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Formulating liquid hydrocarbon fuels for SOFCs

G.J. Saunders*, J. Preece, K. Kendall

Department of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Abstract

The injection of liquid hydrocarbons directly into an SOFC system is considered for application to hybrid vehicles. The main problem is carbon deposition on the nickel anode when molecules such as ethanol or *iso*-octane are injected directly. Such carbon deposition has been studied using a microtubular SOFC with a mass spectrometer analysing the product gases to investigate the reaction sequence and also to investigate the deposited carbon by temperature programmed oxidation (TPO). The results show that only two liquids could be injected directly onto nickel cermet anodes without serious carbon blockage, methanol and methanoic acid. Even then, TPO experiments revealed deposition of small amounts of carbon which could be prevented by small additions of air or water to the fuel. Gasoline type molecules like *iso*-octane killed the SOFC in about 30 min operation, with about 90% of the molecular carbon being deposited on the nickel cermet anode. However, certain mixtures of *iso*-octane, water, alcohol and surfactant were found to produce beneficial results with remarkably low carbon deposition, less than 1% of the molecular carbon appearing on the anode. Such formulations had octane numbers appropriate to internal combustion engine operation.

Keywords: Microtubular SOFC; *Iso*-octane; Alcohol fuels; Carbon deposition; TPO

1. Introduction

Fuels for hybrid vehicles utilising both internal combustion engines (ICEs) and fuel cells (FCs) are limiting the spread of low emission vehicles at present. A number of zero emission vehicles based on Polymer Electrolyte Membrane fuel cells (PEMFCs) have been demonstrated in North America and Japan [1] but these have been limited by their cost and also by the lack of a widespread hydrogen fuelling infrastructure. BMW demonstrated a hydrogen-powered hybrid with an ICE for motive power and a PEMFC for the electrical system [2] but this was limited by liquid hydrogen supplies. The ideal hybrid would comprise an ICE and a FC running on a liquid hydrocarbon fuel which could be available at refuelling stations.

Already, an SOFC exists in every new automobile. It is the oxygen sensor operating in the exhaust manifold to control the composition of the gas entering the catalyst [3]. This is based on yttria stabilised zirconia (YSZ) electrolyte and platinum electrodes and generates only a small amount of electrical power. However, it proves that an SOFC can operate under certain circumstances under real fuel conditions in an ICE vehicle. This raises the question of how much a liquid fuel needs to be modified to make it acceptable to an SOFC hybrid. The objective of this paper was to answer this question by studying liquid fuels injected directly into an SOFC, especially *iso*-octane, a gasoline-like molecule which can operate successfully in spark ignition ICE engines.

2. Experimental

The apparatus is shown in Fig. 1. It consists of an SOFC test unit with a fuel supply system, a mass spectrometer to measure the reaction products and a potentiostat to control the electrical output [4]. A microtubular SOFC made by Adelan [5] was used as the test cell. This was long enough to extend out of the hot zone so that rubber tubes could be sealed onto the inlet and outlet as shown in Fig. 2.

The SOFC was made of an 8 mol% yttria stabilised zirconia (8YSZ) electrolyte tube onto which two anode layers were coated from ink formulations, then fired at 1300 °C [6,7]. The layer next to the electrolyte was a 50/50 mix of nickel oxide and 8YSZ while the second layer was 90% nickel oxide and 10% 8YSZ to allow good electronic conduction to the nickel wire current collector. A two-layer cathode was employed with the first layer a 50/50 mix of 8YSZ and lanthanum strontium manganite (LSM) and a second layer of pure LSM, fired at 1200 °C.

* Corresponding author. Tel.: +44-121-414-5304;
fax: +44-121-414-4324.

