Short communication

Catalysis and oxidation of carbon in a hybrid direct carbon fuel cell

Cairong Jiang, John T.S. Irvine*

School of Chemistry, University of St Andrews, KY16 9ST, United Kingdom

ARTICLE INFO

ABSTRACT

The hybrid direct carbon fuel cell (HDCFC), combining molten carbonate fuel cell and solid oxide fuel cell technology, is capable of converting solid carbon directly into electrical energy without intermediate reforming. Here, we report the investigation of the HDCFC with yttria stabilized zirconia (YSZ) electrolyte, NiO-YSZ anode and lanthanum strontium manganite (LSM) cathode using the eutectic mixture of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3. An open circuit voltage (OCV) of 0.71 V at 800 °C is recorded without the carbonate which increases to 1.15–1.23 V in the presence of the carbonate at the same temperature. In addition, the cell's OCV is enhanced not only by the thermal history but also by the carbonate, which is in excess of 1.57 V after the high temperature treatment. Electrochemical performance analysis indicates a suitable amount of the carbonate enhanced the carbon oxidation. With 1 mm robust thick electrolyte and commercial carbon, the cell (1.13 cm^2 active area) generates the peak density of 50 mW cm^{-2} at 800 °C. There are significant losses from electrolyte resistance, which would be overcome by the application of a thinner electrolyte.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

It is predicted that world coal consumption will have increased from 27% in 2006 to 28% in 2030, which means coal will still be the main energy source in the near future [1]. Therefore, the efficient use of coal is of importance for the low carbon and renewable energy economy [2,3], which is especially critical for non-OECD countries since these countries are responsible for most of the world coal consumption. The direct carbon fuel cell is one of the promising energy sources that could use coal as a fuel without any reforming process with high fuel utilisation and efficiency [4].

Many attempts have been made to develop a fuel cell that can use solid carbons (such as petroleum coke, coal coke, or cracked biomass or pyrolysed hydrocarbon) as fuels. The first direct carbon fuel cell was made by Jacques in the 19th century [5]. The formidable problem for this cell is the reaction of the hydroxide electrolyte with carbon to form the carbonate. Weaver et al. presented a molten carbonate electrolyte for direct carbon conversion in 1979 [6]. Vutetakis employed a stirred approach to promote the coal electrochemical oxidation [7]. The recent work carried out by Cooper and co-workers [4] using a eutectic molten carbonate stimulated research on the direct conversion of solid carbon particulates. The solid carbon can be wetted by the eutectic molten carbonate, which increases the possibility of the electrochemical oxidation of carbon due to the enhanced active reaction area. Our previous report presented the feasibility for carbon directly converting to electricity in the hybrid direct carbon fuel cell (HDCFC), which has an extended anode combining a molten carbonate fuel cell and a solid oxide fuel cell (SOFC) [8–10]. In the basic concept, HDCFCs use a traditional oxide ion conductor, such as yttria stabilized zirconia (YSZ), which transports oxide ions from the cathode to the anode for the oxidation of carbon. One of the advantages is that the separation of the cathode and the anode reduces the possibility of the cathode corrosion in the carbonate which would occur in a molten carbonate based concept [11]. The other advantage is that using air in the cathode chamber eliminates CO_2 circulation in comparison to the traditional molten carbonate fuel cell [12]. We succeeded in the direct conversion of some carbon sources, including coal, starch, graphite and pyrolysed medium density fibreboard (PMDF), on tubular cells and button cells with traditional solid oxide electrolytes, such as YSZ and gadolinium-doped ceria [13,14]. Although the results are encouraging, the research is still underway. In order to approach to commercial interest, many issues need to be clarified and solved, such as the reaction in the anode chamber, the optimised operating conditions, durability and performance improvement and practical system development. The work here aims to further improve the cell performance and to study the electrochemical mechanism. The cell's potential behaviour was recorded using different carbon/carbonate slurries. The cell performance was optimised by varying the carbonate content.

* Corresponding author. Tel.: +44 1334 463817; fax: +44 1334 463808.
E-mail address: jtsi@st-andrews.ac.uk (J.T.S. Irvine).

