

Effect of temperature on the electrochemical oxidation of ash free coal and carbon in a direct carbon fuel cell

Duc-Luong Vu and Choong-Gon Lee[†]

Department of Chemical and Biological Engineering, Hanbat National University,
125, Dongseodaero, Yuseong-gu, Daejeon 34158, Korea
(Received 2 August 2015 • accepted 17 January 2016)

Abstract—The present study proposes the application of ash-free coal (AFC) as a primary fuel in a direct carbon fuel cell (DCFC) based on a molten carbonate fuel cell (MCFC). AFC was produced by solvent extraction using microwave irradiation. The influence of AFC-to-carbonate ratio (3 : 3, 3 : 1, 3 : 0 and 1 : 3 g/g) on the DCFC performance at different temperatures (650, 750 and 850 °C) was systematically investigated with a coin-type cell. The performance of AFC was also compared with carbon and conventional hydrogen fuels. AFC without carbonate (AFC-to-carbonate ratio=3 : 0 g/g) gave a comparable performance to other compositions, indicating that the gasification of AFC readily occurred without a carbonate catalyst at 850 °C. The ease of gasification of AFC led to a much higher performance than for carbon fuel, even at 650 °C, where carbon cannot be gasified with a carbonate catalyst.

Keywords: Ash-free Coal, Carbon, Direct Carbon Fuel Cell, Temperature, Molten Carbonate Fuel Cell

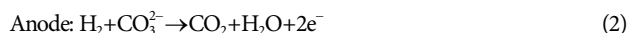
INTRODUCTION

Direct carbon fuel cells (DCFCs) are a special type of high temperature fuel cell. Various types of DCFCs have been investigated, based on alkaline, molten carbonate and solid-oxide electrolytes [1-4]. Among them, molten carbonate electrolytes provide several important advantages: i) they work at rather high temperatures, between 600 and 900 °C, which allows the acceleration of electrochemical reactions and means that the use of noble metals or catalysts can be avoided, ii) they have high conductivity and good stability as electrolytes, iii) they lead to high energy efficiency in the fuel cell, and iv) they have a high operation temperature, allowing the use of various fuels, for example, natural gas, CO, biomass and so forth [5-7].

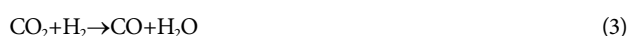
The cathode reaction in a molten carbonate fuel cell (MCFC) is expressed as follows:



When hydrogen is supplied to the anode, the electrode reaction is:



In the anode channel, carbon monoxide is produced by the endothermic reverse water-gas-shift (WGS) reaction:



The open-circuit voltage (E_{OCV}) of a MCFC can be expressed according to the Nernst equation:

$$E_{OCV} = E_0 + \frac{RT}{2F} \ln \left(\frac{[\text{H}_2]}{[\text{H}_2\text{O}][\text{CO}_2]_{an}} [\text{O}_2]^{0.5} [\text{CO}_2]_{ca} \right) \quad (4)$$

As the E_{OCV} is determined by the partial pressures of H_2 , CO and CO_2 at the anode, the WGS reaction can affect the E_{OCV} by changing the gas partial pressures.

Compared to hydrogen, carbon is solid and more convenient for energy storage [8]. As carbon can be oxidized in a DCFC, carbon-containing materials such as natural gas, petroleum, coal and biomass can also be used as the fuel for DCFCs [9,10]. The addition of molten carbonate to the carbon fuel creates a hybrid direct carbon fuel cell (HDCFC). The solid carbon is wetted by molten carbonates in the DCFC, which enhances the reaction rate [11-13]. The ability of direct conversion from carbon to electricity in an HDCFC, especially in the case of a solid oxide fuel cell (SOFC), was investigated by Irvine and co-workers [11-13]. Vutetakis et al. [14] employed a stirred carbon and carbonate mixture to promote electrochemical carbon and coal oxidation. Cherepy et al. [5] tested various carbon materials in molten carbonate electrolytes. Among the carbon species tested, graphite was found to be very conductive and performed well, yielding 0.8 V at $50 \text{ mA} \cdot \text{cm}^{-2}$ and 0.2 V at $120 \text{ mA} \cdot \text{cm}^{-2}$. Chen et al. [15] studied the performance of graphite as a fuel in a DCFC with molten carbonates of Li_2CO_3 - K_2CO_3 - Al_2O_3 . They concluded that graphite alone was not appropriate as the fuel for a DCFC, even though it had regular structure, high electrical conductivity and low electrical resistance.

One of the problems encountered in coal fuelled DCFCs is that the ash content is generally quite high, 5-20% in natural graphite and 10-25% in coal, which affects the power efficiency. Several studies have been dedicated to the development of an efficient fuel cell with ash-free coal (AFC) [16-18]. AFC is a suitable fuel for the anode reaction, owing to the low ash content and dense structure because the mineral matter in coal is extracted into the solvent during the extraction process [19,20]. Recently, Jeon et al. [21] showed the feasibility of using AFC in a solid-oxide based DCFC. The cell voltage was about 1.1 V from 600 to 900 °C. Significant research has

[†]To whom correspondence should be addressed.

