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Short communication

Formulating liquid ethers for microtubular SOFCs

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Abstract

One of the key problems of applying solid oxide fuel cells (SOFCs) in transportation is that conventional fuels like kerosene and diesel do not operate directly in SOFCs without prereforming to hydrogen and carbon monoxide which can be handled by the nickel cermet anode. SOFCs can internally reform certain hydrocarbon molecules such as methanol and methane. However, other liquid fuels usable in petrol or diesel internal combustion engines (ICEs) have not easily been reformable directly on the anode. This paper describes a search for liquid fuels which can be mixed with petrol or diesel and also injected directly into an SOFC without destroying the nickel anode. When fuel molecules such as octane are injected onto the conventional nickel/yttria stabilised zirconia (Ni/YSZ) SOFC fuel electrode, the anode rapidly becomes blocked by carbon deposition and the cell power drops to near zero in minutes. This degeneration of the anode can be inhibited by injection of air or water into the anode or by some upstream reforming just before entry to the SOFC. Some smaller molecules such as methane, methanol and methanoic acid produce a slight tendency to carbon deposition but not sufficient to prevent long term operation. In this project we have investigated a large number of molecules and now found that some liquid ethers do not significantly damage the anode when directly injected. These molecules and formulations with other components have been evaluated in this study. The theory put forward in this paper is that carbon–carbon bonds in the fuel are the main reason for anode damage. By testing a number of fuels without such bonds, particularly liquid ethers such as methyl formate and dimethoxy methane, it has been shown that SOFCs can run without substantial carbon formation. The proposal is that conventional fuels can be doped with these molecules to allow hybrid operation of an ICE/SOFC device.

Keywords: Microtubular SOFC; Ether fuels; Carbon deposition on anode; Hybrid ICE/SOFC

1. Introduction

Present-day fuels, such as gasoline, kerosene or diesel, have largely been developed for internal combustion engines (ICEs) and are specified by octane or by cetane numbers which depend on ignition and oxidation characteristics. Fuels have not yet been specifically defined for solid oxide fuel cells (SOFCs), which demand electrochemical reactivity on catalytic anodes. Consequently there is a problem when standard fuels are used in an SOFC because the fuel cell power drops to near zero in a few minutes under ordinary circumstances when normal fuels like gasoline are injected directly into a fuel cell anode [1,2]. An extensive literature on this effect exists, explaining the anode destruction in terms of carbon deposition on the nickel [13].

Because SOFCs operate between 600 and 1000 °C, they have potential to utilise hydrocarbons such as methane or natural gas and liquid fuels such as gasoline and kerosene [3,4]. However, the commonly used nickel/yttria stabilised zirconia (Ni/YSZ) anode tends to block with carbon when hydrocarbons are used, although steam reforming or partial oxidation can alleviate this problem [5,6]. It has been established that certain molecules without C–C bonds such as methane, methanol and methanoic acid deposit much less carbon on the nickel/zirconia than longer chain C–C molecules like octane and therefore can be used directly in an SOFC [6,7]. The purpose of this paper is to extend that study of gases, alcohols and organic acids to include ethers and more complex potential fuel molecules. In particular we show that molecules containing no C–C bonds such as methyl formate or dimethoxy methane are interesting liquid fuels for direct injection into SOFCs [8]. This suggests that a hybrid internal combustion engine (ICE) could run on a hybrid fuel such as diesel doped with the ether, which could be separated to operate the SOFC. One way in which this could be achieved

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would be to take the volatile ether from the head space in the fuel tank to drive the SOFC [9]. Methyl formate boils at 32 °C and dimethoxymethane at 42 °C, giving a high concentration of ether in the tank headspace compared to diesel fuel which boils above 200 °C.

2. Experimental

Microtubular SOFCs are extremely useful for fuel testing as they are simple to manufacture and have rapid start-up times. The cells used were 2 mm in diameter and comprised a 200 μm thick yttria-stabilised zirconia electrolyte (the white material) to provide mechanical support, a nickel anode and lanthanum strontium manganite cathode (shown in black). The cell length was 20 mm and the total electrolyte length was 55 mm. A silver wire was used to pick up the cathode current and a nickel mesh was inserted down the tube and sealed at the exhaust end as shown in Fig. 1 to collect the anode current.

The microtubular SOFCs were manifolded into drilled Macor® blocks to allow simultaneous exhaust gas analysis and electrical measurements. Gas analysis was done via on-line quadrupolar mass spectrometry: electrical measurement via a datalogging potentiostat.