2. Experiments

2.1. Sample preparation

NiO-YSZ with a weight ratio of 55:45 anode ink (NiO is from Aldrich, 325 mesh) was screen printed on one side of the dense YSZ disk (made from Pi-Kem powder, ~20 mm diameter, 1 mm thickness) and sintered at 1350 °C for 2 h. According to the experiments, the nature and performance characteristics of the anode materials were identified as one of most critical issues in this approach. Initially, a very thin NiO-YSZ anode layer which was about 5 μm was achieved by a screen printing method. The cell presented huge polarisation resistance as well as big series resistance, possibly due to the non-conductive NiO-YSZ layer. So the big semicircles in Fig. 1a show for the thin anode layer the dominant process is likely the diffusion of electrons from the non-conductive NiO-YSZ layer. Consequently, a thicker anode layer (around 90–100 μm) was obtained by screen printing several times. In this case, the electrochemical reaction was not controlled by the electrons diffusion, therefore, significant smaller polarisation resistance (Fig. 1b). The impedance spectra of thicker NiO-YSZ layer consist of three semicircles: one at high frequency (the left side of the spectra, higher than 1 kHz), one at medium frequency (from 1 kHz to 1 Hz), and one at low frequency (lower than 1 Hz). The corresponding process is likely relevant to the electrode–electrolyte interface, charge transfer and mass diffusion. Unless stated to the contrary, all the cells utilised have an anode layer about 90–100 μm thick. Two layers of composite lanthanum strontium manganite (LSM, Pi-chem) and YSZ cathode ink with 50 wt% and 75 wt% $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ and one layer of pure LSM current collection ink were painted on the other surface by the screen printing method after the anode layer was sintered at 1350 °C. The cathode was fired at 1100 °C for 2 h. For each layer of the cathode the thickness is about 7 μm, so the total thickness is around 20 μm.
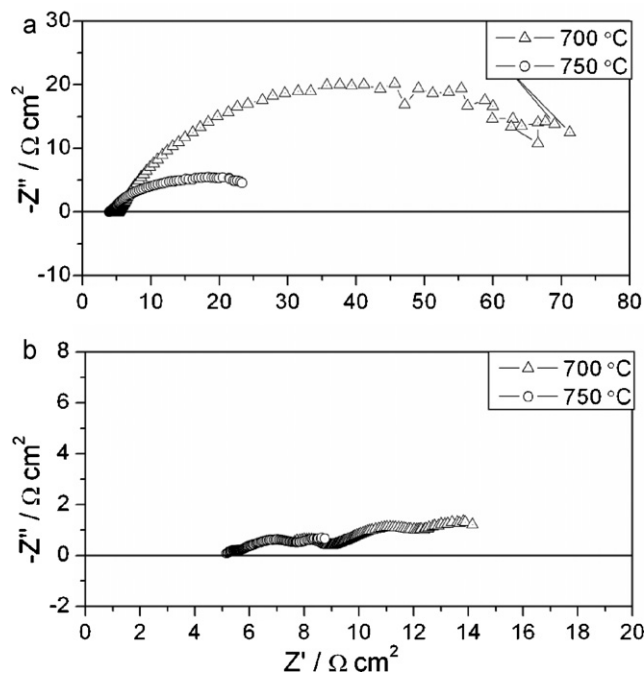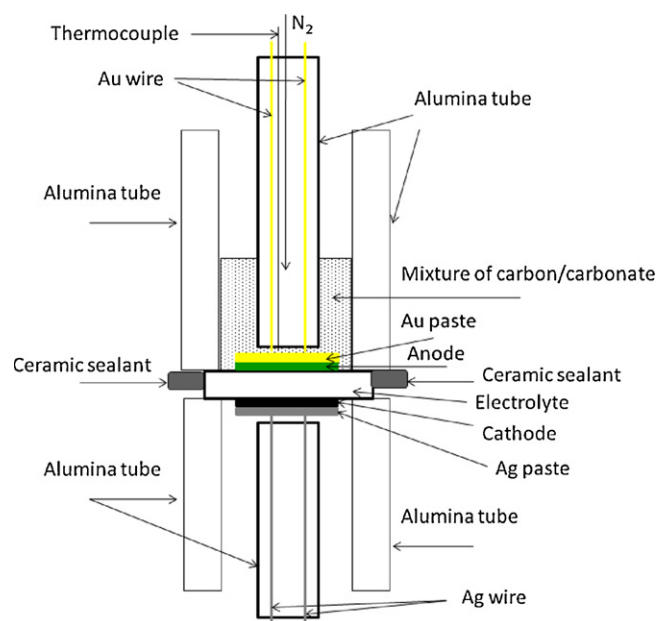

Fig. 2. Schematic design of the hybrid direct carbon fuel cell.