E-mail: leecg@hanbat.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

been performed on DCFCs in order to produce electricity using solid carbonaceous materials instead of gaseous hydrogen. Alternatively, the reforming of coal into gaseous fuels, such as H_2 and CO , has also been studied.

In this work, AFC was prepared by solvent extraction from Arutmin sub-bituminous coal using microwave radiation. AFC, carbon and hydrogen were used as the fuels in a coin-type DCFC. Their electrochemical oxidations were characterized by steady-state polarization, open-circuit voltage and step chronopotentiometry measurements.

EXPERIMENTAL

1. DCFC System

The anode was a porous Ni-Al metal and the cathode was porous Ni. The matrix was made of $LiAlO_2$. The electrodes and matrices were supplied by the Korean Electric Power Research Institute. The carbonate electrolyte was 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 , which was obtained by mixing the two powders (Li_2CO_3 and K_2CO_3) and melting at $500^\circ C$ for 1 h, before cooling and grinding them. The carbonates were of reagent grade. A silver wire was used for the cathode leads, whereas a Ni wire was used for the anode. More details of the cell preparation and operation are described in a previous paper [22].

The cell was installed without carbon fuel in a box furnace, which had a hole in order to penetrate the upper side of the alumina tube of the anode. The temperature of the cell in the furnace was initially raised by $2^\circ C \cdot min^{-1}$ from room temperature to $350^\circ C$ in air. Subsequently, the temperature was increased to 650, 750 and $850^\circ C$, according to the experimental purpose. A mixture of 70 mol% air and 30 mol% CO_2 , at a rate of $0.200 L \cdot min^{-1}$, was supplied to the center of the cathode. A gaseous mixture of $0.125 L \cdot min^{-1}$ H_2 and $0.025 L \cdot min^{-1}$ CO_2 was supplied through a deionized water bubbler to the anode, and the cell performance was measured. Then, the AFC fuel was introduced into the anode with nitrogen-gas purging to prevent air diffusion into the anode chamber. The performance of AFC was also compared with a commercial activated carbon fuel (Junsei). For the solid fuels, a mixture of carbonate with AFC or carbon was filled in a small alumina tube. Both ends of the tube were blocked by Ni foam to allow gas transport from the solid mixture to the electrode surface [23].

2. Preparation of the AFC Fuel

AFC was produced by the extraction of Arutmin sub-bituminous coal with N-methyl-2-pyrrolidone (NMP) as the solvent at around $202^\circ C$ and under atmospheric conditions using microwave irradiation. The proximate and elemental analyses of AFC are shown in Table 1. The carbon fraction in AFC is slightly higher than that in raw coal. The ash content of AFC is about 0.78 wt%, whereas that

of raw coal is 13.32 wt%. AFC was fed to the anode by mixing with carbonate at ratios of 3:3, 3:1, 3:0 and 1:3 g/g (AFC/carbonate).

3. Electrochemical Measurements

The fuel cell performance was measured with a potentiostat (PARSTAT 2273) operated with PowerSuite software. A four-electrode system was used to measure the cell voltage by the applied current. In this configuration, the cathode was the working electrode (WE), the anode served as the counter electrode (CE) and two reference electrodes (RE1 and RE2) were also used. The electrochemical measurements included the E_{OCV} steady-state polarization (SSP) and step chronopotentiometry (SC). Current was applied from 0 to $150 mA \cdot cm^{-2}$ in $10 mA \cdot cm^{-2}$ steps with the SSP method. SC involved increasing the current from 0 to $150 mA \cdot cm^{-2}$ in $50 mA \cdot cm^{-2}$ steps for 60 s and recording the subsequent potential relaxations. The effects of the temperature and the AFC-to-carbonate electrolyte ratio on the cell performance were also investigated over the range of 650 – $850^\circ C$ under atmospheric pressure.

RESULTS AND DISCUSSION

1. Effects of the AFC-to-carbonate Ratio

Fig. 1 presents the E_{OCV} with respect to time at various AFC-to-carbonate ratios in order to investigate the effects of the mixing ratio on the gas-evolution behavior. Measurements were at $850^\circ C$ in order to have sufficient gasification of AFC. The gas evolution from the AFC mostly occurred through the pyrolysis of the hydrocarbon components in AFC and the gasification of carbon components. The pyrolysis of AFC (Eq. (5)) and char gasification (Eq.