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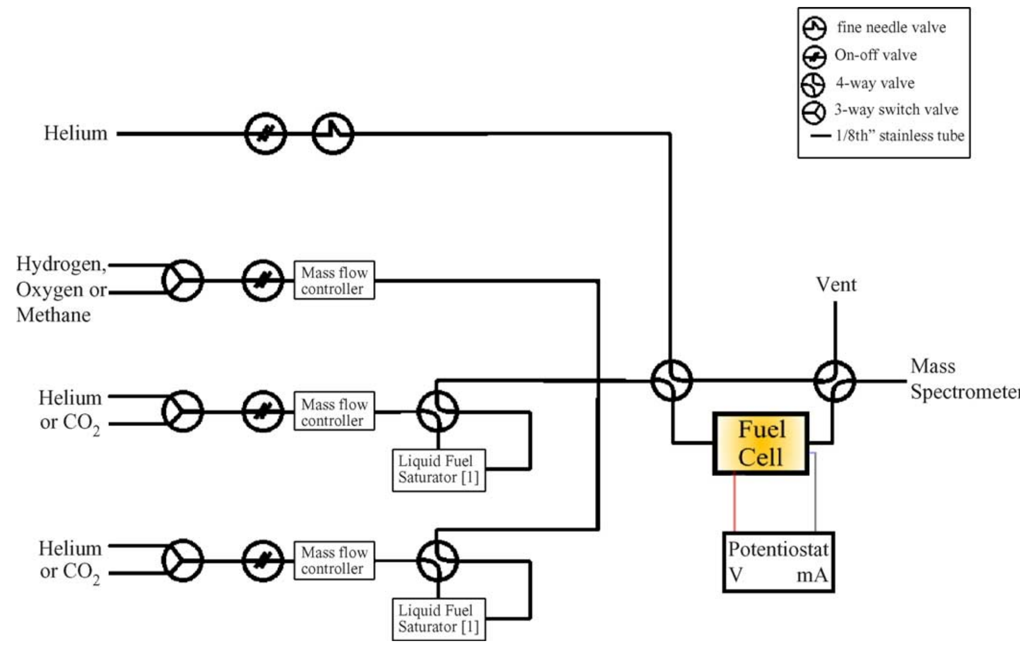

Fig. 1. Test apparatus.

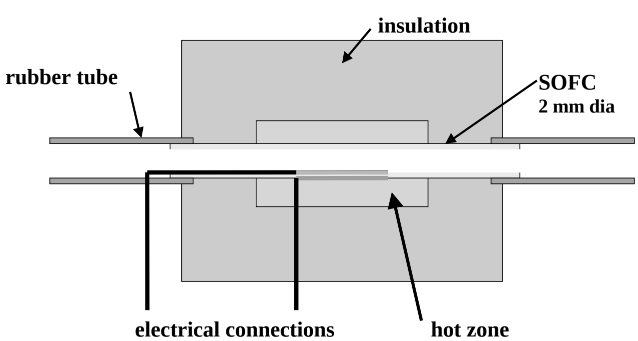

Fig. 2. The microtubular SOFC in the hot zone showing rubber connections.

The anode was reduced in hydrogen for 15 min and the electrical output was then measured, as shown in Fig. 3. The open circuit voltage was 1.25 V on pure hydrogen flowing at 20 ml min^{-1} and the maximum power output was 0.26 W cm^{-2}. When other fuels were directly injected into the anode, the behaviour was observed with time. Methanol gave an SOFC output very similar to that of hydrogen, remaining steady with time, as shown in Fig. 4. Methanoic acid displayed a lower power output but again remained steady, suggesting that little carbon was depositing on the anode. By contrast, ethanol and higher alcohols degraded the SOFC current rapidly. A short time after ethanol injection, the current increased as carbon deposition increased the anode conductivity. But then the carbon began to block the anode sites and the SOFC performance dropped rapidly. Within 30 min, the cell was almost fully blocked with carbon. Ethanoic and higher acids gave similar behaviour [8].

In order to measure the carbon deposited, temperature programmed oxidation (TPO) was employed. The cell was cooled after running for a certain time on the fuel and then oxygen was passed through the cell as the temperature was ramped up steadily. Carbon dioxide was eventually formed as the carbon on the anode oxidised. Measuring this carbon dioxide using the mass spectrometer allowed the amount of carbon to be calculated.

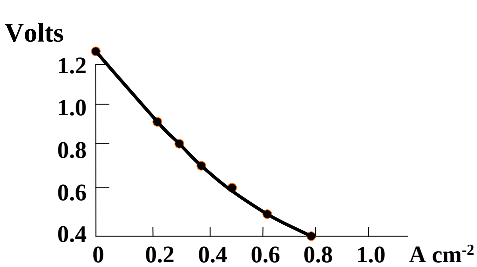

Fig. 3. Output of SOFC on hydrogen at 850 °C.