2.2. Cell sketch and measurement

The test system has been described in detail previously [9], which is shown in Fig. 2. The as-prepared cells painted with gold paste (calcined at 900 °C for 1 h) on the anode and silver paste (calcined at 800 °C for 2 h) on the cathode was sealed to one end of an alumina tube (~20 mm diameter, both ends open) using ceramic sealant (Aremco 552). The mixture of XC-72R (Cabot) and carbonate (62 mol% Li_2CO_3 (Aldrich) and 38 mol% K_2CO_3 (Fisher)) with different carbonate contents was pouring into the alumina tube, which was mixed before using. The other end of the alumina tube was fitted by Swagelok fittings in order to flow various gases. The temperature of the cell was monitored by a thermocouple embedded in a four-hole alumina inner tube in the mixture of carbon and carbonate. In addition, two gold wires through the inner tube were as for the anode current collectors. This integration was vertically sitting on a scaffold, which is cathode compartment with two silver wires for the cathode current collectors. Ar or nitrogen was the purge gas for the anode and cathode was exposed to static air. The system was heated up slowly to 700 °C and tests were carried out at 50 °C intervals until 800 °C. Impedance spectra were measured in the frequency range of 20 kHz to 0.1 Hz with a 10 mV ac perturbation and I–V polarisation curves were obtained at a scan rate of 20 mV s^{-1} using Solartron 1280B. After the I–V test, the cell should be stabilised to equilibrium status before the next measurement.

3. Results and discussion

3.1. Carbon/carbonate slurry

It is desirable to operate the carbon fuel cell at temperatures sufficiently low, e.g. lower than 800 °C, as when the temperature is higher the Boudouard reaction reduces the potential efficiency. Another problem for high temperature operation is the decomposition of the carbonate. The experiments were all performed in the temperature range 700–800 °C.

The electrochemical oxidation of carbon in the presence or absence of the molten carbonate was studied using impedance spectra. At a higher carbon ratio, such as in pure carbon, very high polarisation resistance was presented (Fig. 3). The sluggish reaction rate might be due to the limitation in contact between solid

Fig. 1. Impedance spectra of the HDCFCs with different thickness of Ni/YSZ layer (a) 5 μm and (b) 90 μm using 50 mol% carbonate in carbon fuel at 700 °C and 750 °C.
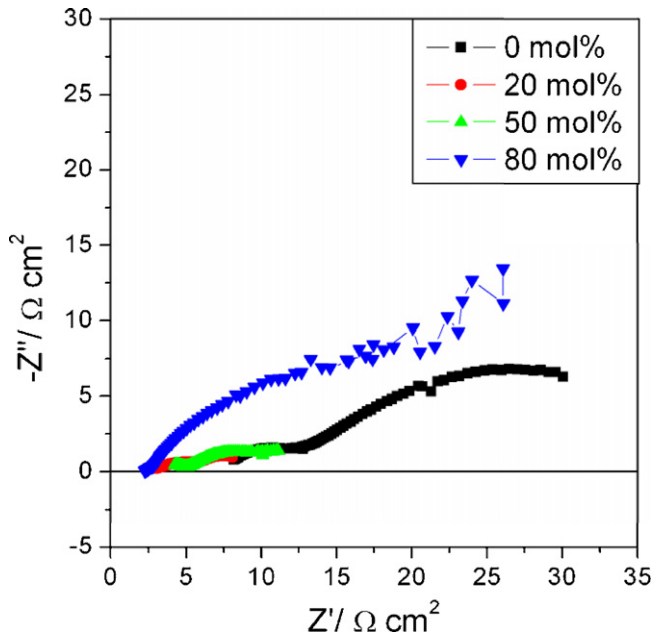
Fig. 3. Effect of the carbonate content in mol% on the HDCFC polarisation resistance at 750 °C.

carbon and the solid electrolyte. In the presence of 20 mol% or 50 mol% carbonate, the polarisation resistance of the carbon oxidation decreased significantly. No further improvement was found when the carbonate amount was increased to 80 mol%, indeed much larger polarisation resistance was observed. Furthermore, another problem resulting from the higher carbonate concentration was the corrosion of the materials and sealing issues. Therefore, a moderate amount of carbonate, 20 mol% (*i.e.* 80 mol% carbon), was utilised in the following cell measurements in order to wet carbon but minimise any corrosion problems.