As shown in scheme of Fig. 2, single phase liquid fuels were delivered by a stepper motor-driven syringe and evaporated at 300 °C before entering the SOFC at 850 °C. Dry helium at 25 ml min^{-1} was used as a carrier gas. The anode was reduced from NiO to Ni at 850 °C for 15 min under a stream of hydrogen before any fuel was added, and experiments were typically run for five hours.

In this project, about 100 formulations were tested in the microtubular SOFC for electrical performance and carbon deposition. The objective was to search for molecules, structures and mixtures which gave low carbon damage to the nickel cermet anode. Two molecules containing no C–C bonds, methyl formate and dimethoxy methane, were found to give much less carbon than expected and these were then tested for comparison with ethanol/water mixtures. The carbon deposition was then measured by temperature programmed oxidation (TPO) to give a sensitive measure of the blocking of the anode. Low carbon deposition, less than 1% of carbon in the inlet fuel, has been shown to lead to good SOFC operation [5], whereas most hydrocarbon fuels deposit 95% of their carbon under direct injection conditions on a Ni/YSZ anode. The results were compared with 1/1 ethanol/water mixtures which had previously been shown to operate successfully in SOFCs [6].

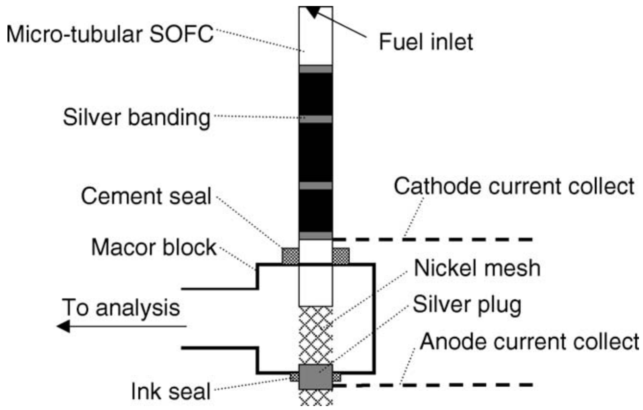

Fig. 1. Arrangement for cell connections.

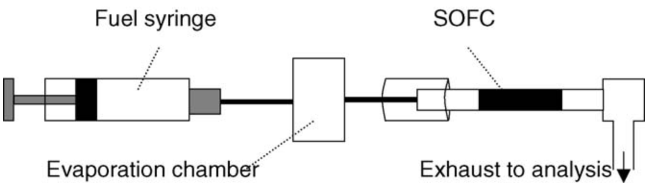

Fig. 2. Injection of liquid fuel into the SOFC.

The selected molecules were then tested in a diesel engine experiment to determine whether a fuel could be formulated to run a diesel ICE/SOFC hybrid vehicle. To carry out an engine test, the pure molecule was added to standard biodiesel at several proportions ranging from 1% upwards. A single cylinder diesel engine was run on standard biodiesel for 5 min and then the fuel was suddenly switched to the ether mixture. The sound of the engine was monitored to detect any change in the combustion as the fuel mixture was introduced. After running the engine for a further 5 min, the fuel was switched back to standard biodiesel and any further change in engine noise detected.

3. Results

Out of the almost 100 molecules and formulations tested, a wide range of electrical performance data were recorded. Selected data are shown in Fig. 3 to illustrate the two types of behaviour observed. Certain molecules like glycerol and *N*-methyl methanamide gave a rapid drop in current with time when injected directly onto the nickel cermet anode. Other molecules like methanoic acid gave performance similar to hydrogen, showing nearly steady current with time over periods of several hours.

From these experiments, it was clear that certain molecules like methyl formate gave much less anode damage than expected in SOFC operation. Therefore, these molecules were selected for special scrutiny. A typical result comparing microtubular cell

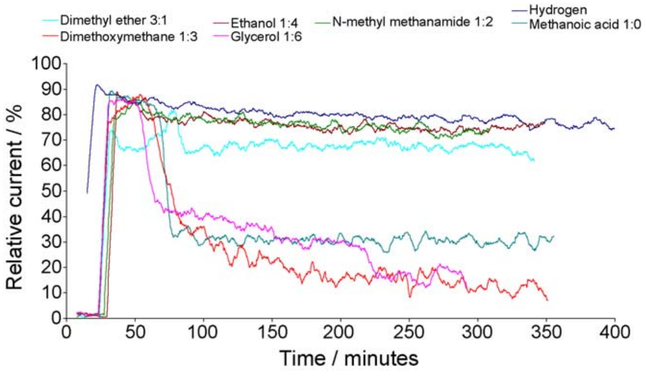

Fig. 3. Selected data showing the range of microtubular SOFC performance with time at 850 °C for different fuel/water formulations for comparison with pure hydrogen. The numbers in the key refer to the fuel/water molar ratio.

