



Characteristics of Solid Fuel Oxidation in a Molten Carbonate Fuel Cell

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ABSTRACT

Oxidation behaviours of ash free coal (AFC), carbon, and H₂ fuels were investigated with a coin type molten carbonate fuel cell. Because AFC has no electrical conductivity, its oxidation occurs via gasification to H₂ and CO. An interesting behaviour of mass transfer resistance reduction at higher current density was observed. Since the anode reaction has the positive reaction order of H₂, CO₂ and H₂O, the lack of CO₂ and H₂O from AFC results in a significant mass transfer resistance. However, the anode products of CO₂ and H₂O at higher current densities raise their partial pressure and mitigate the resistance. The addition of CO₂ to AFC reduced the resistance sufficiently, thus the resistance reduction at higher current densities did not appear. Electrochemical impedance results also indicate that the addition of CO₂ reduces mass transfer resistance. Carbon and H₂ fuels without CO₂ and H₂O also show similar behaviour to AFC: mass transfer resistance is diminished by raising current density and adding CO₂.

Keywords : Ash free coal, Mass transfer, Molten carbonate fuel cell, Overpotential, Oxidation

Received : 9 November 2015, Accepted : 21 March 2016

1. Introduction

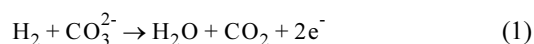
After a long development period, a molten carbonate fuel cell (MCFC) has reached the commercial stage in the US and Korea. It could potentially be used for a large proportion of the world's fuel cells, but to increase its utilization, a longer life and a more economic fuel must be developed. Natural gas is a common fuel for MCFCs, but it is a high price fuel.

To overcome the fuel cost problem, direct use of carbon for the fuel cell has been attempted. Since carbon is a conductive material, it is considered as an electrode as well as a fuel. To oxidise solid carbon the fuel cell generally requires a high temperature of over 700 °C. A recent report has suggested that carbon is gasified to CO with molten carbonate, and then the CO is oxidised to CO₂ [1]. A 100 cm² class MCFC was used for direct carbon fuel, and it was concluded

that carbon oxidation had occurred via CO [2].

Another possible fuel is AFC. It can be prepared by two methods; one is a solvent extraction of organic components from coal followed by separation of solvent and organic materials. The other is dissolution of ash components by acids or bases. AFC has a very low ash content and relatively low gasification temperature compared with carbon. Since AFC has no electric conductivity, it only works as a fuel by gasification to H₂ and CO. Most AFC oxidation was carried out in a DCFC (direct carbon fuel cell) based on SOFC (solid oxide fuel cell) technology [3,4]. To date, no report is available for a DCFC run by AFC based on MCFC technology.

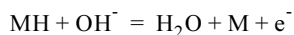
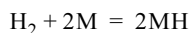
Hydrogen oxidation in molten carbonates is shown in Eq. (1):



However, the oxidation reaction comprises several reaction steps [5]:

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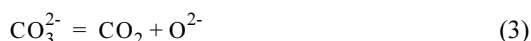
DOI: <http://dx.doi.org/10.5229/JECST.2016.7.2.91>



Due to these reaction steps, the reaction rate has the following relationship for H_2 , CO_2 and H_2O (Eq. 2) [5]:

$$i_0 \propto p(\text{H}_2)^{0.25} p(\text{CO}_2)^{0.25} p(\text{H}_2\text{O})^{0.25} \quad (2)$$

The relationship shown in Eq. 2 indicates that the H_2O and CO_2 species participate in the oxidation with positive reaction orders. In general, it is considered CO_2 is supplied to the anode to prevent carbonate decomposition (Eq. 3).



Moreover, H_2O is also fed to reduce carbon deposition by the water-gas shift reaction (Eq. 4).



Besides the reasons indicated by Eq. 3 and 4, Eq. 2 explains that CO_2 and H_2O are necessary components for H_2 oxidation. Therefore, the much smaller amounts of them than H_2 in conventional hydrogen fuel gives rise to a significant overpotential due to the CO_2 and H_2O species [6].