3.2. Solid carbon and gas fuel

The cell electrochemical polarisation performance was investigated using 20 mol% carbonate in the carbon/carbonate slurry. For comparison purposes, the gaseous fuel, hydrogen, was employed alone in the absence of any solid fuels in the anode compartment. The results revealed an improvement of the electrochemical performance especially under carbon compared to hydrogen (Fig. 4). This might be related to the slightly lower OCV values in 5% hydrogen than that in solid carbon. The carbonate and carbon were mixed before being filled into the anode chamber. The purpose was to extend the contact of carbon particles with the eutectic carbonate since low carbonate contents were used in some cases. The homogeneous dispersion of carbon in the carbonate may promote the electrochemical oxidation rates and the molten carbonate at high temperature enhanced the mass transportation both of which contribute to high power output. With 1 mm thick YSZ electrolyte, power output in excess of 50 mW cm⁻² was obtained at 800 °C (Fig. 4c), and the cell specific area resistance was 8.2 Ω cm² at this temperature. It can bee seen from Fig. 4a and b, for the HDCFC, with the help of the conductive carbon the series resistance is smaller than that of hydrogen fuel cell. However, although at 800 °C the polarisation resistance of the cell with carbon fuel was bigger than that of the cell with hydrogen fuel in comparison to the data at 700 °C, the cell gave good output at this temperature as higher OCV value. There are two semicircles in Fig. 4b, which is charge transfer at high frequency and mass transportation at low frequency, respectively. Considering about the increase in polarisa-
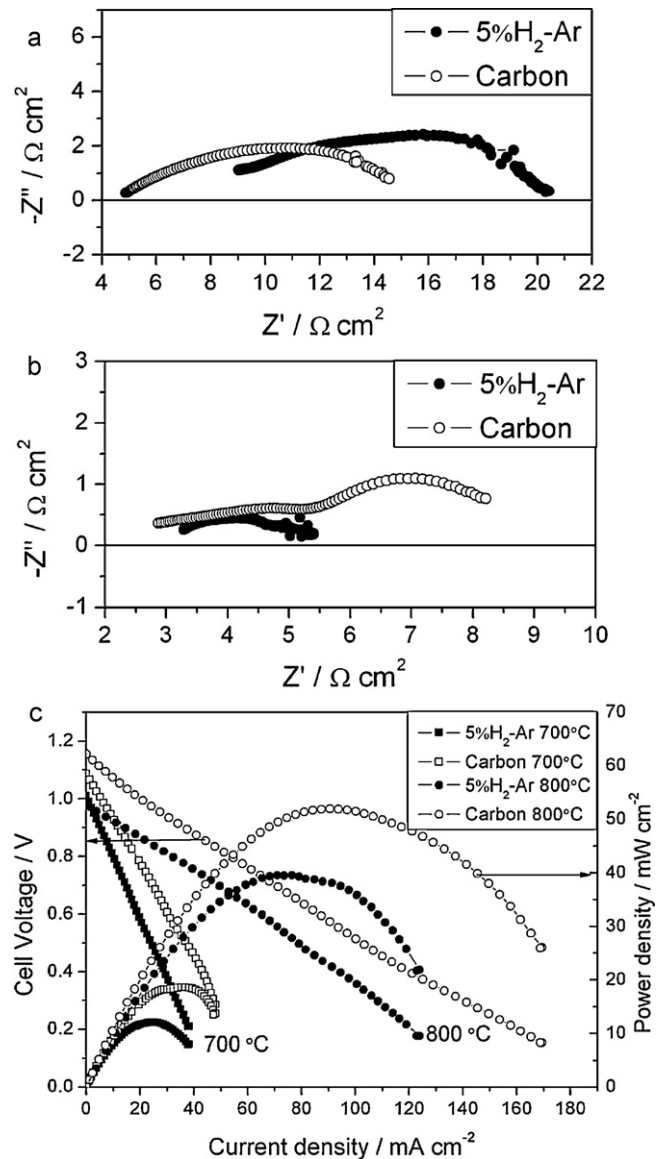

Fig. 4. (a) Impedance spectra of the cells with carbon fuel or hydrogen fuel at 700 °C. (b) Impedance spectra of the cells with carbon fuel or hydrogen fuel at 800 °C. (c) Current–voltage curves of the cells with carbon fuel or hydrogen fuel at 700 °C and 800 °C.