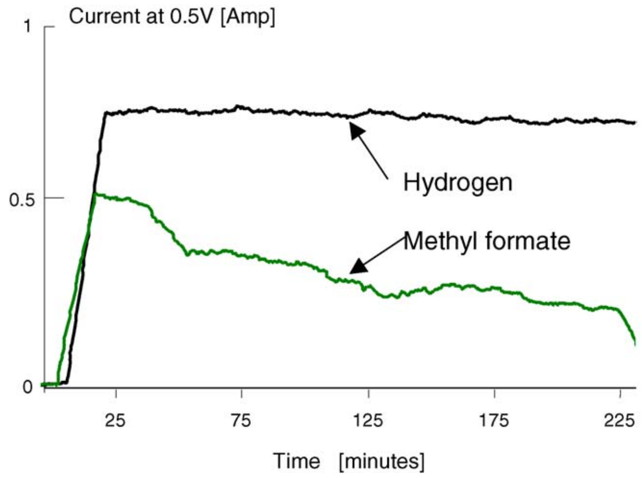

Fig. 4. Output of microtubular cells on hydrogen and methyl formate.

performance at 850 °C as a function of time for hydrogen and methyl formate is given in Fig. 4.

The hydrogen control showed a slight decrease in current with time as the anode sintered, whereas the methyl formate caused a significant current drop as a result of carbon deposition on the anode. However, this fall in current was much better than that for iso-octane which was shown to reduce cell power to almost zero in 30 min by depositing about 90% of the fuel carbon on the nickel cermet [2].

Methyl formate was found to deposit only about 0.14% of the molecular carbon on the cermet as shown by the results in Fig. 5. Dimethoxy methane deposited a similar amount of carbon, around 0.1%. These results were comparable to those using 1/1 molar ethanol/water mixtures.

To reduce the carbon deposition still further, blends of the molecules with methanoic acid and water were tested. The methanoic acid was necessary to give a single phase mixture of water and ether. Under these conditions, both methyl formate and dimethoxy methane gave performance comparable to hydrogen as show in Fig. 6. The time on this graph was measured from the reduction starting point. It was found that the carbon deposition was then almost zero as shown in Fig. 6. The control sample was a 1/1/1 molar mixture of ethanol/water/methanoic acid which had previously been shown to give low carbon deposition values. The ether molecules now showed much better carbon deposition performance than the control formulation containing ethanol (Fig. 7).

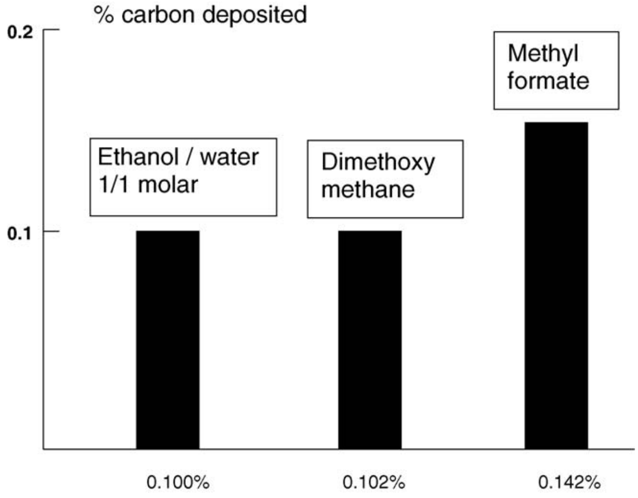

Fig. 5. Carbon deposited on the SOFC anode from three fuel compositions.

