

Performance of Liquid Fuels in a Platinum-Ruthenium-Catalysed Polymer Electrolyte Fuel Cell

HIGHER MOLECULAR WEIGHT COMPOUNDS AS FUELS FOR A PEFC

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Crossover and performance of different 1 M low molecular weight organic fuels with a platinum-ruthenium (60:40) catalyst in a unit fuel cell were studied at different temperatures. Large, negatively charged or complicated molecules were found to have the lowest crossover rates through the Nafion[®] 115 membrane, and methanol had the highest permeability at all temperatures. The smallest molecule, formic acid, dissociates in water, resulting in a less severe crossover problem. In a PtRu-catalysed fuel cell, compounds with only one carbon atom exhibit superior performance compared to molecules having a carbon chain; with methanol and formaldehyde producing power densities up to five times higher than those achieved with molecules having a longer carbon chain. However, it should be noted that PtRu does not catalyse the breaking of the C–C bond; therefore, larger molecules can only be oxidised to derivative products. However, larger organic molecules show a lower rate of crossover through the Nafion[®] membrane, which enables more concentrated solutions to be used to decrease the volume of the fuel. With the addition of a third metal to the PtRu-based catalyst, higher molecular weight molecules are good candidates for energy sources in a fuel cell.

Introduction

Polymer electrolyte fuel cells (PEFCs) are promising electrochemical power generators, especially for transport and portable applications. Pure hydrogen or a hydrogen-rich gas is often used as the fuel in order to obtain high electrical efficiency at ambient temperature. However, storage, transport and refuelling are more problematic for a gaseous fuel than for a liquid. If fuel reforming is used, this renders the system even more complex. Therefore, research has recently been focused on the use of hydrogen carriers such as aqueous solutions of small organic solvents, which offer easier storage, improved safety and high energy densities (between 1750 and 7080 Wh l⁻¹ depending on the component) compared to hydrogen gas (180 Wh l⁻¹ at 1000 psi and 25°C) (1).

At present, of the liquid systems, only the direct methanol fuel cell (DMFC) has been widely

studied (2–7). Disadvantages of methanol include its toxicity, high flammability and tendency to permeate through the widely-used Nafion[®] membrane – a phenomenon known as ‘crossover’. However, several other organic fuels that possess higher boiling points and lower crossover rates than methanol have shown promising preliminary results (8–13).

At low temperatures, Pt nanoparticles are widely used as catalyst materials for organic fuels in the fuel cell anode. However, pure Pt catalysts only extract the hydrogen atoms from the carbon chain. They cannot cleave the carbon–carbon bond or oxidise the carbon–oxygen bond at the range of potentials normally encountered in a liquid-fuelled fuel cell. Therefore, Ru is added to offer a possible catalyst site for water to decompose to hydrogen and hydroxyl (OH) groups at lower potentials (6, 14), enabling the organic fuel to be oxidised completely to carbon dioxide.

The aim of the present study is to compare the behaviour of different liquid fuels for a PtRu (60:40) catalysed PEFC. The chosen fuels are all short-chained carbon compounds. The crossover rates of the fuels through the commonly used Nafion[®] 115 (N-115) membrane were explored, followed by their performance in a PEFC with a Nafion[®] 115 membrane as the electrolyte.

Measurement Conditions and MEA Preparation

The solutions used were prepared from methanol (Fluka, p.a.), formaldehyde (Merck, p.a.), formic acid (Riedel-de Haën, p.a.), ethanol (Altia, Grade A), acetaldehyde (Merck, p.a.), 1-propanol (Merck, extra pure), 2-propanol (Merck, p.a.), ethylene glycol (Aldrich, 99.89%), glycerol (Fluka, p.a.) and ultrapure water (Milli-Q[®] (MQ), Millipore, 18.2 M Ω cm).

To observe the crossover phenomenon with as few variables as possible, the crossover experiments were performed in a two-compartment diffusion cell. The Nafion[®] 115 membrane was pressed between the two compartments, then one side of the cell was filled with a 1 M solution of the fuel and the other with deionised water. 30 μ l samples were taken every 10 min for 60 min and were analysed with a gas chromatograph (HP 6890 GC) using an HP Innowax column at a heating rate of 5°C min⁻¹. An internal standard of 10 μ l of 1,4-dioxane was added to each sample.