tion resistance at high temperature, the dissolution and corrosion of the electrode and electrolyte might not be negligible, especially at higher temperatures. This is one of the reasons that the carbonate contents were being decreased to a certain level. We can also see from Fig. 1 more processes were involved in since 50 mol% carbonate is used, while less processes when 20 mol% carbonate is used for Fig. 4. The another possible reason for the bigger polarisation resistance at 800 °C is related to the decomposition of carbonate, especially at high temperatures the carbonate decomposes much more quickly according to the following equation (Fig. 5):

$$CO_3^{2-} \rightarrow CO_2 + O^{2-} \tag{1}$$

Reaction of the carbonate with carbon (Eq. (2)) might also be responsible for the degradation,

$$C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^- \tag{2}$$

This will be further considered in Section 3.3 where CO_2 gas was introduced into the system. For all the cell tests, we used the robust thick YSZ electrolyte. The ionic resistance of a 1 mm YSZ
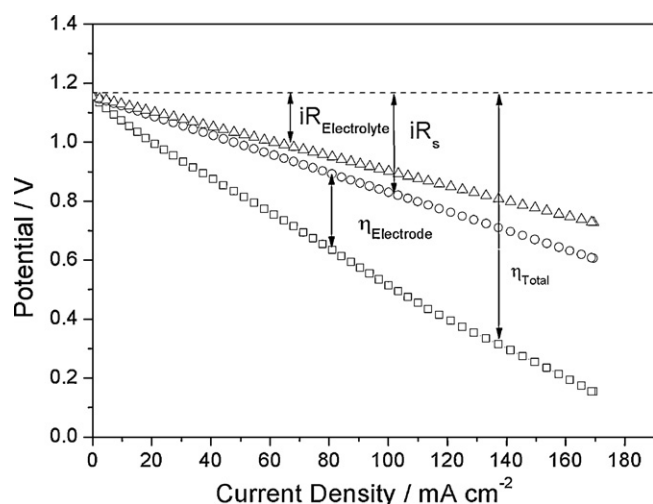
Fig. 5. Potential of the HDCFCs with 1 mm YSZ electrolyte, Ni/YSZ anode and LSM/YSZ cathode using 20 mol% carbonate in carbon fuel at 800 °C.

electrolyte should be $2.23 \pm 0.02 \, \Omega$ at 800 °C. This alone amounts to some 80% of the ohmic losses (R_s, series resistance shown in Fig. 4b) and would be even larger if electrode area is not fully utilised. When the electrolyte is made thinner, of the order of a few tens of micrometers, much higher current density is expected.

3.3. Enhanced OCV with carbon and carbonate

The OCV of the cell with solid carbon is higher than that with hydrogen fuel. With the same cell structure, one of cells using 5% H_2–Ar as the fuel without carbon and carbonate has 1.01 V open circuit voltage at 700 °C, while another one the solid carbon fuel and carbonate shows 1.08 V open circuit voltage and the temperature has a positive effect on the OCV. Without carbonate, the electrochemical reaction rate is sluggish so that the OCV is limited, which is only 0.71 V (Fig. 6).

Considering the electrochemical reaction of the whole cell the cathode reaction is simply as follows:

$$\text{Cathode}: O_2 \rightarrow O^{2-} + 2e^- \tag{3}$$

However, the reaction that happens in the anode compartment is more complex. Although many researchers have made an effort
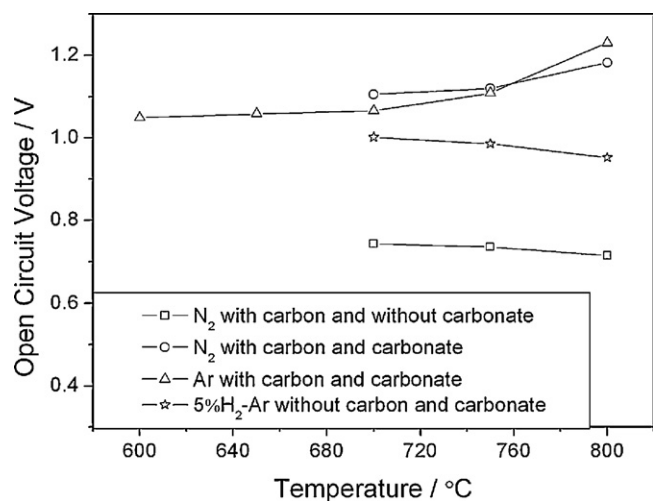