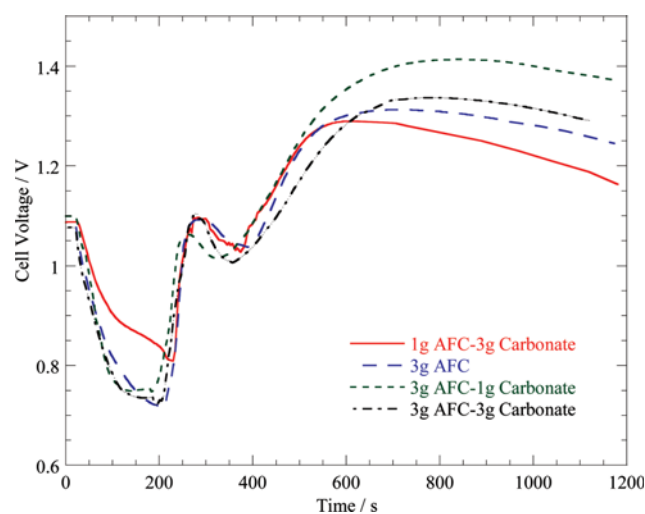
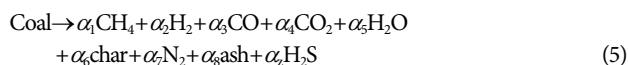


Fig. 1. Behavior of open-circuit voltages (E_{OCV}) with different AFC-to-carbonate ratios at $850^\circ C$.

Table 1. Proximate and ultimate analyses of Ash free coal and Arutmin raw coal

| Sample | Proximate analysis (wt%) | | | | Ultimate analysis (wt%) | | | | |
|---------------|--------------------------|-----------------|--------------|-----------|-------------------------|------|------|-------|------|
| | Moisture | Volatile matter | Fixed carbon | Ash (dry) | C | H | N | O | S |
| Raw coal | 6.96 | 40.04 | 39.68 | 13.32 | 69.12 | 5.12 | 4.71 | 20.81 | 0.24 |
| Ash free coal | 0.42 | 50.40 | 47.91 | 0.78 | 76.06 | 5.65 | 2.92 | 15.30 | 0.07 |

(6)) are combined in the gasification, forming mainly H_2 , CO , CO_2 and CH_4 [24,25]:



where α is the number of moles of the species, $\sum \alpha_i = 1$. The reverse Boudouard reaction is given by:



When the carbonate is mixed with AFC, the carbon reacts with the carbonate to produce CO [26]:



As the carbonate maintains the equilibrium with CO_2 and O^{2-} ions, we can write the following relationship:



The two minima in the voltage are related to gas generation. The first minimum at 200 s is attributed to H_2 generation, and the second at 400 s is attributed to CO generation, because gas generation from AFC is initially from H_2 , followed by CO generation [27]. H_2 generation is thought to be from the pyrolysis of hydrocarbon sources in AFC and, therefore, it is rapid. CO generation, however, is relatively slow, owing to the chemical processes of Eqs. (6) and (7). Both of these reactions reduce the CO_2 partial pressure at the anode, which raises the E_{OCV} value according to the following relation:

$$E_{OCV}(H_2/H_2O) = E_{H_2/H_2O}^0 + \frac{RT}{2F} \ln \left(\frac{[H_2]}{[H_2O][CO_2]_{an}} [O_2]^{0.5} [CO_2]_{ca} \right) \quad (9)$$

All of the curves showed the same behavior, as shown in Fig. 1. The E_{OCV} reached a considerably high value after 650–700 s, and then the voltage gradually decreased. For a low amount of AFC (1 g), the E_{OCV} decreased more rapidly. Different AFC-to-carbonate mixtures gave different maximum E_{OCV} values of 1.28, 1.31, 1.41 and 1.34 V at 1:3, 3:0, 3:1 and 3:3 g/g mixture ratios, respectively.

Fig. 1 also shows that the E_{OCV} value for the composition with only AFC being comparable to the other AFC and carbonate mixtures. In general, a carbonate catalyst is required for the gasification of carbon [29]. However, AFC contains many hydrocarbon compounds and the pyrolysis decomposes the AFC to H_2 and CO [27,28]. Indeed, a cell temperature of 850 °C was enough to gasify the AFC without a carbonate catalyst. Therefore, the cell could run with AFC only. The smallest amount of AFC, at an AFC-to-carbonate ratio of 1:3 g/g, showed the lowest E_{OCV} value over 600 s, because the amount of generated gas is smallest for this composition and the diffused oxygen from the outside reduced the H_2 and CO partial pressures. In addition, the composition with only AFC had a lower voltage than the other 3 g AFC and carbonate mixtures. This is contrary to the previous result [27]. AFC is gasified to H_2 and CO , thus, only a very small amount of CO_2 raises the E_{OCV} . The reason for this is not currently clear, but the low activity of AFC may be a reason.