The membrane electrode assembly (MEA) was made by spraying a mixture of 2 mg cm⁻² catalyst

powder (anode: Pt:Ru (60:40) on Vulcan XC-72 carbon (40%); cathode: Pt on Vulcan (40%)), Nafion[®] liquid ionomer (5 wt.%, Aldrich) and 2-propanol on the surface of the Nafion[®] 115 membrane. After spraying both sides, the MEA was hot pressed at a temperature of 130°C and a pressure of 50 kN for 2 min.

All measurements were performed in a fuel cell with an active area of 7.26 cm². The 1 M liquid fuels were fed to the anode compartment at room temperature at a rate of 1.5 ml min⁻¹, and the gas (Instrument Oxygen 5.0, AGA) to the cathode at 270 ml min⁻¹. The cell was allowed to stabilise overnight (liquid fuel 0.2 ml min⁻¹ and oxygen 30 ml min⁻¹ at 30°C) before the measurements were taken. Prior to each fuel change, the cell was rinsed with MQ-water for 2 h. All measurements were made at temperatures of 30°C, 50°C and 70°C.

Fuel Cell Efficiency and Crossover Rates

The results obtained show that fuel cell efficiency, defined as current density at a particular cell voltage, is temperature-related. Fuel cell efficiency increases with increasing temperature for all the fuels tested, as shown in Figure 1 for a DMFC. However, the crossover rate also increases with temperature, as shown in Figure 2. Figures 1 and 2 present the behaviour of methanol; the results for the other fuels are similar.

Increasing the temperature of the DMFC from 30°C to 50°C increases the fuel cell efficiency by

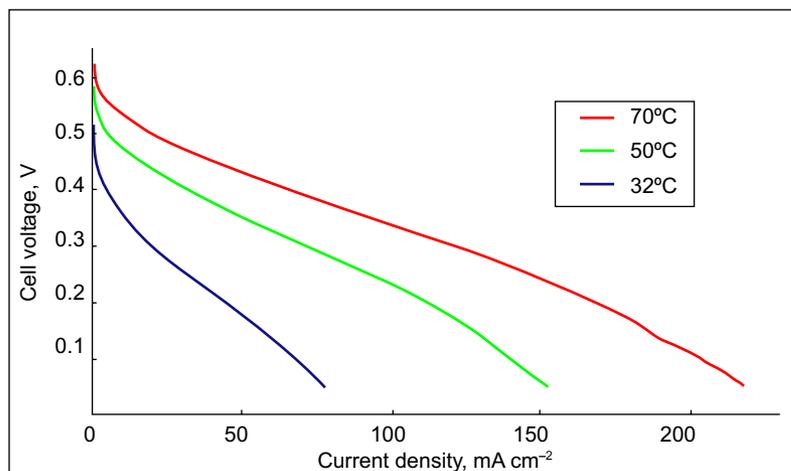


Fig. 1 Effect of temperature on the efficiency of the direct methanol fuel cell (DMFC)

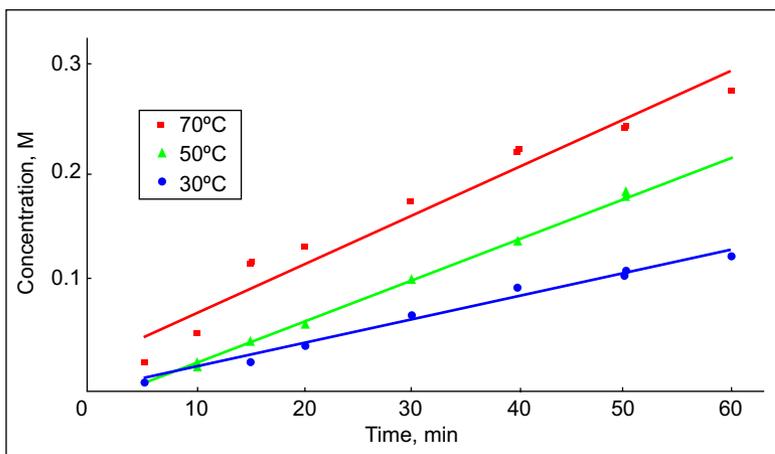


Fig. 2 Effect of temperature on the crossover of 1 M methanol through the Nafion® 115 membrane

