Reactions of hydrocarbons in small tubular SOFCs

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Abstract

The benefits of SOFCs are likely to be optimally realised using fuels other than pure hydrogen, which is best employed in PEMFCs. This paper examines a number of plausible fuels including pure alkanes such as methane and *iso*-octane. Other compounds such as ammonia, methanol and methanoic acid have been shown to react very cleanly when injected directly into the SOFC. More complex fuels, e.g. ethanol and ethanoic acid tend to produce carbon deposits unless the inlet stream is much diluted, e.g. with argon or carbon dioxide. More complex real fuels such as natural gas, landfill gas and gasoline are also mentioned. The experiments involved mixing the fuel with a carrier gas and passing the composition down a zirconia fuel cell tube to examine electrochemical output, while analysing the reaction products using mass spectroscopy. Any carbon deposited was measured by temperature programmed oxidation at the end of the experiment. Windows of operation were found for many of the fuels examined. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The ability of SOFCs to reform hydrocarbons internally and directly at the anode makes them suitable for use in portable/mobile applications [1]. Ordinarily the reforming process makes use of one or a number of methods; steam reforming, dry reforming and autothermal reforming; each method adds a level of complexity to the fuel cell system. Fuels typically studied include methane/natural gas, biogas, propane/butane and methanol [2–4]. Normally, the pure fuel is fed into the cell and the reaction processes are observed. Sometimes, impurities such as H_2S, higher hydrocarbons or additives are studied because these can cause difficulties. This project had a new approach of considering the ideal mixture of molecules for fuelling SOFCs. Several types of molecules were selected, including linear and branched alkanes, alcohols and organic acids. These were studied individually and in mixtures to determine their behaviour in the cell and to see if any benefit could be gained from blending a fuel mixture.

Fuel vapour was carried on helium to a 2 mm diameter zirconia cell having a (internal) nickel/zirconia anode and a (external) lanthanium/strontium manganite cathode. Mass spectroscopy was used to identify reaction products and carbon deposits [5].

2. Theory

Thermal cracking of hydrocarbons usually leads to rapid cell failure by carbon deposition. Some hydrocarbons may decompose in a way that is useful or at least less destructive than others. Functional groups, present in additives, may react more effectively with certain hydrocarbons or isomers than others. The mechanism of decomposition may vary with temperature although any significant changes in mechanism are expected to occur below the fuel cell operating temperature window, which is 973–1173 K in the system used in this project. For example, branched hydrocarbons decompose to different products compared with linear hydrocarbons.

Under conditions promoting pyrolysis, scission of a linear hydrocarbon tends to occur towards the centre of the chain, producing an alkane and alkene of the same/similar carbon number. Branched hydrocarbons tend to dehydrogenate to form an *iso*-alkene. Linear alkenes tend to be less stable than *iso*-alkenes and could produce polymerides and aromatic hydrocarbons. These products tend to be more destructive than some others in a nickel based cermet anode.

Organic acids have the potential to decompose in a number of ways, e.g formic acid thermal cracking.

$$HCOOH \leftrightarrow CO_2 + H_2 \tag{1}$$

or

$$HCOOH \leftrightarrow CO + H_2O \tag{2}$$

Reaction products from decomposition of formic acid at the anode could be useful in processing other fuel molecules.

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The proportions of these products could also have an impact on other reaction mechanisms occurring at that anode.

Alcohols have the potential to dehydrolyse, with secondary and tertiary alcohols being more prone to dehydrolysis than primary alcohols. On the one hand, this feature may be useful in influencing other reaction mechanisms. On the other hand, under certain cell conditions it will promote carbon deposition. Either way alcohols are useful for producing microemulsion mixtures of polar and non-polar components that may work well together in the cell. Blending a number of fuel components together to take advantage of certain reaction products for further reaction, to influence other reaction mechanisms and to influence the rate of reactions by competitive adsorption at the anode could improve cell lifetime and performance.

It has been shown that SOFCs operating at high fuel:steam or CO_2 ratios can survive for a considerable time under certain conditions [6]. A blended fuel might be able to provide or improve conditions under which an SOFC can directly process fuel thereby improving performance and cell lifetime.