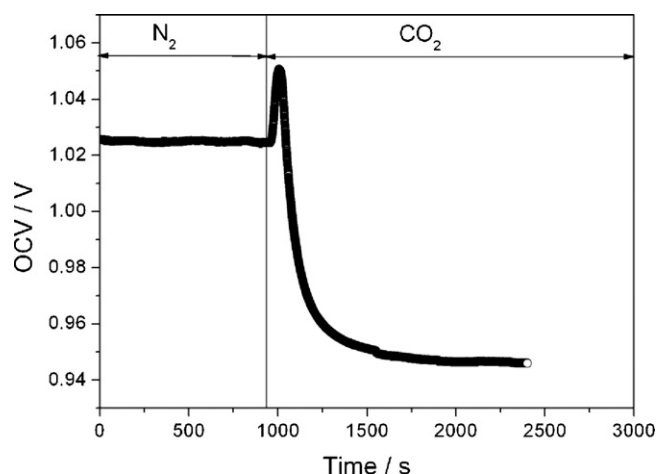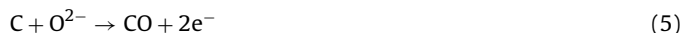**Fig. 6.** Open circuit voltage of the HDCFCs with various purge gases or different carbon/carbonate slurry.

Fig. 7. Open circuit voltage of the HDCFC under N_2 or CO_2 using 80 mol% carbonate in carbon fuel at 700 °C.

to explore the reactions at the anode, the mechanism is still unclear. The possible several reactions are as follows:

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \tag{4}$$

$$C + O^{2-} \rightarrow CO + 2e^- \tag{5}$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{6}$$

$$CO_2 + C \rightarrow 2CO \tag{7}$$

As well as involving Eqs. (1) and (2).
The total reaction of the cell is,

$$C + O_2 \rightarrow CO_2 \tag{8}$$

In order to simplify the calculation, only Eq. (4) is considered as the main reaction in the anode compartment.

So, the open circuit voltage of the cell can be described as,

$$E_{cell} = E_0 - \frac{RT}{nF} \ln \frac{a_{CO_2}}{a_C \times a_{O_2}} \tag{9}$$

Here, $E_0 = \Delta G_0/nF$, and ΔG_0 is the reaction Gibbs function of Eq. (8), n is the number of electrons in the electrochemical reaction, a_{CO_2}, a_C and a_{O_2} are the activity of CO_2 and C at the anode, and O_2 at the cathode. Theoretical E_0 values are similar at various temperatures because the entropy change is nearly zero. The observed open circuit voltages were higher than the theoretically expected values, which is because no gas pressures were involved in this theoretical calculation. a_C is 1 because carbon is solid and the oxygen activity is 0.21 at the cathode since air is used, while at the anode, the activity significantly relies on the gas composition. Cooper et al. utilized CO_2 as the carrying gas at their anodes and obtained an OCV around 1.00 V [4]. In our case, we purged inert gas, nitrogen or argon (Fig. 6). Therefore, the main gas component at the anode is nitrogen or argon, while the produced gases, CO_2 and CO, only make up a low percentage of the gases components. Thus a quite low CO_2 activity value contributes a lot to the open circuit voltage. The open circuit voltage of the cell under CO_2 flowing was also tested, which is shown in Fig. 7. The OCV was 1.02 V at 700 °C in nitrogen, which was slightly lower than the value in Fig. 4c, which might be due to a small leak. The OCV started to increase slightly and then moved to a low value when the gas was switched from nitrogen to CO_2. The stable OCV reached 0.95 V in CO_2 (Fig. 7). This suggests the above evaluation on the OCV is reasonable.