96%, and from 50°C to 70°C by 43% (Table I). This is due to the faster electrode kinetics at the anode and the cathode when the temperature is increased. For other fuels, a temperature change from 30°C to 50°C leads to an increase in efficiency of between 36% and 109%, while an increase from 50°C to 70°C increases efficiency by 31% to 77% (Table I). The open circuit potential (OCP) of the fuel cell represents the difference in potential between the anode and the cathode when there is no external current flow. This also shows a slight increase when the temperature is raised, but this phenomenon is

related to the catalyst material of the electrodes and the fuel used. Therefore, only the OCP for each fuel at 50°C is presented in Table I.

Raising the temperature also increases the fuel crossover from the anode to the cathode (Figure 2). Changing the temperature from 30°C to 70°C more than doubles the amount of methanol being transported to the cathode, causing a decrease in fuel cell performance. The crossover rate of the fuel depends not only on the temperature but also on the fuel and membrane used (15). Crossover through the Nafion® 115 membrane during the

Fuel	Number of carbons in chain	OCP at 50°C, V	Increase in fuel cell efficiency with temperature, %	
			From 30°C to 50°C	From 50°C to 70°C
Methanol	C ₁	0.58	96	43
Formaldehyde	C ₁	0.57	79	43
Formic acid	C ₁	0.64	36	32
Ethanol	C ₂	0.53	73	49
Acetaldehyde	C ₂	0.54	54	77
Ethylene glycol	C ₂	0.46	109	76
1-Propanol	C ₃	0.44	63	50
2-Propanol	C ₃	0.81	55	48
Glycerol	C ₃	0.44	107	31

* All measurements were carried out at a potential of 0.05 V

first 60 minutes in the diffusion cell at 25°C is presented for all the studied fuels in Figure 3. The crossover information for formic acid and glycerol was not included because of very low crossover for these fuels and the difficulty of analysing very small volumes of dilute formic acid samples.

Figure 3 demonstrates that methanol, being a small and neutral molecule which behaves similarly to water, permeates easily through the membrane. This results in losses in fuel cell efficiency. In contrast, formaldehyde, an even smaller molecule, has a lower crossover rate, due to the formation of methylene glycol with water (16) which due to its larger size permeates less easily through the Nafion[®] 115 membrane.

Permeability of alcohols through the membrane decreases with increasing size and complexity of the molecule, which justifies the interest in higher alcohols. Even though the crossover of ethanol and 2-propanol is not as severe as that of methanol, these fuels have shown a tendency to swell the membrane, influencing the MEA structure (17, 18). This results from the fact that the alcohols replace water molecules in the proton conducting membrane, decreasing the mobility of the protons, which increases electrolyte resistance. As shown in Figure 3, for most fuels the crossover through the Nafion[®] 115 membrane at 25°C over 60 minutes is linear, but for 1-propanol and ethylene glycol the crossover increases sharply after 30 minutes. This fact strongly supports the idea that these larger organic molecules might interact

with the membrane, causing changes to the membrane morphology.

Open Circuit Potentials with Different Fuels

For all the fuels, the theoretical OCP can be calculated from thermodynamic values. For the fuels studied, the calculated OCP values lie between 1.00 V and 1.25 V under standard conditions. However, in real processes, the OCP is substantially lower due to mixed potentials caused by fuel crossover lowering the total potential of the cathode, and activation overpotentials caused by surface phenomena at both electrodes.

Figure 4 shows that the observed OCP of a PtRu-catalysed fuel cell lies between 0.4 V and 0.6 V at 50°C for all the fuels tested except 2-propanol, which produces a higher OCP of 0.8 V (Table I), in accordance with previous results (13, 18). The high OCP of 2-propanol is presumably the result of two different phenomena. Firstly, 2-propanol has a low crossover rate through the Nafion[®] 115 membrane (Figure 3), resulting in lower cathode overpotentials. Secondly, when the OH-group is situated on the central carbon atom of the molecule, the electronegative oxygen draws electrons from the carbon, which then attracts electrons from the C–C bonds. This changes the adsorption of the molecule to the catalyst surface, which leads to a different oxidation path to that seen for primary alcohols. This causes lower overpotentials at the anode, again resulting in a higher OCP.