In this work, the oxidation behaviours of AFC and carbon were investigated by comparison with hydrogen fuel in a coin type MCFC. The overpotential was analysed in terms of gas composition with a gas chromatograph (GC) and current densities with the electrochemical analysis methods of steady state polarisation, step chronopotentiometry (SC) and electrochemical impedance spectroscopy (EIS).

2. Experimental Section

A coin type MCFC was built with electrodes ca. 4 cm in diameter. The anode was a porous Ni alloy, and the cathode was porous in-situ oxidised NiO. The matrix was made of LiAlO_2 powder and the electrolyte was a Li_2CO_3 - K_2CO_3 eutectic. The coin cell was installed in a furnace and the anode had a long alumina tube of 3 cm I.D. to introduce the coal fuel. More details were described in a previous work [1].

The AFC was prepared from a bituminous Indonesian Berau coal. It was extracted with a microwave at 202 °C with an organic solvent of NMP (N-methyl-2-pyrrolidinone) [7]. The carbon was home-made from oak at 400 °C in a N_2 environment. The AFC or carbon was used to fill a small alumina tube of O.D. 1.5 cm, and then it was supplied to the anode chamber. Specifically, 3 g of carbon was supplied to the fuel cell as a eutectic mixture with 3 g of 38 mol% Li_2CO_3 and 62 mol% K_2CO_3 . Prior to the introduction of AFC or carbon, the cell was operated with a normal H_2 fuel ($0.125 \text{ L min}^{-1} \text{ H}_2 + 0.025 \text{ L min}^{-1} \text{ CO}_2 + 14 \% \text{ H}_2\text{O}$) and a cathode gas ($0.150 \text{ L min}^{-1} \text{ air} + 0.100 \text{ L min}^{-1} \text{ CO}_2$). The H_2 fuel was used to check the cell performance. When the AFC or carbon was introduced, the H_2 fuel was stopped while the cathode gas was kept constant. To prevent O_2 diffusion into the anode, the anode chamber was maintained at a higher pressure than outside by flowing N_2 into the anode. More detailed preparation and operation procedures were described in a previous work [1,7].

Gas composition from the AFC was measured with a GC (Model HP G1530A). The AFC and carbonate mixture (3 g AFC and 3 g Li-K carbonates) were placed in a closed alumina tube, which was heated to 850 °C. To measure the gas generation rate, nitrogen at 0.1 L min^{-1} was flowed into the tube. Then the outlet gas compositions were measured with the GC and gas generation rates were obtained by comparison with the nitrogen composition.

Electrochemical methods of steady state polarisation, SC, and EIS were employed. The steady state polarisation was carried out with a potentiostat (PAR 2273) in the current range up to 150 mA cm^{-2} . The SC showed voltage relaxations by 50 mA cm^{-2} steps in the current for 60 s up to 150 mA cm^{-2} . There were therefore three steps in the SC measurement. The EIS was measured in an open circuit state by applying 5 mV rms in the frequency range from 1 kHz to 0.01 Hz.

3. Results and Discussion

Fig. 1 compares current-voltage behaviours of AFC+ N_2 fuel (AFC 3 g + N_2 0.1 L min^{-1}), AFC+ CO_2 fuel (AFC 3 g + CO_2 0.025 L min^{-1}), and H_2 fuel (H_2 0.125 L min^{-1} + CO_2 0.025 L min^{-1} + 14 % H_2O) at 850 °C. The equilibrium constant (K_{eq}) of the water-gas shift reaction (Eq. 5) is about 0.91 at 850 °C. The value

was obtained by the interpolation of Gibbs energy of the reaction (5) between 1100 and 1200 K [8].



Thus, the calculated open circuit voltage (E_{OCV}) of the H_2 fuel at 850 °C is 1.053 V according to Eq. 6.

$$E_{\text{OCV}} = E^0 + \frac{RT}{2F} \ln \frac{p(\text{H}_2)p(\text{O}_2)^{0.5}p(\text{CO}_2)_{\text{ca}}}{p(\text{H}_2\text{O})p(\text{CO}_2)_{\text{an}}} \quad (6)$$