Takanohashi et al. [16,17] reported that AFC contained a high concentration of oxygen surface functional groups, which demonstrates a broad alignment with the increase in the electrochemical

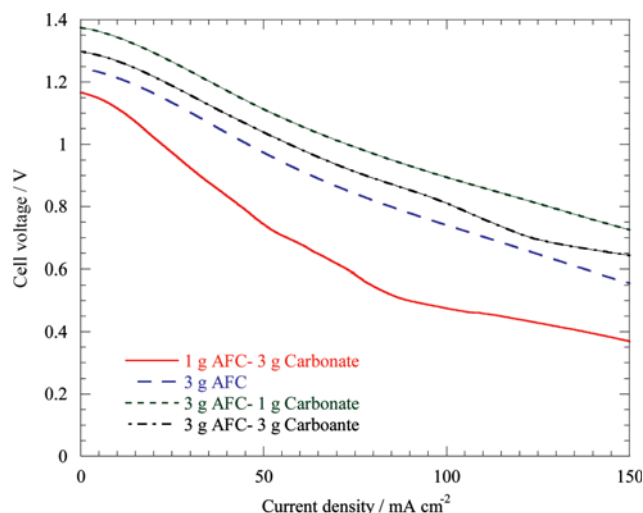


Fig. 2. Comparison of current-voltage indicated with different AFC-to-carbonate ratios at 850 °C.

reactivity. In addition, they suggested that the high surface area or pore volume of AFC showed an improvement in the anodic reaction by increasing the contact between the solid fuels and carbonate liquids. In this study, the surface area and pore size effects are not discussed; however, they may affect cell performance and further research is needed.

Fig. 2 presents the current-voltage behavior for the different ratios of AFC and carbonate at 850 °C. As we can see, the curves of the three compositions with a 3 g AFC mixture exhibit very similar slopes. The voltages of 0.725 V for 3:1 g/g (AFC-to-carbonate), 0.643 V for 3:3, 0.368 V for 1:3 and 0.555 V for AFC only are observed at 150 mA·cm⁻². This indicates that the AFC mixing ratio does not have a significant effect on the internal or mass-transfer resistances. However, for the 1:3 g/g AFC-to-carbonate ratio, the lowest voltage and steepest slope was observed, indicating that large mass-transfer resistance exists because of the low gas generation from it.

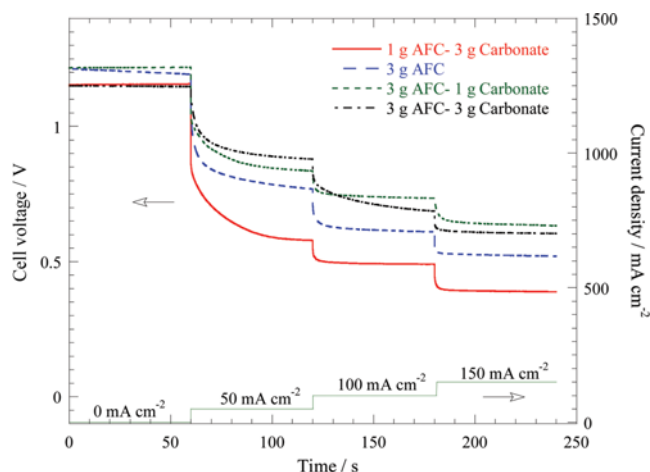


Fig. 3. Comparison of step chronopotentiometry behavior with different AFC-to-carbonate ratios at 850 °C.

Fig. 3 shows the SC results for the four compositions at 850 °C. They had large relaxation gaps at lower current densities, with the mixture of 1 g AFC and 3 g carbonate showing the slowest voltage relaxation. However, at current densities over 100 mA·cm⁻², the voltage relaxation patterns became similar. Different relaxation behavior, according to the current density, is also observed in the current-voltage curves shown in Fig. 2. The curves have a steeper slope at lower current densities, whereas they become milder at higher current densities, meaning that the mass-transfer resistance becomes milder at higher current densities, irrespective of the composition. The reason for this is currently under investigation and will be reported soon. According to the voltage-time characteristics depicted in Fig. 3, the minimum voltages for the AFC-to-carbonate ratios of 3:3, 3:1, 1:3 and 3:0 g/g are 0.63, 0.60, 0.39 and 0.52 V, respectively.

2. Temperature Effects

The E_{OCV} behavior for AFC and activated carbon at 650, 750 and 850 °C is presented in Figs. 4(a) and 4(b). During the first 20 s,