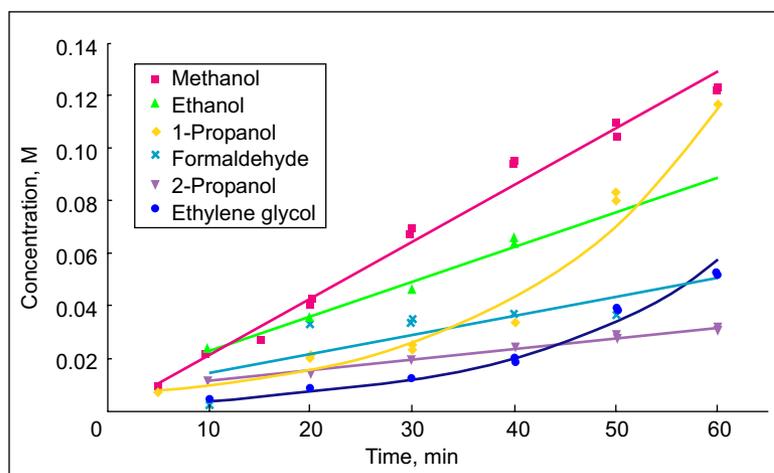


Fig. 3 Crossover of one-, two- and three-carbon fuels through the Nafion[®] 115 membrane at 25°C

Another fuel also reaches slightly higher overpotentials than other alcohols and aldehydes. Formic acid produces an OCP of 0.64 V (Table I). Formic acid has previously been shown to have a very small crossover through cation exchange membranes, due to the anionic nature of the dissolved molecule (19). Formic acid has also shown higher electrochemical activity compared to methanol (20). These phenomena would be expected to result in a higher OCP than that seen for light alcohols with high crossover rates.

The lowest OCP values (under 0.5 V) are attained with 1-propanol, ethylene glycol and glycerol (Table I). The low OCP of 1-propanol is probably caused by the dramatic increase in 1-propanol crossover after the fuel has been in contact with the Nafion[®] 115 membrane for 40 minutes (Figure 3). The OCP values of ethylene glycol and glycerol are around 0.1 V lower than those of methanol and ethanol. It is reasonable to assume that this is due to the OH-groups connected to every carbon atom in the diol and triol, changing the adsorption mechanisms on the PtRu surface.

Performance of One-Carbon Fuels

Figure 4 shows that organic molecules containing only one carbon atom are superior fuels for the PtRu-catalysed fuel cell, producing current densities at least three times higher than larger molecules. The difference between methanol and formaldehyde performance is surprisingly minor.

Methanol has a higher energy density and a higher OCP, therefore it might have been expected to offer better performance. The observed result indicates that the performance loss when using methanol as a fuel is significant, likely due to severe methanol crossover. Investigation of new membrane materials to decrease methanol crossover may eventually lead to increased OCP and improved efficiency of the DMFC.

Formaldehyde exhibits a much lower crossover than methanol and performs better at lower current densities, but when higher current densities are reached, its performance declines gradually. As mentioned earlier, formaldehyde forms methylene glycol in water, and this greatly increases the size of the reactant. At the high current densities as the reaction rate increases, neither the products nor the reactant are able to diffuse from or to the surface fast enough, causing a rapid decrease in performance starting from 90 mA cm⁻² (Figure 4). Therefore, the rate determining step for formaldehyde seems not to be the electrode kinetics as is the case for methanol.

The smallest one-carbon molecule, formic acid, produces roughly half the current density of the other C₁ fuels, even though the crossover of formic acid is nearly negligible. However, when using a more concentrated solution, formic acid performs better because the current density rises with more concentrated solutions, which is not the case for alcohols (19).

