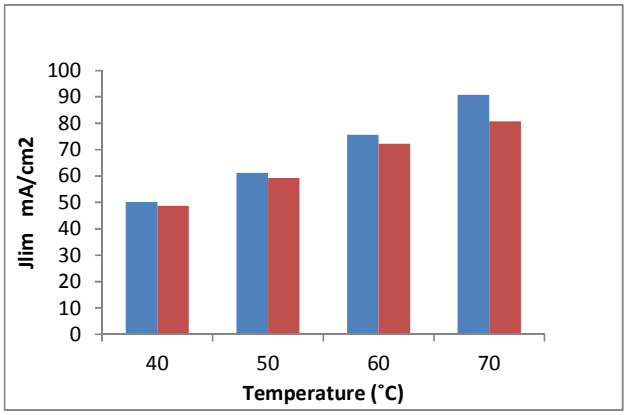


Figure 12. Nafion 117, 0.5% loading. Crossover current density as a function of temperature for a DMFC using a standard Nafion 117 MEA and an MEA containing a 0.5% mordenite with a composite layer.

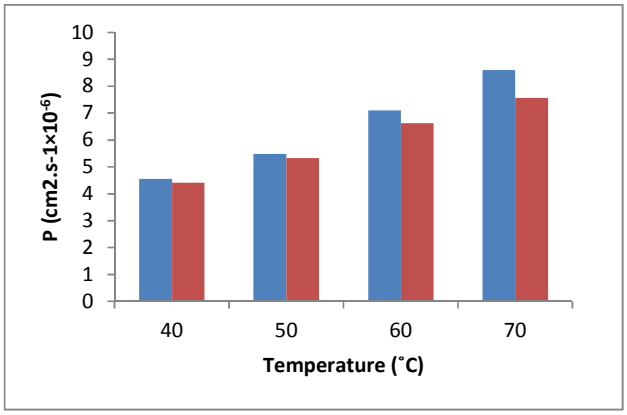


Figure 13. Nafion 117, 0.5% loading. Methanol permeability as a function of temperature for a DMFC using a standard Nafion 117 MEA and an MEA containing a 0.5% mordenite with a composite layer.

Discussion

The composition of the MEA which gave the best DMFC performance was the MEA featuring a composite layer with a mordenite loading of 0.5% (by total weight) which equated to a composition of 13.67% mordenite within the composite layer itself. This MEA had a lower methanol permeability than the standard MEA under all of the DMFC operating temperatures and methanol feed concentrations tested. This offered improvements in power density over a standard Nafion 117 MEA at 70°C of 60%, 33% and 124% using 1M, 2M and 4M methanol feeds respectively. These peak power densities were obtained at current densities that were 66%, 36% and 102% higher than those with the standard MEA.

The best overall DMFC performance is obtained with a loading of 0.5% mordenite and decreases thereafter as the mordenite content is increased within the methanol resistant layer. The passage of both methanol and protons through the MEA should be inhibited because of the low proton conductivity of mordenite, which is only around 1% of Nafion, indicating a different effect influencing the performance of the fuel cell other than the inorganic moiety simply stopping the methanol at the Nafion/mordenite interface and allowing the protons to pass unimpeded.

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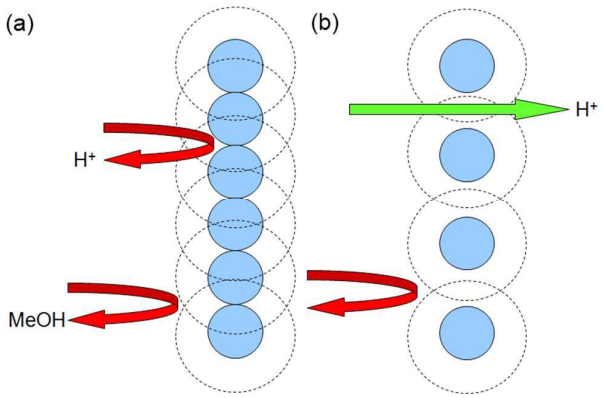

Figure 14 (a) A coherent mordenite layer prevents the passage of protons whereas; **(b)** a dispersed composite structure which features an ideal dispersion of mordenite in Nafion could allow the transport of protons through the Nafion and a sphere of organic influence formed by preferentially absorbed water and/or the repulsion of methanol preventing the flow of methanol into the bulk membrane.

It is likely that the mordenite within the barrier layer improves performance due to a blocking mechanism. When an optimum loading of mordenite is used an aqueous layer is retained at the Nafion/mordenite interface surrounding the inorganic moiety this will allow the passage of protons but partially block the passage of methanol. It is clear from Figures 9 and 10 that at 0.5 % mordenite, the optimum concentration of mordenite has been achieved in terms of the trade-off between a detrimental effect on proton conductivity coupled with a positive effect on reducing methanol crossover.

Figure 14(b) shows an idealised structure for the barrier layer that incorporates a mordenite layer that is dispersed to an extent that a sphere of organophobic influence could repel the methanol without overly prohibiting the passage of protons.

The retention of methanol at the catalyst surface as it is repelled by the mordenite layer also decrease the mass transport losses observed and increases the current density at which the maximum power densities are gained.

Conclusions

In this work we have shown that while organophobic materials do not have good proton conductivity relative to Nafion, if they are dispersed correctly and in the optimum location, they can have a significant effect on methanol permeability without adversely affecting the proton conductivity. The optimisation of the barrier layer depends on the inorganic material and the operating conditions of the cell but for MPTS functionalised mordenite, 0.5 wt% of mordenite as a percentage of the total Nafion in the cell gives a significantly enhanced performance at all measured temperatures and concentrations of methanol. Clearly, a coherent layer of mordenite would have the same (poor) proton conductivity as the zeolite and hence we have suggested a mechanism by which a 'hydrated zone' around the zeolite particles partially excludes methanol without significantly impeding proton conductivity.

It has been shown[21] that the link between methanol permeability and proton conductivity is not linear in that reduction in methanol crossover and proton conductivity do not scale equally. As such, for this system, under these conditions the 'optimum' balance is achieved when 0.5 wt% is used. In this work, the only variable has been the concentration of inorganic material with all other conditions constant for comparison. However, it follows that this approach would also be applicable to other inorganic materials with hydrophilic (hence organophobic) properties but that these would probably need to be optimised, and possibly functionalised, in the same way.

When using a methanol concentration of 4M the power density and current density obtained for this MEA are comparable to the standard MEA using a 1M methanol feed at the same temperature. This would be useful for portable and standalone devices as less fuel would need to be carried for an equal performance. Alternatively, much higher performance under the same conditions may be desirable for some systems.

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Notes and references

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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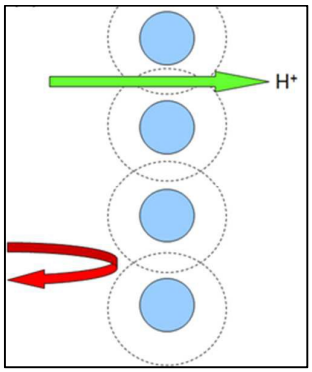
GRAPHICAL ABSTRACT



The targeted addition of an ‘organophobe’ increases the power density of a Direct Methanol Fuel Cell by up to 50%.