The measured E_{OCV} of the H_2 fuel of 1.052 V is very close to the theoretical one. On the other hand, the E_{OCVs} of the AFC fuels are 1.300 V for AFC+N₂ and 0.885 V for AFC+CO₂ fuel. Since the E_{OCV} is determined by temperature and gas composition as shown in Eq. 6, the E_{OCVs} for AFC represent a deviation of gas compositions from the H_2 fuel. In particular, the high E_{OCV} of 1.300 V for AFC+N₂ was due to the very small amounts of CO₂ and H₂O at the anode because the AFC was fed in a dry state. The addition of CO₂ to the AFC+CO₂ fuel raised the CO₂ partial pressure, and the lowest E_{OCV} of 0.885 V was obtained. The H_2 fuel shows clear linearity by applying current, which indicates that the MCFC reactions are mass transfer control processes [9]. The mildest slope was also observed for the H_2 fuel, representing the lowest mass transfer resistance among the fuels. The steepest slope is obtained for AFC+N₂ fuel although it has the highest E_{OCV} . It means the

AFC+N₂ fuel has the largest mass transfer resistance among them. An interesting point is that the AFC+N₂ fuel had milder slopes at higher current densities. This indicates that the resistance had been changed by the current and less resistance existed at higher currents. However, the AFC+CO₂ fuel had a consistent slope much milder than that of AFC+N₂.

Fig. 2 shows gas generation rates for AFC. H₂ and CO are the main gases from AFC, and CO₂ and CH₄ are the minor components. Those gases are mostly generated for 30 min, however the cell continued for several hours with 3 g of AFC. Since the current density of 150 mA cm⁻² is 1.05 A, which corresponds to ca. 7.3 mL min⁻¹ of H₂, thus the cell could be operated for several hours. H₂O could not be detected by the GC, but the amount must be very small because the AFC was kept dry and the H₂O composition in the AFC was about 2 wt% [7]. Identical gas generation behaviour for AFC has also been reported [3]. Therefore it is clear that the large mass transfer resistance of the AFC+N₂ fuel shown in Fig. 1 was due to the low amounts of CO₂ and H₂O. Although the steady state polarisation in Fig. 1 was measured within 30 min of the AFC being supplied, the steep decrease of gas generation rates resulted in a large mass transfer resistance, especially due to CO₂ species. Consequently, the CO₂-added fuel of AFC+CO₂ had much less resistance than AFC+N₂ fuel because the added CO₂ raised its partial pressure and reduced resistance according to Eq. 2.

Fig. 3 compares SC results for the three fuels -H₂ fuel, AFC+N₂, and AFC+CO₂ - at 850 °C. The SC

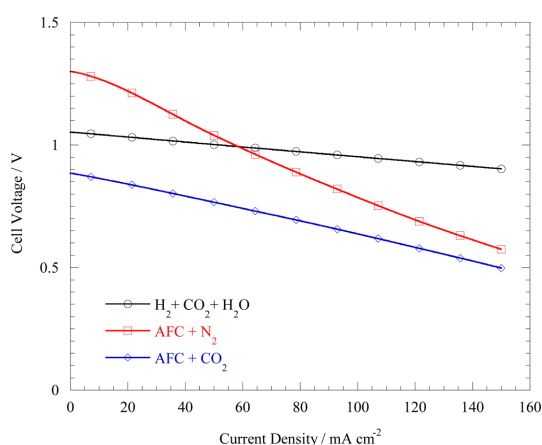


Fig. 1. Current-voltage behaviours of 3 g AFC + 0.1 L min⁻¹ N₂ (AFC+N₂), 3 g AFC + 0.025 L min⁻¹ CO₂ (AFC+CO₂), and 0.125 L min⁻¹ H₂ + 0.025 L min⁻¹ CO₂ + 14 % H₂O (H₂+CO₂+H₂O) fuels at 850 °C.