3. Apparatus

Tubular electrolytes were prepared by extruding a zirconia paste through a 2.5 mm diameter die. The tubes were fully densified at 1773 K. Wall thickness after firing was 200 mm. A nickel/zirconia slurry was coated onto the inside of the electrolyte tube and fired at 1573 K. Lanthanum/strontium manganite was applied to the outside and fired at 1373 K [7]. A nickel coil was inserted into the cell to make contact with the anode and silver wire was wrapped around the outside for cathode current collection (Fig. 1). The wires were connected to a potentiostat, which was used to measure voltage and draw current. Each cell anode was reduced in hydrogen at 1073 K.
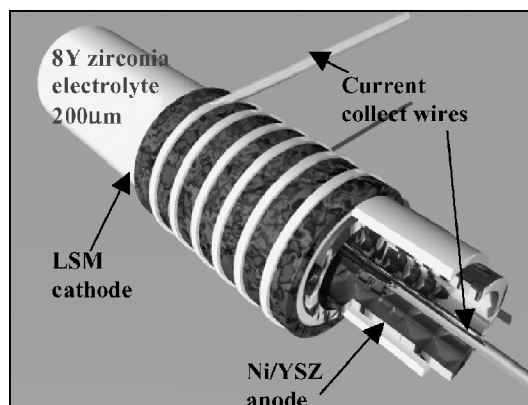

Fig. 1. Outline of a microtubular SOFC.

Fig. 2 shows the test equipment used to study the reactions of various fuels and mixtures at the SOFC anode. The cell was placed in an electrically heated furnace. Temperature programmed surface reactions were performed by heating the furnace from 323 K up to 1173 K at a rate of 5 K min^{-1}. Cell electrical performance was studied between 973 and 1173 K. Analysis of carbon deposits was by temperature programmed oxidation (323–1173 K at 5 K min^{-1}) of the anode.

The cell was connected (outside the furnace) to the gas manifold with silicone tubing. The gases at either the cell inlet or exhaust could be fed to the mass spectrometer for analysis.

4. Experimental results

Temperature programmed surface reaction studies of methanol, ethanol, propan-1-ol, propan-2-ol, *n*-octane, 2,2,4-trimethylpentane, formic acid, acetic acid followed by TPO analysis of the anodes yielded reaction products,
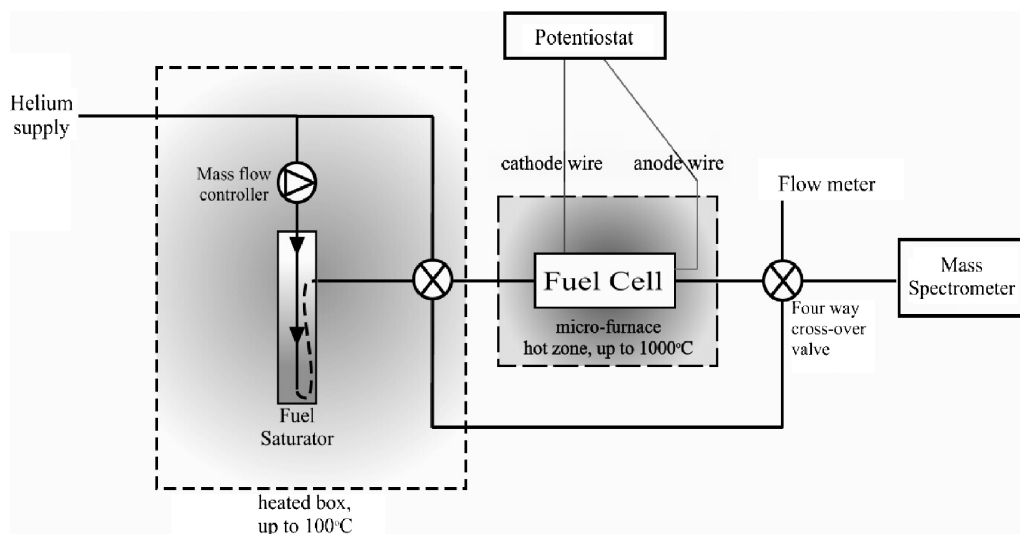

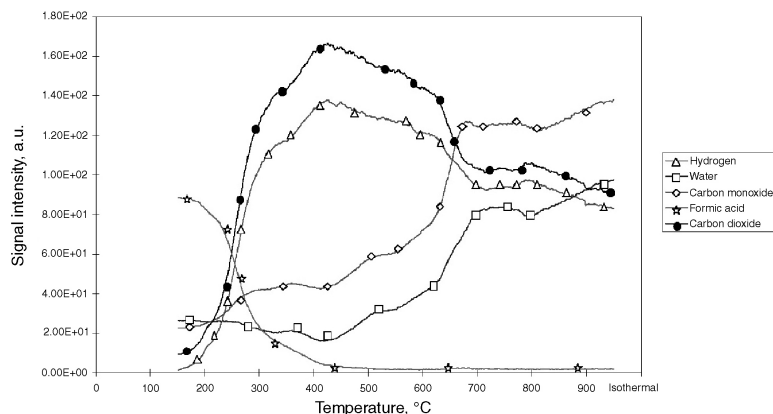Fig. 2. Liquid fuel test ring.