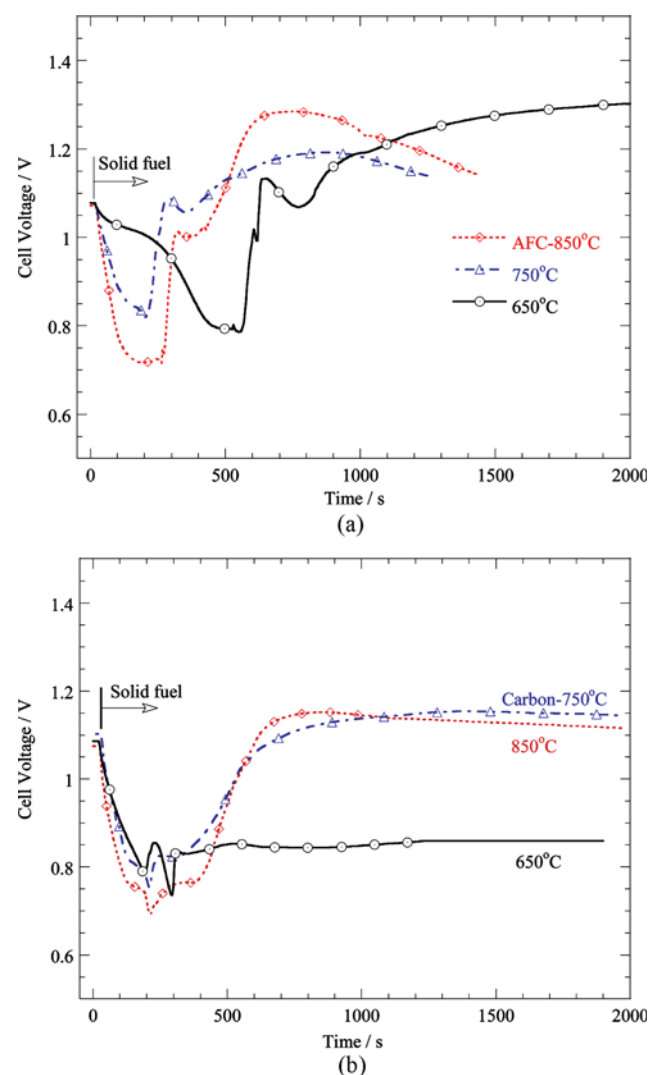


Fig. 4. Behavior of E_{OCV} for 3 g AFC and 3 g carbonate mixtures (a) and 3 g carbon and 3 g carbonate mixtures (b) at 650, 750 and 850 °C.

hydrogen fuel (0.125 L·min⁻¹ H₂ and 0.025 L·min⁻¹ CO₂ through a bubbler) was supplied to the anode, and, for instance, an E_{OCV} value of about 1.08 V was observed at 850 °C. Then, the hydrogen fuel was cut, and simultaneously the E_{OCV} decreased and reached 0.74 V after 150 s. At around 200 s, an AFC-to-carbonate mixture of 3:3 g/g was introduced into the anode by filling it into an alumina tube. To prevent oxygen diffusion from outside into the cell, there was a nitrogen gas flow in the anode chamber. After solid fuel introduction, the E_{OCV} increased quickly again. At around 600 s, the E_{OCV} value reached 1.30 V at 850 °C. Similar behavior was also observed at 650 and 750 °C. In particular, AFC fuel at 650 °C shows an E_{OCV} value of about 1.3 V at around 2,000 s, although this E_{OCV} change is much slower than those at 750 and 850 °C. This means the gasification of AFC can even be obtained at 650 °C, which is very different from the behavior of carbon fuel. Fig. 4(b) compares the E_{OCV} change following the introduction of carbon fuel into the cell at different temperatures. The cell at 650 °C shows a very low E_{OCV} value, compared to those at 750 and 850 °C, when the carbon and carbonate mixtures are supplied. When we substitute hydrogen fuel for solid carbon, the E_{OCV} of around 1.1 V becomes a mini-

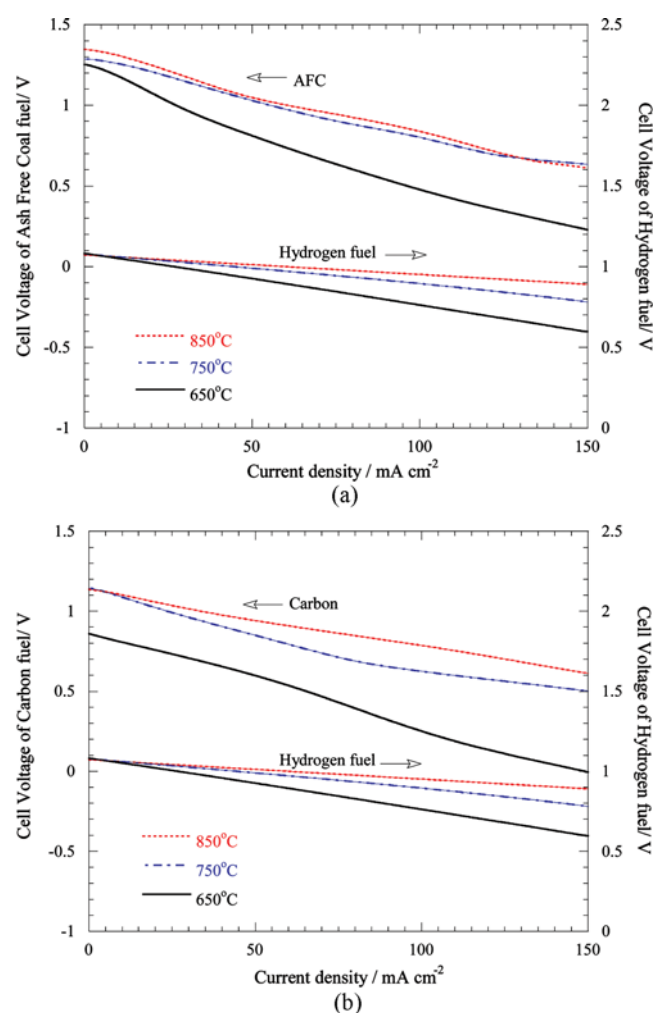


Fig. 5. Current-voltage behavior for 3 g AFC and 3 g carbonate mixtures (a) and 3 g carbon and 3 g carbonate mixtures (b) at 650, 750 and 850 °C.