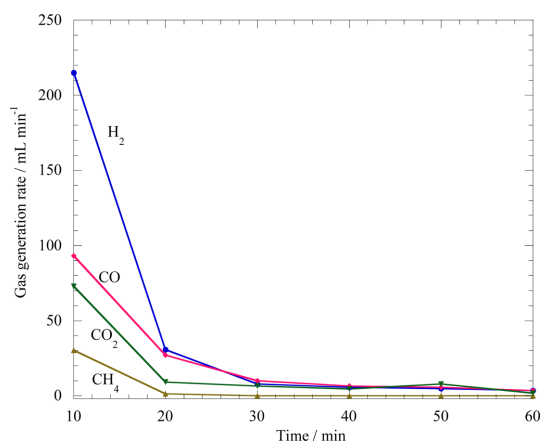


Fig. 2. Gas generation rates of various gases from AFC at 850 °C.

method reveals reaction characteristics by voltage relaxation. The H_2 fuel showed consistent and very fast voltage relaxations at the three current steps, showing that H_2 oxidation is very fast with a low mass transfer resistance. However, $\text{AFC}+\text{N}_2$ fuel had a very large and very slow voltage relaxation for the first current step up to 50 mA cm^{-2} , indicating that AFC oxidation is very slow with a large mass transfer resistance. A possible reason for this large resistance is due to the lack of CO_2 and H_2O species in the reactant gases because AFC generates very small amounts of CO_2 as seen in Fig. 2, and H_2O as mentioned above. In particular, the voltage relaxations of the $\text{AFC}+\text{N}_2$ fuel become faster and smaller at higher current densities. This can be explained by the production of H_2O and CO_2 in the reaction at the anode as shown in Eq. 1. A higher current density generates more H_2O and CO_2 at the anode, which reduces mass transfer resistances of the species. The effect of CO_2 at the anode is confirmed by the $\text{AFC}+\text{CO}_2$ fuel, which shows much smaller and faster voltage relaxations at the current steps than those of the $\text{AFC}+\text{N}_2$ fuel. Consequently, the addition of CO_2 reduces its mass transfer resistance, although E_{OCV} is decreased according to Eq. 6.

Fig. 4 shows the voltage relaxation values for each of the current steps for the three fuels. They were measured by voltage relaxation for 60 s. Steps 1, 2, and 3 mean the current steps from 0 to 50 mA cm^{-2} , 50 to 100 mA cm^{-2} , and 100 to 150 mA cm^{-2} , respectively. The H_2 fuel has the lowest values for the steps, indicating it has a very low overvoltage. The

$\text{AFC}+\text{N}_2$ fuel shows a decrease in the values with increasing current. As mentioned before, the product species of H_2O and CO_2 reduce the mass transfer resistance, so that the relaxation values decrease. The $\text{AFC}+\text{CO}_2$ fuel shows much lower and more stable values than $\text{AFC}+\text{N}_2$. It shows that the addition of CO_2 to AFC significantly reduces the mass transfer resistance of the species. Much larger voltage relaxations for $\text{AFC}+\text{CO}_2$ than those for the H_2 fuel would be due to the insufficient gas generation from AFC, thus a larger mass transfer resistance exists for the $\text{AFC}+\text{CO}_2$ fuel.

Fig. 5 shows the EIS results for the two fuels $\text{AFC}+\text{N}_2$ and $\text{AFC}+\text{CO}_2$ at 850°C . Since the real values at the highest frequency are the same in both fuels, the cell has identical internal resistance for both fuels. In particular, the $\text{AFC}+\text{N}_2$ fuel shows very large impedance in the low frequency region. This shows that a very large mass transfer resistance exists for the fuel. The reason is the very small amount of H_2O and CO_2 species at the anode compared with the H_2 fuel. This can be confirmed by addition of CO_2 to AFC. The CO_2 -added fuel of $\text{AFC}+\text{CO}_2$ gives very small impedance compared with $\text{AFC}+\text{N}_2$ because the addition of CO_2 reduces the resistance.

The CO_2 addition effect was also attempted for carbon fuel. Fig. 6 shows the SC results for carbon and 0.1 L min^{-1} of N_2 ($\text{C}+\text{N}_2$), carbon and 0.025 L min^{-1} of CO_2 ($\text{C}+\text{CO}_2$), and H_2 (H_2 0.125 L min^{-1} + CO_2 0.025 L min^{-1} + 14% H_2O) fuels at 850°C . Carbon is also a solid fuel, so that its direct oxidation to CO_2