In our previous report the effect of high temperature heat treatment on the OCV had been demonstrated [9]. It was believed that the decomposition of the carbonate at high temperature and leaving Li_2O in the anode compartment changed the activity of CO_2
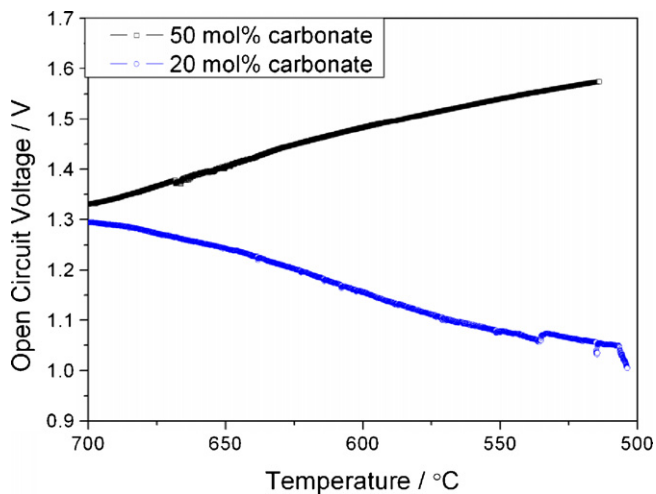
Fig. 8. Effect of the carbon/carbonate slurry on OCV behaviour as temperature is decreased from 700 °C.

to contribute to the increase in the OCV. Here we found the OCV behaviour was not only dependent on thermal history but also on the carbon/carbonate slurry. High temperature heat treatment was effective for the fuel with high carbonate contents and has no influence on the OCV behaviour if a low amount of the carbonate was used. If 50 mol% content of the carbonate was used, the OCV value increased with decreasing temperature and reached in excess of 1.57 V at 550 °C after high temperature treatment (Fig. 8). However, with other contents of the carbonate (such as 20 mol%), OCV values decreased with decreasing temperature (Fig. 8). It means that the carbonate content is of importance for cell properties, with more carbonate the by-product of CO increases. In this case, Eq. (6) is the dominant electrochemical reaction at the anode. Therefore, the OCV increased with decreasing temperature. The enhanced OCV values might be related to the decomposition, which was elicited in our previous paper [9].

4. Conclusions

A hybrid direct carbon fuel cell using a solid carbon fuel in the presence of the secondary electrolyte carbonate as well as in the absence of the carbonate was investigated and appreciable current densities are obtained after the optimization of the anode structure and composition. The open circuit voltages of the cell without the carbonate and with different amounts of the carbonate were recorded. The addition of the carbonate led to a much higher OCV values, 1.23 V at 800 °C. The carbon/carbonate slurry also plays an important role in the OCV behaviour. It was demonstrated that the carbon oxidation process is not only temperature but also electrode/electrolyte (carbon to carbonate) component dependent.

Acknowledgements

References

[1] International Energy Outlook, 2009, http://www.eia.doe.gov/oiaf/ieo/coal.html.
[2] Renewable and low carbon fuel regulation enacted, http://www2.news.gov.bc.ca/news_releases_2009-2013/2009EMPR0024-000796.htm.
[3] Carbon trust to explore opportunities to cut carbon and support UK business in China, http://www.carbontrust.com/EN/CECIC.aspx.
[4] N.J. Cherepy, R. Krueger, K.J. Fiet, A.F. Jankowaki, J.F. Copper, J. Electrochem. Soc. 152 (2005) A80.
[5] W.W. Jacques, US patent no. 555,551 (1896).
[6] R.D. Weaver, S.C. Leach, A.E. Bayce, L. Nanis, SRI, Menlo Park, CA 94025, SAN-0115/105-1.
[7] D.G. Vutetakis, D.R. Skidmore, J. Eelectrochem. Soc. 134 (1987) 3027.
[8] S.L. Jain, Y. Nabae, B.J. Lakeman, K.D. Pointon, J.T.S. Irvine, Solid State Ionics 179 (2008) 1417.
[9] Y. Nabae, K.D. Pointon, J.T.S. Irvine, Energy Environ. Sci. 1 (2008) 148.
[10] S.L. Jain, B.J. Lakeman, K.D. Pointon, J.T.S. Irvine, Ionics 13 (2007) 413.
[11] K. Ota, S.I. Mitsushima, S. Kato, S. Asano, H. Yoshitake, N. Kamiya, J. Electrochem. Soc. 139 (1992) 667.
[12] J.R. Selman, J. Power Sources 160 (2006) 852.
[13] S.L. Jain, J.B.J. Lakeman, K.D. Pointon, R. Marshall, J.T.S. Irvine, Energy Environ. Sci. 2 (2009) 687.
[14] Y. Nabae, K.D. Pointon, J.T.S. Irvine, J. Electrochem. Soc. 156 (2009) B716.