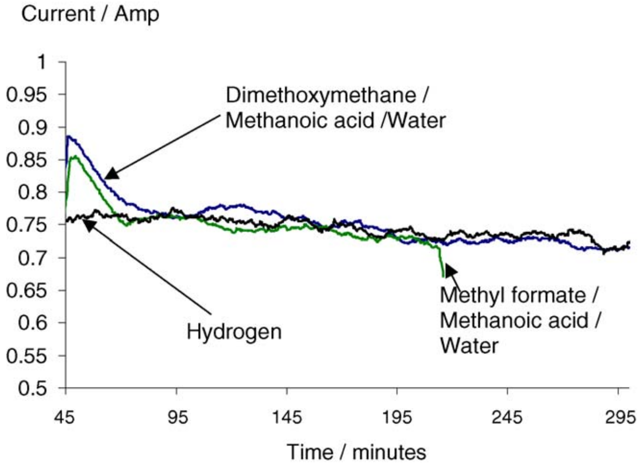

Fig. 6. Performance of 1/1/1 molar ether/methanoic acid/water mixtures at 850 °C.

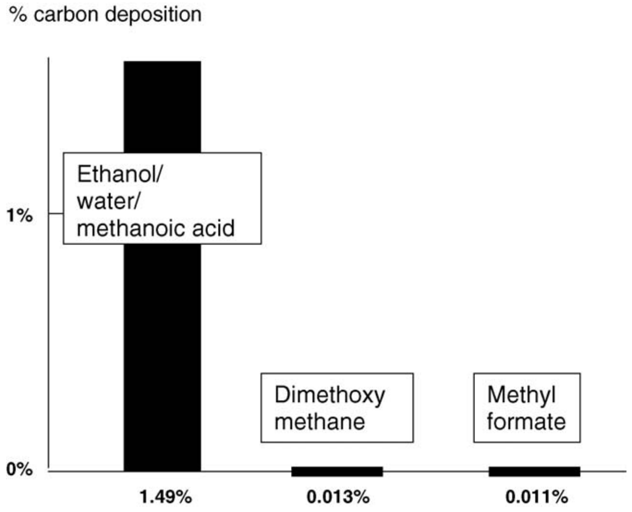

Fig. 7. Carbon deposition from fuel blends with molecules mixed 1/1/1 molar with water and methanoic acid.

Methyl formate and dimethoxy methane have not been much studied previously in catalytic reforming and fuel cell investigations. Methyl formate has been mentioned in connection with methanol synthesis [10]. Dimethoxymethane has been reformed on precious metals but not on Ni, and has been considered for fuel cell use [11,12].

4. Discussion

With the blended ethanol/methanoic acid/water fuel, we see an increase in carbon deposition. This indicates that methanoic acid is not as good an oxidising agent as water. The reduction in carbon deposition for both fuels A and B may be a consequence of more efficient mixing in the single phase fuel. It is evident that methanoic acid operates as a significant mixing agent for water and hydrocarbon fuels.

One mechanism of carbon deposition on a nickel catalyst is known to proceed via the breaking of C–H bonds and the formation of C–Ni bonds. When there is no carbon atom directly adjacent to the Ni-bonded carbon, permanent deposition may be inhibited. This may be a steric effect or the formation of a stronger C=O bond. It is evident from this study that molecules without C–C bonds can deposit less carbon and are therefore candidates for hybrid IC engine SOFC hybrids. The present list of potential fuels includes methane, methanol, methanoic acid, methyl formate and dimethoxymethane.

To test this idea, biodiesel fuel operating in a small engine was switched over to a mixture of biodiesel with 1% methyl formate. Since there was no change in the sound of the engine on changing over to the mixture and on changing back to standard biodiesel, it was concluded that the engine running was not affected by the additive and that the fuel mixture could be used to power diesel engines. Since the methyl formate is more volatile than diesel, it forms a concentrated vapour in the fuel tank and this can be drawn off to operate the SOFC. Thus, a hybrid diesel/SOFC fuel might be formulated, with separation occurring in the fuel tank [9]. But the pure ethers themselves would not keep the diesel engine going. When an engine running on standard biodiesel was switched over to pure methyl formate, the combustion became noisy and the engine stopped.

5. Conclusions

When used directly in SOFCs, certain molecules with no C–C bonds deposited less carbon on a nickel cermet anode than their carbon content would suggest. In particular, methyl formate and dimethoxy methane can produce very little carbon deposition when injected directly into a microtubular SOFC, especially in the presence of water and methanoic acid.

When blended with water and methanoic acid, electrical performance was comparable to that of hydrogen. Carbon deposition was reduced to negligible levels.

A 1% mixture of methyl formate in biodiesel was used to drive a diesel engine successfully. Since the ether was more volatile than the biodiesel, the methyl formate could be separated easily from the diesel fuel to power an SOFC. The ethers could therefore be used as additives to diesel fuel to operate SOFC/ICE hybrids.

Acknowledgement

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