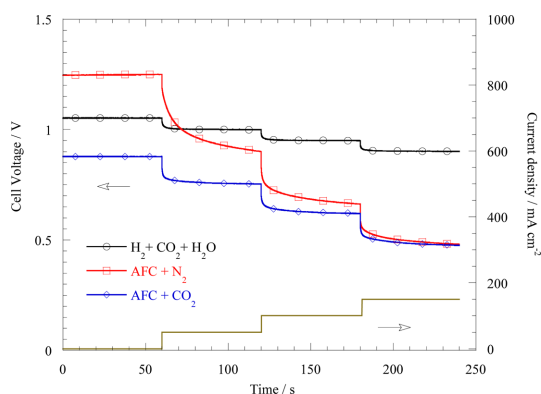


Fig. 3. Step chronopotentiometric results of 3 g AFC + 0.1 L min^{-1} N_2 ($\text{AFC}+\text{N}_2$), 3 g AFC + 0.025 L min^{-1} CO_2 ($\text{AFC}+\text{CO}_2$), and 0.125 L min^{-1} H_2 + 0.025 L min^{-1} CO_2 + 14 % H_2O ($\text{H}_2+\text{CO}_2+\text{H}_2\text{O}$) fuels at 850°C .

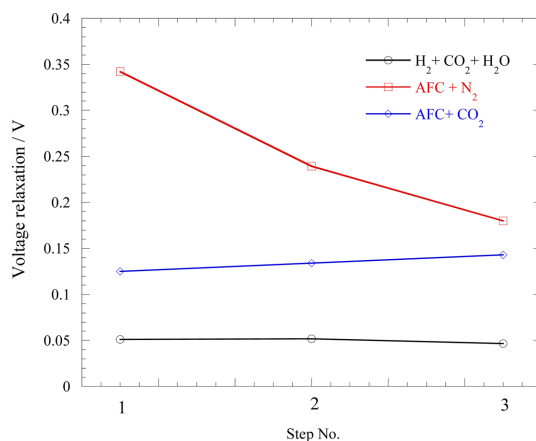


Fig. 4. The relaxed voltages for 60 s at every current step of Fig. 3. Step 1 is that at the current step from 0 to 50 mA cm^{-2} , step 2 to 100 mA cm^{-2} , and step 3 to 150 mA cm^{-2} .

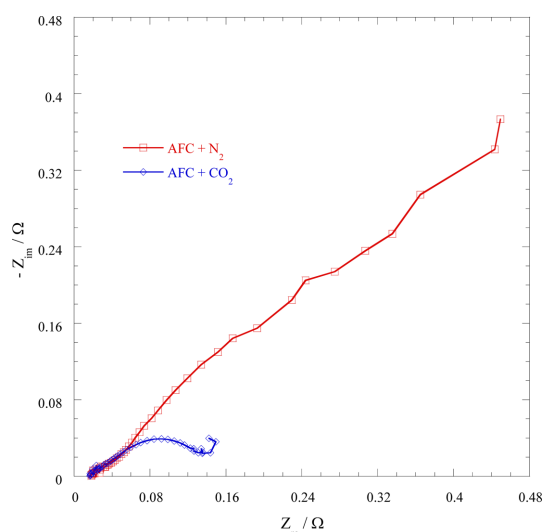


Fig. 5. Electrochemical impedance spectroscopy results of 3 g AFC + 0.1 L min⁻¹ N₂ (AFC+N₂) and 3 g AFC + 0.025 L min⁻¹ CO₂ (AFC+CO₂) fuels at 850 °C, open circuit voltage state.

would be difficult [1]. In general, it is accepted that carbon oxidation in a fuel cell proceeds via carbon monoxide [1,10]. The carbon is gasified with molten carbonates over 700 °C and CO is the main species [11]. Therefore, 3 g of carbon and 3 g of carbonates were mixed and supplied to the anode as a carbon fuel in this work. Since the C+N₂ fuel has a very small CO₂ and H₂O content, the mass transfer from them would be significant. Therefore, much larger voltage decreases are observed for C+N₂ compared with the H₂ fuel. However, faster and smaller voltage relaxation is also observed at the higher current density steps. This behaviour is very similar to that of AFC, showing they have similar oxidation paths, and a deficiency of CO₂ produces a large mass transfer resistance. On the other hand, the CO₂-added fuel (C+CO₂) shows very stable voltage relaxations, although the E_{OCV} is decreased for the same reason as for AFC+CO₂. The consistent voltage relaxations for the C+CO₂ fuel indicate that the added CO₂ sufficiently reduced the resistance.

