Short communication

Effect of carbon monoxide addition to the anode of a molten carbonate fuel cell

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Abstract

This study attempts to characterize the gas-phase reactions at the anode of a molten carbonate fuel cell by the addition of carbon monoxide and carbon dioxide. Carbon dioxide addition causes a rapid negative voltage shift. A constant voltage is maintained during the addition at open-circuit state. This indicates that the water gas shift (wgs) reaction which accompanies the addition of carbon dioxide is a fast reaction. Addition of carbon monoxide results in slow shifts in negative and positive voltages and suggests that carbon monoxide gives rise to complex gas-phase reactions at the anode. The Boudouard reaction prevails at the anode on addition of carbon monoxide at low partial pressures of carbon dioxide, i.e. $H_2:CO_2 = 90:10$ to $80:20$ mol%, while the wgs reaction is dominant at higher carbon dioxide ratios. In a polarized state, the wgs reaction appears to be dominant, as opposed to the Boudouard reaction, even at a low CO_2 partial pressure of $H_2:CO_2 = 90:10$ mol%. This is probably due to an increase in the partial pressure of carbon dioxide caused by the anodic reactions.
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1. Introduction

Molten carbonate fuel cells (MCFCs) are based on carbonate electrolytes, and operate at relatively high temperatures ($\sim$923 K). This gives rise to very fast electrode reactions and thus precious metal catalysts are not required in the electrodes. Although carbonate electrolytes allow use of carbon monoxide as a fuel according to the following reaction:

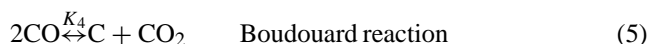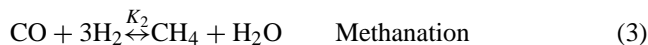$$CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^- \qquad (1)$$
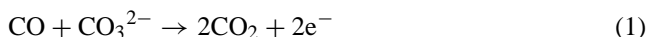
The direct electro-oxidation of carbon monoxide is very sluggish [1], and may cause appreciable overpotentials. To provide a practical method for using carbon monoxide, conversion to hydrogen through a gas-phase reaction, i.e. a water gas shift (wgs) reaction, has been considered, namely:

$$CO + H_2O \overset{K_1}{\leftrightarrow} CO_2 + H_2 \qquad (2)$$

A MCFC generally uses hydrogen as a fuel, and both carbon dioxide and steam are supplied to the anode to prevent decomposition of the carbonate electrolyte and carbon deposition. Mechanistic studies also have suggested that hydrogen oxidation progresses with steam and carbon dioxide

[2]. Thus, H_2, CO_2, H_2O, and CO are usually present in the anode. Under these conditions, the following chemical reactions are available in the gas phase on the carbon monoxide addition, including the wgs reaction:

$$CO + 3H_2 \overset{K_2}{\leftrightarrow} CH_4 + H_2O \qquad \text{Methanation} \qquad (3)$$

$$CO + H_2 \overset{K_3}{\leftrightarrow} C + H_2O \qquad \text{CO hydrogenation} \qquad (4)$$

$$2CO \overset{K_4}{\leftrightarrow} C + CO_2 \qquad \text{Boudouard reaction} \qquad (5)$$

This study characterizes the gas-phase reactions at the anode in a MCFC by the step-functional addition of CO and CO_2 to the anode.

2. Experimental

The MCFC used in this work was a 100-cm^2 single cell with a Ni–10 wt.% Cr anode and an in situ oxidized NiO cathode. The electrolyte was $(62 + 38)$ mol% $(Li + K)CO_3$. The cell was maintained at 923 K under atmospheric conditions. A mixture of 80 mol% H_2 and 20 mol% CO_2 was humidified by passage through water at 53 °C (14 mol% H_2O) and served as the anode gas. The cathode gas was a mixture of 70 mol% air and 30 mol% CO_2. More details of the single cell and its operation have been presented elsewhere [3].