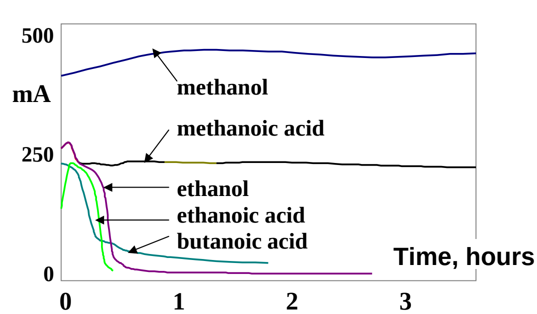

Fig. 4. Performance of SOFC with direct injection of several fuels.

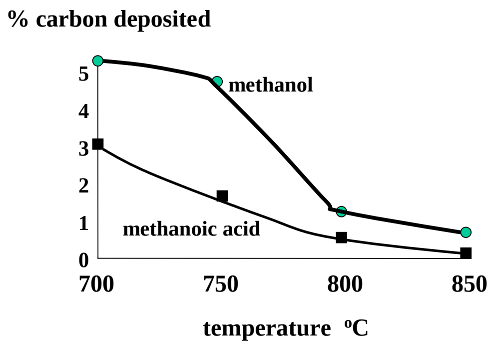

Fig. 5. Carbon on anode measured by TPO for methanol and methanoic acid after running the SOFC at several temperatures.

3. Results on methanol

Fig. 5 shows the results obtained by running the SOFC on methanol at several temperatures, starting at 700 °C which left 5% of the carbon in the methanol deposited on the anode. Higher temperature runs demonstrated that less carbon was deposited at 750 and 800 °C with only 0.6% deposited at 850 °C. Methanoic acid showed similar behaviour. Three percent of the carbon in the molecule was deposited at 700 °C causing eventual blockage, whereas only 0.2% of the carbon was deposited at 850 °C, where the SOFC could run cleanly for long periods.

In order to inhibit the carbon formation observed using pure methanol as fuel, two formulations were tested; one using water mixed with the methanol; the other employing air as the carrier gas to inject the fuel into the anode compartment. Fig. 6 shows the results when water was mixed with the methanol, then injected into the SOFC.

Bubbling air through the pure methanol to inject a methanol/air mix into the anode chamber was also successful at inhibiting carbon deposition. Fig. 7, which shows the current output as a function of methanol concentration, demonstrates that the SOFC performance levelled off above 15% methanol. From 15 to 50% concentration of methanol, there was no significant carbon deposition on the nickel cermet anode.

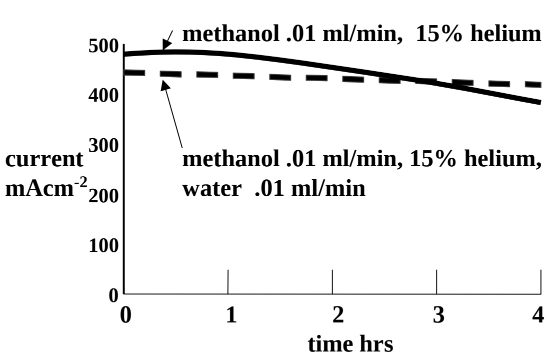

Fig. 6. Pure methanol injected with helium into the SOFC degrades performance with time because of carbon deposition. Adding water prevents the degradation.

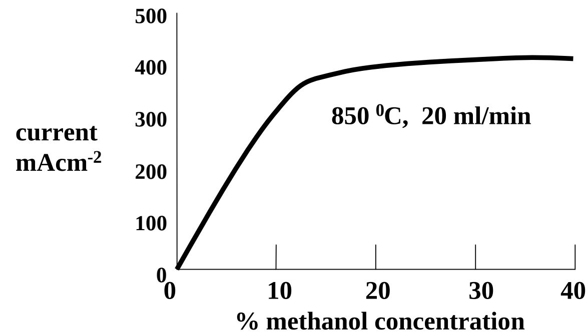

Fig. 7. Effect of bubbling air through methanol and injecting into the anode.

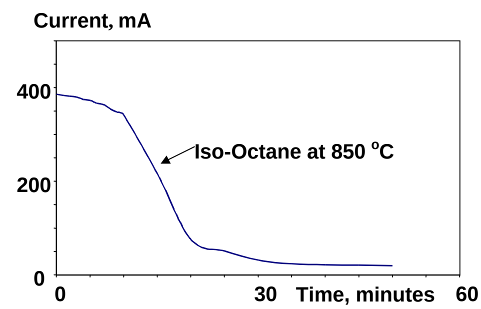

Fig. 8. Degradation of SOFC performance using *iso*-octane as fuel.