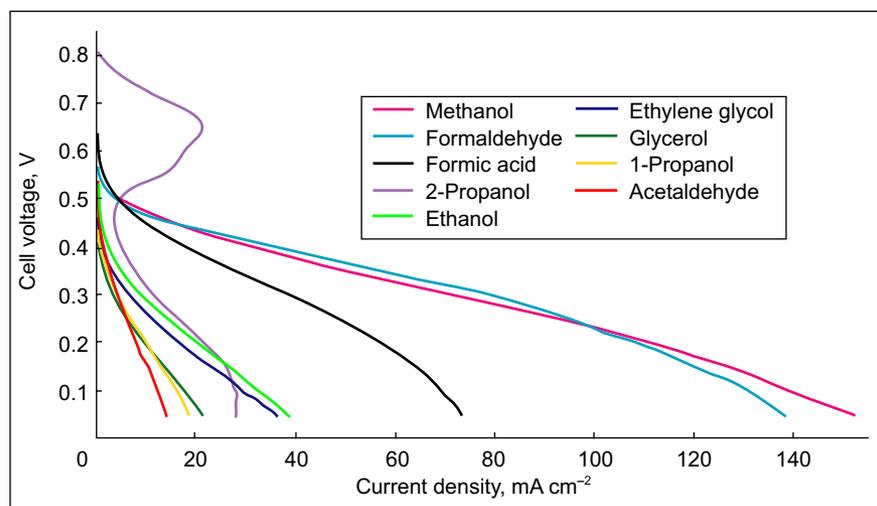


Fig. 4 The efficiency of the investigated one-, two- and three-carbon liquid fuels in a single cell at 50°C

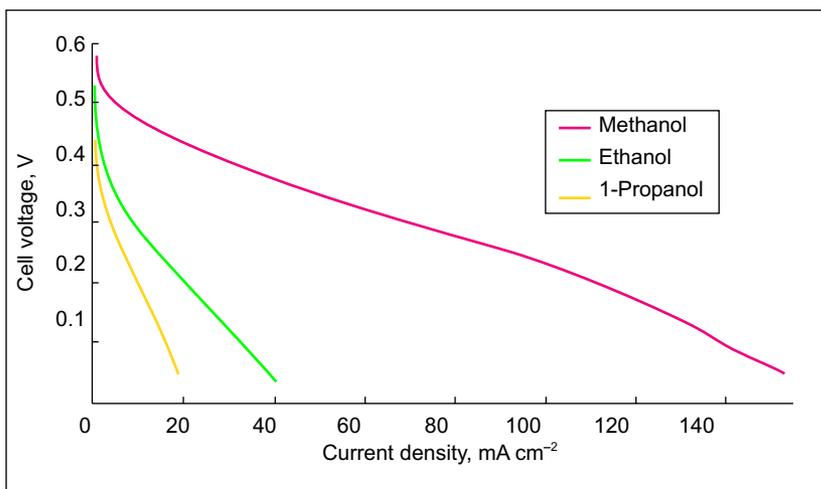


Fig. 5 Comparison of the efficiency of primary alcohols in a single cell at 50°C

To explore more carefully the effect of the length of the carbon chain in the fuel, the performances of the studied primary alcohols are presented in Figure 5. This figure illustrates that current density with methanol is more than three times higher than has been obtained with ethanol, and up to seven times higher than with 1-propanol. The longer the carbon chain, the lower the performance. This is due to partial oxidation of molecules with several carbon atoms, which is not seen in one-carbon molecules. These results are in accordance with a previous study (21), suggesting that the PtRu catalyst cannot effectively dissociate the C–C bond. However, it is clear that PtRu is an excellent catalyst for C₁ fuels at low temperatures.

Performance of Two- and Three-Carbon Fuels

In contrast to the case of C₁ molecules, ethanol shows more than double the current densities measured for its corresponding aldehyde, acetaldehyde, even though the OCP values of the two fuels remain nearly identical (Figure 6). This indicates that at low temperatures on the PtRu electrode, oxidation of ethanol and acetaldehyde stops at acetic acid, which is not oxidised further. Therefore, acetaldehyde displays inferior performance to ethanol. Experiments with acetic acid as a fuel gave such poor performance that the data have been excluded from this study. The other C₂ alcohol, ethylene glycol, performed in an almost identical way to ethanol, despite the fact that the

