Examining the role of water in the performance of solid oxide fuel cells; an isotopic investigation

Matthew Drewery,[a]* **Scott Molloy,**-[a] **Bogdan Dlugogorski,** [b] **Eric Kennedy,** [a] **Michael Stockenhuber** [a]

[a]*Chemical Engineering, The University of Newcastle, Callaghan NSW 2308, Australia*
[b]*School of Engineering and Information Technology, Murdoch University, Murdoch WA 6150, Australia*
**Matthew.Drewery@uon.edu.au*

Abstract: Reducing environmental impacts associated with energy production has engendered interest and research activities into the use of SOFCs. Hydrocarbon feeds can deactivate the cell via carbon formation on the catalyst. To limit this, fuel streams are usually humidified, requiring high steam:carbon ratios which decrease cell efficiency. The role of water was examined by comparing operation of the SOFC with deuterated and non-deuterated species. It was found that there is a small but significant difference in the rate of electron production when water is replaced with deuterated water, suggesting its involvement in the rate determining reaction step within the cell anode.

Keywords: SOFC, isotope, water.

1. Introduction

The environmental impact of energy generation has stimulated interest in the development of sustainable energy supplies. One potential replacement is SOFCs, which produces energy at high efficiencies through electrochemical reactions. Small chain hydrocarbons are considered to be the most viable fuel option due to ease of supply, but there is also the potential to use higher molecular weight hydrocarbons such as those produced from biofuel waste streams. Utilising hydrocarbons as fuels increases the potential to deposit carbon and subsequently deactivate the catalytic anode, presenting severe problems for SOFC operation[1-3]. Literature has identified that humidifying the anode inlet stream minimises and potentially eliminates the formation of carbon[1,2], indicating that the presence of water in the fuel stream plays an important role in anode chemistry by preventing catalyst deactivation. In spite of this, the role of water is still not clearly understood in SOFCs. While a high H_2O content in the fuel stream would decrease the cell performance and efficiency according, to the Nernst Equation[4-8], the mechanism by which water interacts with the fuel on the anode surface is not clearly understood, with some research identifying low H_2O concentrations in the feed playing a crucial part in SOFC operation[9-13].

It has been hypothesised that the presence of water may assist in hydrogen transport, where a theoretical study has identified dissociatively adsorbed water molecules assisting in hydrogen transfer by decreasing the activation energy of the spill-over mechanism[14]. The aim of this study was to identify the role of water in anode surface chemistry through comparative isotopic investigations. It is theorised that water not only participates in heterogeneous chemical reactions, but that it potentially participates in a rate determining step; a charge transfer reaction.

2. Experimental

A planar solid oxide fuel cell test system was sourced from Fuel Cell Materials utilising glass seals supplied by Kerafol as discussed in previous publications[15]. The cell consists of a 150 µm scandia doped zirconia electrolyte with screen printed 28 cm^2 electrodes of LSM/LSM-GDC cathode and Ni-YSZ/Ni-GDC anode. An indigenous constant voltage dynamic load combined with a Datataker 505 was used to simultaneously monitor cell potential and current with gas compositions measured via a Varian 490 micro-GC equipped with a TCD.

3. Results and discussion

As the reactions are assumed to be at or near equilibrium, it is assumed that the addition of water in the anode stream would decrease the power by shifting the equilibrium towards the reactants[4,6,7]. In order to investigate the net effect of humidification on reaction rate, the current produced (indicative of rate) was measured over varying partial pressures of water. A slight decrease in current produced by the cell with increasing water concentration was found, most likely caused by slight dilution of hydrogen and shift of equilibrium as humidification is increased, supported by similar changes observed in cell open circuit voltage (OCV).

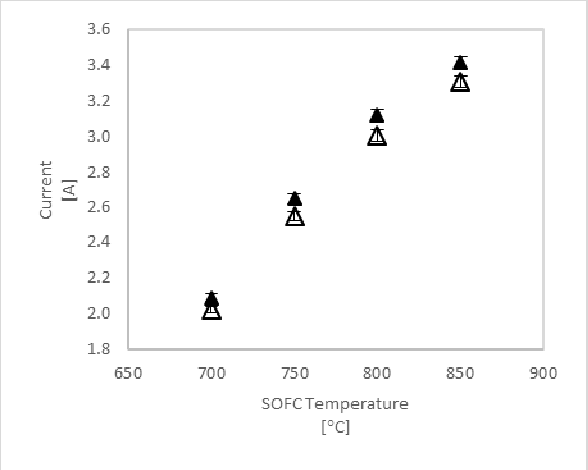

Figure 1. Current at 0.7 V over SOFC temperatures with H_2 concentration of 70% in N_2 and flow of 300 mL.min^{-1}. Isotope effect compared with H_2O (filled) and D_2O (hollow) humidification

As previously discussed, if water is involved in a rate limiting step in the SOFC reactions, it is expected that the reaction rate, as indicated by cell current measurements, would vary when using water compared to the isotope – deuterated water (D_2O). If there is a variation in reaction rate because of the energy required to break OD bonds compared to OH bonds, this would be evidenced by variations in the current-voltage characteristics. The electron flow, as measured by the cell current, is indicative of the reaction rate where two moles of electrons are produced for every mole of hydrogen reacted. Cell currents measured with operating temperatures between 700 and 850°C showed there were significant differences in reaction rate when changing between water and deuterated water, visible in Figure 1. Cell current differences between deuterated and non-deuterated were similarly reflected in variations in the extent of fuel reacted. Hydrogen humidified with water showed a consistently higher percentage of fuel reacted in the anode compared to deuterated humidification.

4. Conclusions

The observed variation in cell performance when changing between isotopes indicates that water participates in a rate limiting step in anode chemistry. It is theorised that the rate limiting step in the process involves the transfer of a proton across the three-phase boundary, the rate of which is enhanced in the presence of water vapour. In this instance, the hydrogen fuel is dissociatively adsorbed onto the nickel anode while water is dissociatively adsorbed on the electrolyte surface as hydroxyl groups, which then facilitates the migration of hydrogen ions to the electrolyte for oxidation before being desorbed as water.

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