Fig. 3. Formic acid decomposition, OCV.

types and amounts of carbon formed at various temperatures. The fuels were studied in a working cell so that anode morphology and reaction environment was the same as in a typical cell. The cell was at open circuit voltage for the TPSR and TPO experiments. Current data for individual fuels and mixtures was obtained at 1073 K and a constant load at 0.5 volts.

4.1. Alkanes

The cracking products of the octanes were hydrogen, carbon, methane, C_2 and C_4 alkanes/alkenes. No C_3 hydrocarbons were detected in the *n*-octane exhaust gas suggesting concurrent polymerisation and degradation of alkene intermediates. Intermediate cracking products of 2,2,4-trimethylpentane tended to break down more readily resulting in significantly higher carbon deposition in the 1023–1123 K temperature range. *n*-Octane tended to produce filamentous carbon whereas *iso*-octane produced more of the nickel encapsulating type graphite. Swelling of the anode by the formation of filamentous carbon cause cell failure not by complete deactivation on the anode but by physical blockage at the cell inlet.

4.2. Organic acids

Organic acids cracked to produce a mixture of hydrogen, carbon (for $>C_1$ acids) carbon monoxide, carbon dioxide and water. The ratio of hydrogen + carbon dioxide to water + carbon monoxide was strongly temperature dependent up to the lower cell operating temperature (973 K). Above this temperature the change in product concentration was much less (Fig. 3). A cell was fuelled with formic acid and operated at load for many days with little reduction in performance. Higher organic acids caused cell failure within 30 min.

4.3. Alcohols

Alcohols cracked to produce hydrogen, carbon (for $>C_1$ alcohols) and carbon monoxide. Methanol was a very clean fuel at typical cell operating temperatures (973–1173 K). However, between 300 and 700 K a significant portion of the syngas product reacted to form methane (Fig. 4)—this may have implications for thermal cycling of a cell/stack where anode exhaust gas recycling is in use [8] or when considering anode dopants. Thermal cracking of methane in
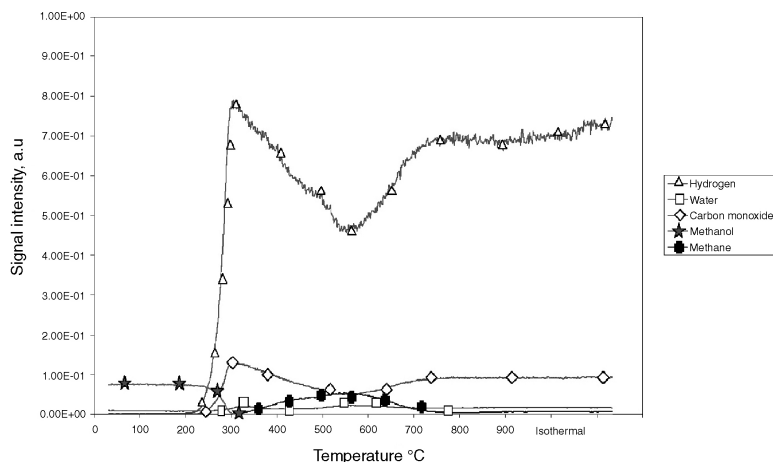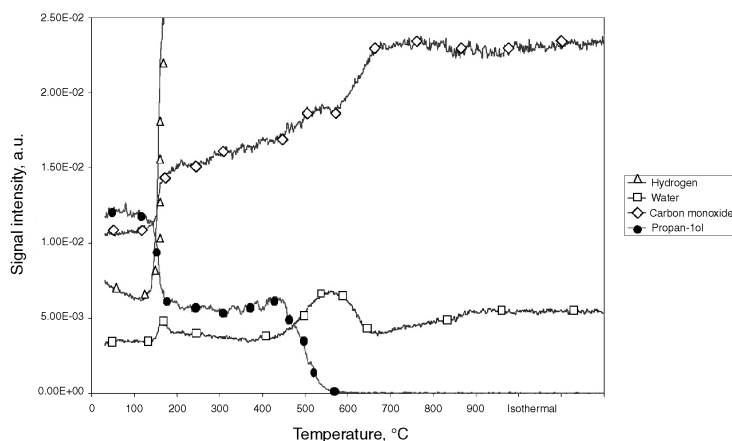

Fig. 4. Methanol decomposition, OCV.