num and then rises again at 750 and 850 °C. However, the cell at 650 °C shows a very small increase to approximately 0.85 V, whereas the E_{OCV} values at 750 and 850 °C are over 1.1 V at around 800 s, indicating that the gasification of carbon fuel is not enough at 650 °C and a relatively high temperature is required to oxidize solid carbon fuel.

Figs. 5(a) and 5(b) show the voltage-current behavior at 650, 750 and 850 °C at a potential scan rate of $0.25 \text{ mV}\cdot\text{s}^{-1}$ for an AFC-to-carbonate fuel ratio of 3:3 g/g and a carbon-to-carbonate fuel ratio of 3:3 g/g, as well as for hydrogen fuel ($0.125:0.025 \text{ L}\cdot\text{min}^{-1}/\text{L}\cdot\text{min}^{-1} \text{ H}_2/\text{CO}_2$ through a bubbler). The theoretical E_{OCV} values for the hydrogen fuel are 1.078 V at 850 °C, 1.106 V at 780 °C and 1.132 V at 650 °C. Thus, lower E_{OCV} values should be obtained at higher temperatures. Although the behavior is not clear, a slightly lower E_{OCV} was observed at higher temperatures. For the hydrogen fuel, the voltage linearly decreased with current. Lee et al. [30] suggested that mass-transfer processes control the electrode reactions in the MCFC, and thus a linear decrease of voltage is obtained. Fig. 5(a) shows that the voltage for the AFC and carbonate mixture has a much steeper slope than for the H_2 fuel and has several various slopes according to the current densities. The steepness of the AFC fuel slope indicates that larger resistance exists in AFC oxidation. In a previous study [27], AFC was gasified to H_2 and CO before being oxidized. The complexity is reflected in the steep and non-linear current-voltage curves of the AFC fuel. The E_{OCV} values of the AFC fuel were 1.35 V at 850 °C, 1.28 V at 750 °C and 1.25 V at 650 °C. A larger E_{OCV} value at higher temperatures is attributed to the higher H_2 and CO partial pressures from more active gasification, which is in agreement with prior results [31–33]. The voltage at $150 \text{ mA}\cdot\text{cm}^{-2}$ was 0.625 V at 850 °C, 0.595 V at 750 °C and 0.25 V at 650 °C. A very low voltage at 650 °C, compared with the voltages at higher temperatures, was observed. The current densities were in the mass-transfer controlled region, and less gasification and a reduced volume of gas at 650 °C could be the reason for this low voltage.

Another effect of temperature is a reduction in cathodic polarization. As reported in a previous study [34], the polarization decrease as a result of temperature increase is significant, especially at the cathode, because mass-transfer resistance through the liquid-carbonate film is a dominant factor and oxygen solubility and diffusivity in the carbonates are temperature sensitive.

Temperature also has an important effect on the conductivity. The conductivity of the electrolyte is generally a function of temperature and obeys Arrhenius' law [35]:

$$\sigma_{\text{electrolyte}} = \sigma_{\text{electrolyte}}^0 \exp(-E_a/RT) \quad (10)$$

where $\sigma_{\text{electrolyte}}^0$ is a pre-exponential factor of the electrolyte conductivity ($\text{S}\cdot\text{m}^{-1}$). Eq. (10) indicates that higher temperatures result in better electrolyte conductivity as a consequence of decreasing viscosity, which reduces the resistance of the cell and increases cell performance.

Fig. 5(b) shows current-voltage behavior of carbon and carbonate mixed fuels at different temperatures. A clear difference is observed between the AFC and carbon fuels: the carbon fuel has a lower voltage than the AFC fuel at all temperatures. In particular, the voltage of carbon fuel at 650 °C is much lower than that of the