* Corresponding author. Tel.: +82-42-865-5395; fax: +82-42-865-5374.
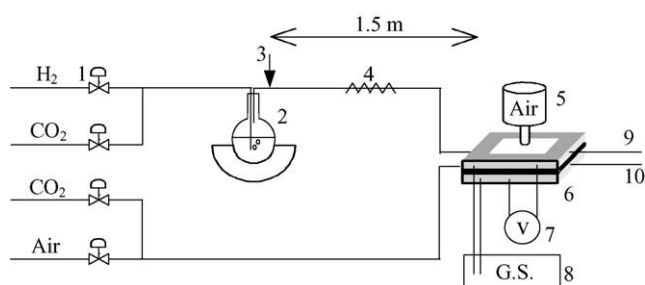*E-mail address:* leecg@kepri.re.kr (C.-G. Lee).

Fig. 1. Schematic diagram of the experimental apparatus: 1, mass flow controller; 2, humidifier; 3, carbon monoxide gas inlet port; 4, line heater; 5, air press; 6, single cell; 7, oscilloscope; 8, galvanostat; 9, anode outlet; 10, cathode outlet.

To investigate the effects of addition of CO and CO_2 to the anode, an addition port was installed approximately 1.5 m ahead of the cell (Fig. 1). This modification is similar to that employed previously in the study of inert gas addition [3]. The amounts of CO and CO_2 were regulated with a mass flow controller and were added in a step-wise function. The voltage shifts were then recorded with an oscilloscope (LeCroy 534A) as a function of current load, $H_2:CO_2$ ratio, and steam amount. The current load was applied with a galvanostat (Sycopel Powerstat) up to 150 mA cm^{-2}. The $H_2:CO_2$ was varied from 90:10 to 60:40 mol% at a total flow rate of 0.217 l min^{-1}. The amount of steam in the anode ranged from 20 to 40 mol% by controlling the humidifier temperature at fixed H_2 and CO_2 flows. The gas compositions at the anode outlet were analyzed with a gas chromatograph (HP 5890II).

Table 1
Comparison of OCV calculated from theoretical gas composition with measured voltages with and without CO_2 addition (0.3 l min^{-1}) to a total anode flow of 0.253 l min^{-1}

	Gas composition (mol%)				Calculated OCV (V)	Measured OCV (V)
	H_2	CO_2	H_2O	CO		
Without CO_2	51.9	7.5	23.7	9.7	1.073	1.059
With CO_2	15.3	48.5	22.7	16.2	0.949	0.967

3. Results and discussion

The effect of CO_2 addition on the open-circuit voltage (OCV) is shown in Fig. 2. The CO_2 reduces the concentration of the other gases in the anode. A gas-phase chemical reaction determines the gas compositions mostly via the wgs reaction (Eq. (2)). Since the equilibrium constant of this reaction (K_1) at 923 K is about 2.0 [4], CO_2 addition increases the partial pressure of CO_2 and reduces that of H_2. The OCV therefore decreases according to the Nernst equation, i.e.

$$E = E^{o} + \frac{RT}{nF} \ln \left(\frac{P(H_2) \, P(O_2)^{0.5} \, P(CO_2)_{ca}}{P(CO_2)_{an} \, P(H_2O)} \right) \quad (6)$$

where E^{o} is the standard potential. Measured and calculated OCVs with and without CO_2 addition are listed in Table 1. Although there is some deviation between the calculated and measured OCV values, the calculated value corresponds with the measured value by showing a negative voltage shift on CO_2 addition. A slower voltage relaxation is observed at the moment of CO_2 interruption, because the interruption
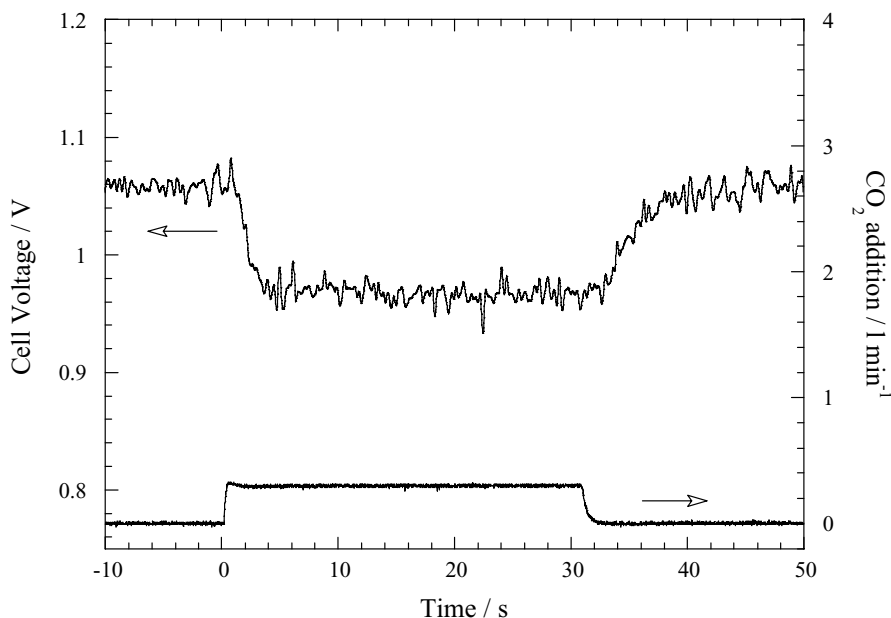