Fig. 7 shows the SC results for H₂ only and H₂+CO₂ fuels at 850 °C. When the anode was supplied only with H₂, smaller and faster voltage relaxation was observed at higher current densities. This is very similar to the AFC+N₂ fuel due to a larger mass transfer resistance with a smaller amount of CO₂.

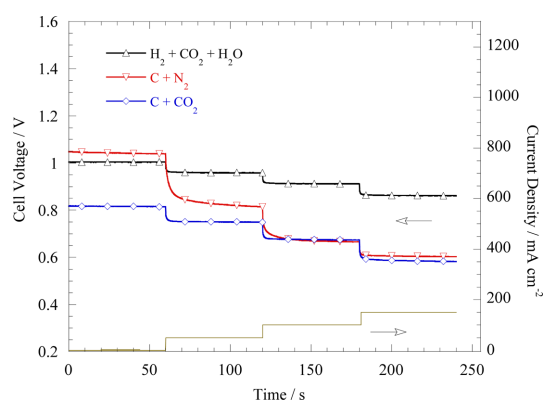


Fig. 6. Step chronopotentiometric results of 3 g C + 0.1 L min⁻¹ N₂ (C+N₂), 3 g C + 0.025 L min⁻¹ CO₂ (C+CO₂), and 0.125 L min⁻¹ H₂ + 0.025 L min⁻¹ CO₂ + 14 % H₂O (H₂+CO₂+H₂O) fuels at 850 °C.

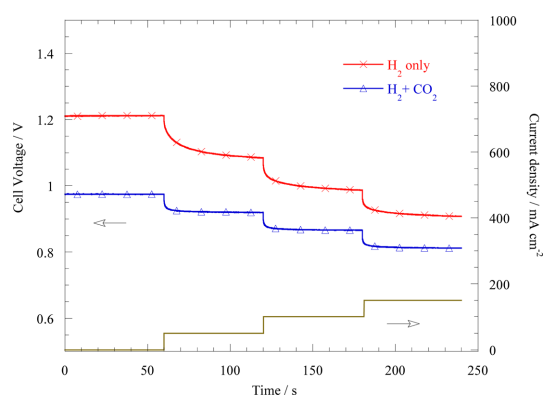


Fig. 7. Step chronopotentiometric results of 0.125 L min⁻¹ H₂ (H₂ only) and 0.125 L min⁻¹ H₂ + 0.025 L min⁻¹ CO₂ + 14 % H₂O (H₂+CO₂+H₂O) fuels at 850 °C.

Therefore, deficiency of CO₂ species at the anode results in significant mass transfer resistance regardless of fuel species. The CO₂-added fuel of H₂+CO₂ shows a much faster and smaller voltage relaxation than H₂ only fuel, although CO₂ addition decreases the E_{OCV} .

4. Conclusions

The oxidation behaviours of solid (AFC and carbon) and gas (H₂) fuels were investigated with a coin type MCFC single cell. The cell temperature was 850 °C, and oxidation of the fuels was successfully predicted. Since the solid fuel of AFC was gasified at that temperature, a very high E_{OCV} of 1.300 V was

obtained whereas that for H₂ was 1.052 V. The high E_{OCV} of AFC was due to the very small amounts of CO₂ and H₂O generated by it. Therefore, AFC showed a very large mass transfer resistance compared to H₂ fuel because the anode reaction requires CO₂ and H₂O as well as H₂ according to the H₂ oxidation mechanism in Ref. 5. The resistance was reduced at higher current densities because the current generates CO₂ and H₂O as anode product gases. For the same reason, the addition of CO₂ to AFC reduced the resistance. Similar behaviour was also observed for the carbon and H₂ fuels. The oxidation behaviour of carbon is very similar to AFC because addition of CO₂ to the carbon reduces resistance, although E_{OCV} also decreases. When we supplied only H₂ to the anode, a very large mass transfer resistance was obtained similar to the AFC and carbon cases. The addition of CO₂ to the H₂ gas reduced the resistance as CO₂ enhanced the mass transfer rate.

Acknowledgements

This research was supported by the research fund of Hanbat National University in 2014.

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