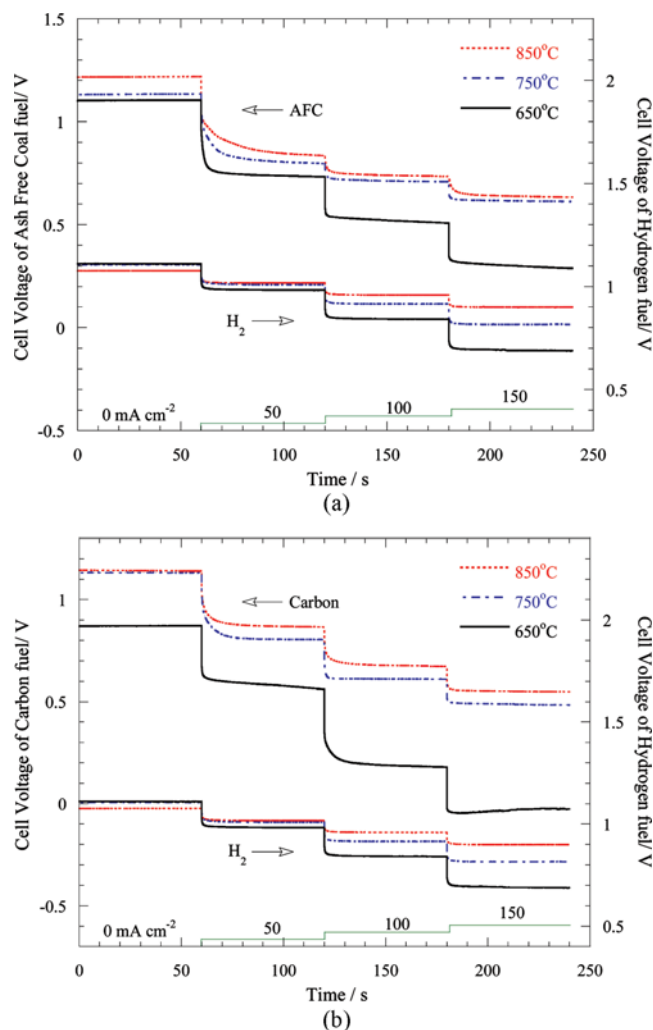


Fig. 6. Step chronopotentiometry (SC) behavior for 3 g AFC and 3 g carbonate mixtures (a) and 3 g carbon and 3 g carbonate mixtures (b) at 650, 750 and 850 °C.

AFC fuel. The E_{OCV} value of carbon at 650 °C is about 0.860 V, whereas that of AFC at the same temperature is 1.250 V. The large differences in the E_{OCV} values and the voltages during polarization are attributed to the difficulty of gasification of carbon at 650 °C. A previous study [27] reported that carbon is difficult to gasify using a carbonate catalyst at 650 °C.

Figs. 6(a) and 6(b) compare the SC results of the AFC and carbon fuels with respect to hydrogen fuel at different temperatures (650, 750 and 850 °C). Hydrogen fuel shows very stable and uniform voltage relaxations with the current step at the different temperatures. The largest voltage steps were observed at 650 °C. Lowering the temperature, as mentioned above, increases the internal, charge and mass-transfer resistances at the electrodes. Thus, the largest voltage steps are inevitably at the lowest temperature of 650 °C.

On the contrary, the AFC fuel shows very large and slow voltage relaxations, especially at 650 °C, as shown in Fig. 6(a). At higher temperatures of 750 and 850 °C, the voltage relaxations become faster in the higher current density region. The changes are drastic according to the applied current densities seen in the figure.

When we compare the voltage relaxations between the hydrogen and AFC fuels, the difference is mostly ascribed to oxidation at the anode. Therefore, the temperature effect is found to be significant for AFC oxidation at the anode.

Fig. 6(b) shows the SC results with carbon fuel at the various temperatures. Compared with the AFC fuel, much slower voltage relaxations are observed for all temperatures. The size of the voltage steps is reduced by the current density at 750 and 850 °C. However, the size of the voltage steps at 650 °C becomes larger with increasing current density. This is quite different from other voltage steps at higher temperatures. This unique behavior at 650 °C is mostly attributed to the difficulty of carbon gasification. The small amount of reactant gases signifies mass-transfer resistance at higher currents; thus, larger and slower voltage relaxations are obtained at 650 °C.

CONCLUSIONS

The electrochemical oxidation of behavior ash-free coal and carbon was investigated in a coin-type DCFC using a molten carbonate electrolyte. The electrochemical behavior of the fuels was compared with conventional hydrogen fuel in terms of the AFC-to-carbonate ratio and operating temperature. The following content was concluded from this work. The addition ratio of AFC-to-carbonate was not a dominant factor for cell performance. The AFC composition without carbonate also showed indifferent E_{OCV} values and voltages at polarization compared to compositions with carbonate added, indicating that AFC does not require a carbonate catalyst for its gasification. From 650 to 850 °C, AFC showed an E_{OCV} value over 1.2 V throughout the temperature range, whereas carbon gave an E_{OCV} value of approximately 1.1 V at 750 and 850 °C, and 0.85 V at 650 °C. Thus, AFC has a very high performance at 650 °C compared to carbon, owing to the ease of AFC gasification at lower temperatures. In the current-voltage curves, the solid fuels had many regions with different slopes, indicating the complexity of oxidation due to gasification. The AFC and carbon solid fuels had much larger polarizations and lower performance compared to hydrogen fuel.

ACKNOWLEDGEMENTS

This research was supported by Cooperation of Industrial R&D Programs through the Korea Institute of Energy Technology Evaluation and Planning funded by the Ministry of Trade, Industry and Energy (20143010031830).