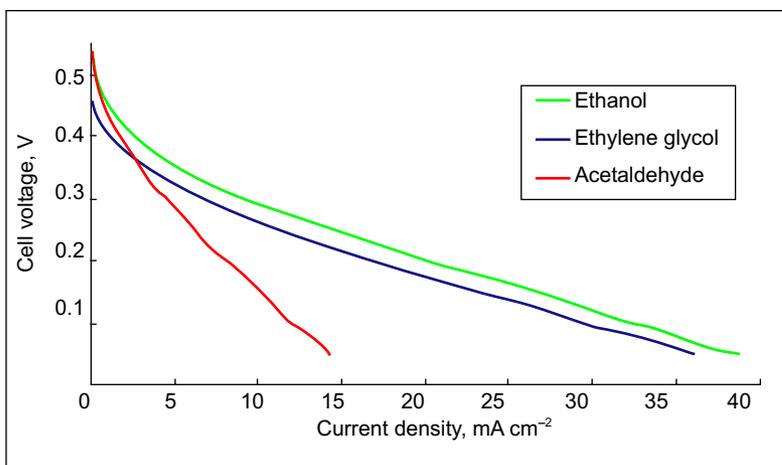


Fig. 6 Comparison of the efficiency of C₂ fuels in a single cell at 50°C

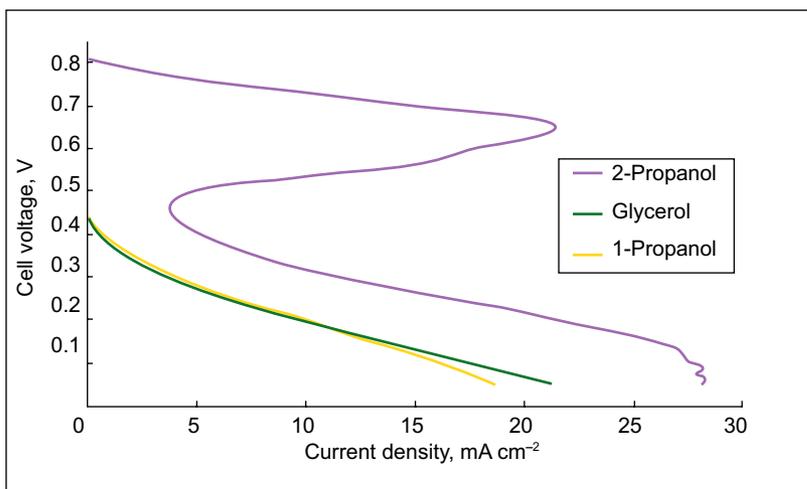


Fig. 7 Comparison of the efficiency of C_3 fuels in a single cell at $50^\circ C$

OCP of the former molecule was nearly 0.1 V lower. This indicates that the electrode processes of ethylene glycol differ from those of ethanol. Further studies need to be carried out to determine specific reaction mechanisms.

Figure 7 shows the performance of C_3 alcohols in terms of fuel cell efficiency. Similarly to the C_2 alcohols, the primary alcohol (1-propanol) and glycerol perform equally. However, in this case the primary alcohol also has a low OCP. These C_3 alcohols produce roughly half the current density of C_2 alcohols. Furthermore, the polarisation curve of the secondary alcohol 2-propanol behaves differently to that of the other compounds. Firstly, the OCP of 2-propanol is very high at 0.81 V, which is almost 0.3 V higher than that measured

for methanol. Secondly, even at low current densities, 2-propanol reacts to form an intermediate, most likely acetone (22), which does not undergo further oxidation but remains at the surface, impeding the adsorption of 2-propanol. Therefore, when a current density of 20 mA cm^{-2} is reached, the surface of the catalyst is completely blocked by this intermediate, resulting in a rapid drop in current. At lower potentials, around 0.5 V, the intermediate either desorbs into the solution, allowing 2-propanol to adsorb on to the catalyst sites, or is oxidised further.

In contrast to our results, two separate research groups have reported fuel cell performances for 2-propanol involving no rapid current drop (13, 18). However, Qi *et al.* (13) also conclude that