4. Results on *iso*-octane

Hydrocarbon fuels such as gasoline, kerosene and diesel are formulated to give ignition, combustion and lubrication performance within ICEs. When injected directly into nickel SOFC anodes, such fuels block the system with carbon within minutes. The intention of the present work was to formulate a hydrocarbon fuel without the many molecules which are specially added to improve ICE performance. Instead, the idea was to formulate a hydrocarbon based fuel which could operate cleanly in an SOFC, then to provide an octane rating suitable for an ICE. *Iso*-octane was used as the model molecule.

Fig. 8 shows the SOFC performance degradation when *iso*-octane was injected directly onto an SOFC anode, using helium as the carrier gas. The current output was satisfactory for a few minutes, but then dropped substantially over a 30 min period.

Temperature programmed oxidation was used to measure the carbon deposited at various temperatures as shown in Fig. 9. The behaviour was found to be opposite to methanol. Little carbon was found at 700 °C but almost complete blocking was found at temperatures above 800 °C. About 90% of the carbon in the *iso*-octane molecule was found to be deposited on the nickel cermet under these conditions. This suggested that a mixture of *iso*-octane and alcohol could behave in a synergistic manner, evening up the deposition over the full temperature range.

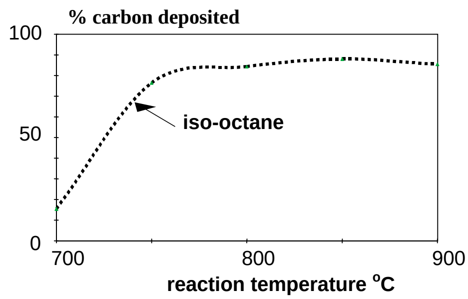

Fig. 9. Carbon deposited from *iso*-octane at various temperatures.

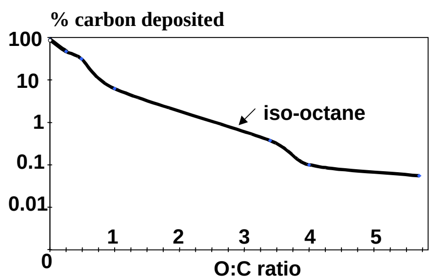

Fig. 10. Reduction in carbon deposition as water was added at 850 °C.

Another experiment showed the carbon deposited when mixtures of water and *iso*-octane were fed onto the SOFC anode. Fig. 10 demonstrates that an oxygen/carbon ratio of 3 was necessary to reduce the carbon below 1% of the carbon in the *iso*-octane molecule. The SOFC could operate cleanly under these conditions.

Experiments were then performed on mixtures of *iso*-octane, water, alcohol and surfactant to produce emulsions which did not phase-separate so that they could readily be injected using a syringe pump into an evaporator at 250 °C which fed directly into the SOFC anode. The best mixture found was composed of 20 ml *iso*-octane, 20 ml water, 2.5 ml isopropanol and 5 ml Brij 30 surfactant. This mixture formed a single phase micro-emulsion which was readily stored, then pumped into the evaporator for injection into the SOFC. A simple estimate of expected carbon deposition was found by working out the oxygen to carbon ratio and using Fig. 10 to give a deposition figure, which was 14%. The experimental results, by contrast, gave a deposition of 0.5% which was very much better than expected and which allowed the SOFC to run cleanly for long periods [9].

5. Conclusions

The carbon deposition from fuel molecules onto a nickel cermet anode has been measured by temperature programmed oxidation over a number of operating conditions. Methanol and methanoic acid were the only molecules which could run directly in the SOFC and even these produced a small amount of carbon deposit. Such deposits were reduced by formulating the methanol fuel with water or air to inhibit carbon formation.

Iso-octane has been studied to illustrate the effect of injecting gasoline-type molecules directly onto the SOFC anode. Mixing the *iso*-octane with water, alcohol and surfactant to produce an oil in water micro-emulsion was successful in reducing the carbon formation significantly, while retaining a high octane number. Consequently, such a fuel formulation may prove useful in ICE-SOFC hybrid vehicles.

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