REFERENCES

1. J. R. Selman, *J. Power Sources*, **156**, 128 (2006).
2. D. Cao, Y. Sun and G. Wang, *J. Power Sources*, **167**, 250 (2007).
3. A. L. Dicks, *J. Power Sources*, **156**, 128 (2006).
4. J. F. Cooper, *Proc. 2nd International Conference on Fuel Cell Science, Engineering and Technology*, Rochester, NY, 375 (2004).
5. N. J. Cherepy, R. Krueger, K. J. Fiet, A. F. Jankowski and J. F. Cooper, *J. Electrochem. Soc.*, **152**, A80 (2005).
6. J. R. Selman in *Fuel cell systems* (Eds. L. J. M. J. Blomen, M. N. Mugerwa), Plenum Press, New York, 384 (1993).
7. K. Joon, *J. Power Sources*, **61**, 129 (1996).
8. S. Zecevic, E. M. Patton and P. Parhami, *Carbon*, **42**, 1983 (2004).
9. Y. Nabae, K. D. Pointon and J. T. S. Irvine, *J. Electrochem. Soc.*, **156**, B716 (2009).
10. Q. H. Liu, Y. Tian, C. Xia, L. T. Thompson, B. Liang and Y. D. Li, *J. Power Sources*, **185**, 1022 (2008).
11. S. L. Jain, Y. Nabae, B. J. Lakeman, K. D. Pointon and J. T. S. Irvine, *Solid State Ionics*, **179**, 1417 (2008).
12. Y. Nabae, K. D. Pointon and J. T. S. Irvine, *Energy Environ. Sci.*, **1**, 148 (2008).
13. S. L. Jain, B. J. Lakeman, K. D. Pointon and J. T. S. Irvine, *Ionics*, **13**, 413 (2007).
14. D. G. Vutetakis, D. R. Skidmore and H. J. Byker, *J. Electrochem. Soc.*, **134**, 3027 (1987).
15. M. Chen, C. Wang, X. Niu, S. Zhao, J. Tang and B. Zhu, *Intl. J. Hydrogen Energy*, **35**, 2732 (2010).
16. T. Yoshida, T. Takanohashi, K. Sakanishi, I. Saito, M. Fujita and K. Mashimo, *Energy Fuels*, **16**, 1006 (2002).
17. C. Li, T. Takanohashi, I. Saito, M. Iino, H. Aoki and K. Mashimo, *Energy Fuels*, **18**, 97 (2004).
18. M. Muthuvel, X. Jin and G. G. Botte, in *Encycl. Electrochem. Power Sources*, Vol. 3 (Ed. Jurgen Garche), Elsevier, 158 (2009).
19. S. D. Kim, K. J. Woo, S. K. Jeong, Y. J. Rhim and S. H. Lee, *Korean J. Chem. Eng.*, **25**, 758 (2008).
20. N. Okuyama, N. Komatsu, T. Shigehisa, T. Kaneko and S. Tsuruya, *Fuel Process Technol.*, **85**, 947 (2004).
21. J. P. Kim, H. Lim, C. H. Jeon, Y. J. Chang, K. N. Koh and S. M. Choi, *Intl. J. Hydrogen Energy*, **37**, 11401 (2012).
22. C.-G. Lee, H. Hur and M.-B. Song, *J. Electrochem. Soc.*, **158**, B410 (2011).
23. C.-G. Lee, *Fuel Cells*, **12**, 550 (2012).
24. D. Vamvuka, E. T. Woodburn and P. R. Senior, *Fuel*, **74**, 1452 (1995).
25. D. Vamvuka, E. T. Woodburn and P. R. Senior, *Fuel*, **74**, 1461 (1995).
26. K. Nagase, T. Shimodaira, M. Itoh and Y. Zheng, *Phys. Chem. Chem. Phys.*, **1**, 5659 (1999).
27. C.-G. Lee and W.-K. Kim, *Intl. J. Hydrogen Energy*, **40**, 5475 (2015).
28. C.-G. Lee, W.-K. Kim and D.-L. Vu, *Korean J. Chem. Eng.*, **32**, 1784 (2015).
29. D. W. Mckee and D. Chatterji, *Carbon*, **16**, 53 (1978).
30. C. G. Lee, B. S. Kang, H. K. Seo and H. C. Lim, *J. Electroanal. Chem.*, **540**, 169 (2003).
31. J. Ruffin, A. D. Perwich II, C. Brett, J. K. Berner and S. M. Lux, *J. Power Sources*, **213**, 275 (2012).
32. L. Guo, J. M. Calo, E. Dicooco and E. J. Bain, *Energy Fuels*, **27**, 1712 (2013).
33. Q. Liu, Ye. Tian, Ch. Xia, Levi T. Thompson, B. Liang and Y. Li, *J. Power Sources*, **185**, 1022 (2008).
34. C.-G. Lee, *J. Electroanal. Chem.*, **701**, 36 (2013).
35. T. Kojima, Y. Miyazaki, K. Nomura and K. Tanimoto, *J. Electrochem. Soc.*, **154**, F222 (2007).