Fig. 5. Propan-1-ol decomposition, OCV.

the recycle gas during system warm-up may cause damage to the anode. The high partial pressure of CO in the off gas tended to promote the Boudouard reaction at intermediate temperatures more so for methanol than for other alcohols.

Dehydrogenation activation temperatures were typically around 473 K. Partial dehydrogenation of the alcohol groups to form carbonyls occurred at lower reaction temperatures (473–673 K). At around 673 K dehydrolysis to form alkenes starts—consideration should be given to the possibility of polymerisation to form aromatics. At around the same temperature methane synthesis also starts to occur—again this could be contributed by concurrent polymerisation and degradation mechanisms. At typical cell operating temperatures (973–1173 K) the main products are hydrogen, carbon monoxide (and filamentous carbon for >C1 alcohols).

Differences in the amounts of some reaction products were observed for propan-1-ol and 2-ol, with propan-2-ol having a greater tendency to dehydrolyse at intermediate temperatures (Figs. 5 and 6).

Relative amounts of carbon deposited at the anode by pyrolysis of a number of fuels are shown in Fig. 7. Hydrocarbons tend to deposit more carbon with increasing temperature as dehydrogenation becomes thermally and kinetically more favourable. Carbon deposition tends to decrease with increasing temperature for low molecular weight alcohols. This is because, dehydrolysis to produce carbon and water from the alcohols group, is succeeded by dehydrogenation to form carbon monoxide and hydrogen only at higher reaction temperatures.

Fig. 8 shows the current drawn from a cell at 1023 K and 0.5 V when fuelled with various hydrocarbons. Cells fuelled with methanol or formic acid can be seen to operate quite successfully whilst other fuels rapidly destroy the anode.

A fuel was blended from 2,2,4-trimethylpentane, ethanol, octanol and formic acid or water. A cell was operated at 1023 K and supplied with the blended fuel vapour on helium carrier gas. Fig. 9 illustrates cell performance on separate components and on the blended fuel. Complete deactivation of the anode cermet occurred within 30 min for all separate hydrocarbon components except methanol and formic acid.
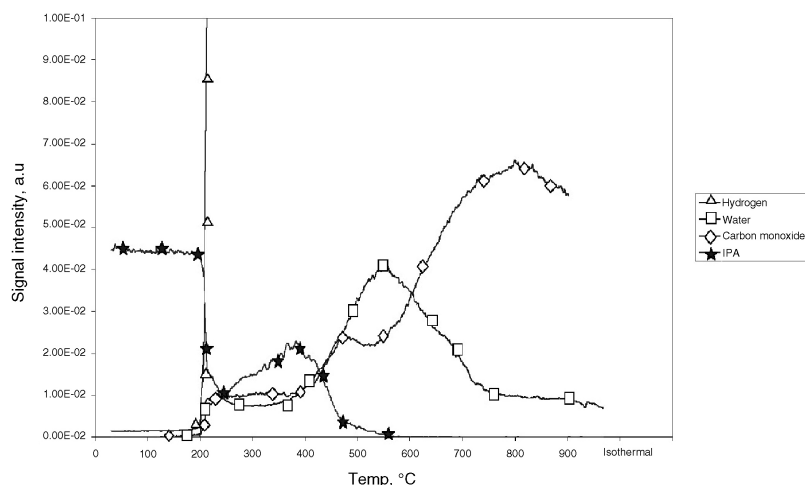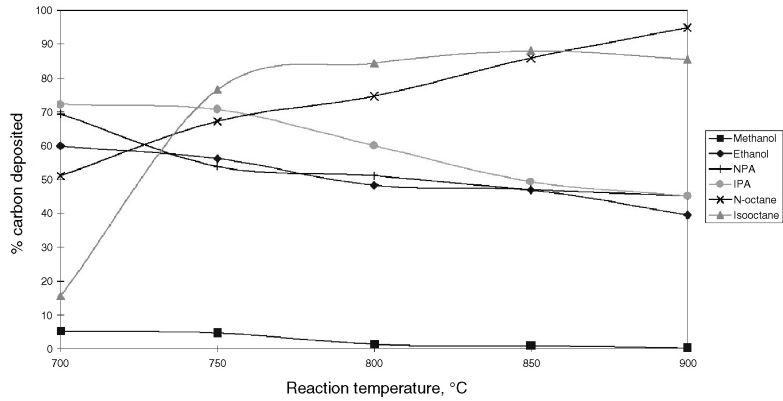