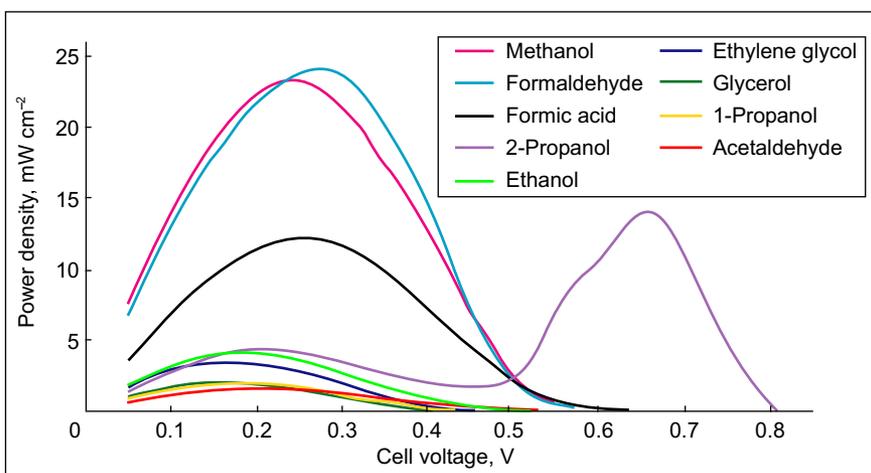


Fig. 8 The power densities of all the investigated one-, two- and three-carbon fuels in a single cell at $50^\circ C$

the electrode surface of the PtRu catalyst is being poisoned with intermediates of 2-propanol oxidation and suggest a periodic cleaning of the surface by an electrical pulse.

Power densities of the fuels can be calculated from the cell voltage and current density (Figure 8). The highest power densities were reached with C₁ fuels, providing almost five times more power than fuels with a carbon chain. Almost all the fuels studied have their power density maximum between 0.15 V and 0.3 V. However, 2-propanol produces an additional power density peak at a potential of 0.66 V. Even though 2-propanol cannot produce higher power density than C₁ fuels (due to the catalyst used), it can still provide the highest power density of the fuels containing a carbon chain at 0.22 V.

Fuel Choice for a PtRu-Catalysed Fuel Cell

The results found during this study are in agreement with previous work by several groups (6, 23, 24) showing that a PtRu catalyst performs best for methanol and other C₁ fuels. The crossover of methanol is the most severe of all the organic components studied. Methanol also produces the highest current density when used with a PtRu catalyst, therefore much research on DMFCs has concentrated on the development of impermeable electrolyte materials. However, the highest power density is produced by formaldehyde, which also seems to oxidise completely on the PtRu surface. Formaldehyde exhibits a lower crossover than methanol through the Nafion[®] 115 membrane, therefore it may be another possible candidate fuel for use in a PEFC.

Formic acid produces only half the current density of other C₁ fuels, even though it has the lowest crossover rate through the Nafion[®] 115 membrane and therefore, the highest OCP of the C₁ fuels. Formic acid has shown promising results when used in a fuel cell at high concentrations, even as high as 12 M (19). On the other hand, the PtRu catalyst appears not to be the optimum catalyst material for formic acid oxidation. Palladium-based and platinum-bismuth catalysts have both shown higher performances than the PtRu catalyst (25, 26).

Unfortunately, the PtRu catalyst shows no activity towards breaking the C–C bond, resulting in only partial oxidation of fuels with carbon chains. To improve the performance of the oxidation reaction for organic molecules with higher molecular weight, a second or third metal must be introduced with the Pt catalyst. For instance, tin alloyed with Pt has shown promising results towards ethanol oxidation (27, 28). Electrooxidation kinetics for organic molecules with higher molecular weight are extremely complicated and difficult to control. However, their crossover through the Nafion[®] 115 membrane is low and therefore they are interesting candidates and worthy of further study.

Of all the investigated organic molecules with a carbon chain, 2-propanol exhibits the most interesting results, producing the highest OCP and power density. However, there remains a problem with the formation of an intermediate which blocks the catalyst surface at higher current densities, causing a rapid drop in current. Further work is needed to characterise this intermediate and prevent its formation. Nevertheless, of the fuels tested in this study, 2-propanol appears to be the only light organic compound containing more than one carbon atom that has an appropriately high OCP. Therefore it would be an interesting focus for further research.

Conclusions

This paper presents the main features of temperature dependence, crossover and fuel cell efficiency for different fuels oxidised using a PtRu catalyst in a fuel cell. When the temperature of a fuel cell is increased, the performance increases. However, at the same time more fuel is transferred from the anode to the cathode compartment through the membrane. This crossover depends on the size and the charge of the fuel molecule, as well as the concentration of the fuel solution. Therefore, organic compounds with high molecular weight might offer a solution to the crossover problem.

Acknowledgements

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