Fig. 6. Propan-2-ol decomposition, OCV.

Fig. 7. Percentage of carbon deposited by pyrolysis of various fuels at OCV.

Carbon deposition was greatest near the cell inlet where the anode is exposed to the highest concentration of hydrocarbons.

A cell was successfully operated under load (0.5 V) on the blended fuel for over 4 h without excessive loss in performance, despite the bulk fuel being 2,2,4-trimethylpentane. The presence of water and CO_2 (from formic acid decomposition) at the anode assisted in reforming the other hydrocarbons and keeping the cell cleaner. Carbon was deposited but more evenly along the anode.
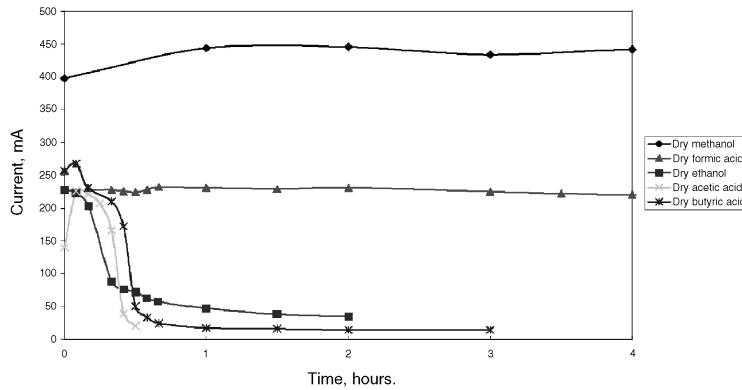

Fig. 8. Current drawn for various fuels at 1023 K, 0.5 V.
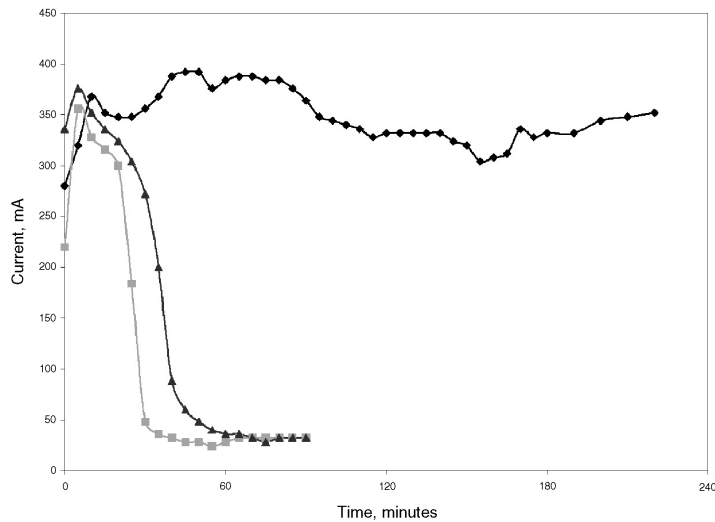

Fig. 9. Cell performance on separate and blended fuel components.

5. Conclusions

Methanol and formic acid can be used directly at the anode of an SOFC with good electrical performance and clean operation. Other hydrocarbons can rapidly destroy the anode unless steam or CO_2 is supplied in adequate amounts with the fuel. Carbon deposits from certain hydrocarbon isomers (e.g. whisker carbon from *n*-octane) cause cell failure to occur more rapidly by swelling the anode and physically blocking the anode chamber at the inlet.

Alcohols can be used to incorporate oxygenated fuel components in a bulk liquid hydrocarbon fuel to improve the performance and lifetime of a cell/stack whilst reducing or even eliminating the steam/CO_2 supply element of a solid oxide fuel cell system.

A cell fuelled with a mixture of *iso*-octane, ethanol, octanol and formic acid operated for much longer than on *iso*-octane, ethanol or octanol alone.

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