Fig. 2. Effect of CO_2 addition (0.3 l min^{-1}) on OCV at 923 K, 1 atm. Anode flow rate = 0.253 l min^{-1} ($H_2:CO_2:H_2O$ = 69:17:14 mol%). Cathode flow rate = 0.883 l min^{-1}.

reduces the gas flow and more time is then required to re-plenish the anode gas in the cell. A consistent OCV is observed while the added CO_2 flows in the cell. Since the OCV is only a function of gas composition and temperature, the constant OCV suggests that the gas composition and temperature in the cell are invariant to CO_2 addition and the wgs reaction is rapidly completed with the addition.

It should be noted here that the wgs is an exothermic reaction, thus the CO_2 addition progresses the wgs reaction reversibly and is accompanied by heat absorption. This heat absorption may change the temperature on the electrode surface and thus shift the OCV. The constant OCV on CO_2 addition does, however, indicates that the change in temperature at the anode due to the wgs reaction is insignificant. The relatively large heat capacity of the cell frame due to its thickness (about 2.5 cm) may account for this.

The shift in OCV with the CO addition is shown in Fig. 3. Clear voltage changes with very slow relaxations are observed on the addition and the interruption of CO, which contrasts significantly with the OCV behavior with CO_2 addition, where the voltage shift reached a steady state within 10 s. Assuming the temperature change due to CO addition is negligible, the voltage shifts are then responsible for the gas composition changes ascribed to the gas-phase chemical reactions. In particular, the CO addition yields two negatively and positively shifted voltage peaks. This is in contrast with CO_2 addition, which caused only a negative voltage shift and indicates that CO addition causes complex gas-phase reactions.

The available gas-phase reactions with CO addition can be estimated from the voltage peaks. When CO is added to the anode, the OCV shifts negatively. According to the Nernst equation, this effect suggests a decrease in the par-tial pressure of H_2 and an increase in that of CO_2 and H_2O. As noted in Section 1, the possible chemical reactions arising from CO addition include the wgs, methanation, CO hydrogenation and Boudouard reactions, i.e. Eqs. (2)–(5), respectively. Among these, only the CO hydrogenation and Boudouard reactions can account for negative voltage shifts. Since the wgs reaction consumes H_2O and produces CO_2 and H_2, positive voltage shifts are expected with CO addition. Nevertheless, the negative voltage shift shown in Fig. 3 suggests that the wgs reaction might not be the dominant reaction with CO addition. The methanation reaction is also negligible because of the very low equilibrium constant at 923 K ($K_2 \approx 0.37$) [4].

When 100 s have elapsed after the addition CO, the decreased voltage rises again and relaxes to a steady-state value, as shown in Fig. 3. This indicates that the disturbance in the gas composition caused by CO addition disappears and an equilibrium in the gas composition is reached. In this case, the equilibrium would be determined by the wgs reaction, because this reaction prevails at the steady state. On the other hand, CO interruption raises the OCV. This also results from deviation of the gas compositions from the equilibrium compositions of the wgs reaction. The reverse reactions of the negative voltage shift are responsible for the positive peak.

The gas compositions measured at the anode outlet by gas chromatography (GC) at the marked points in Fig. 3 are presented in Fig. 4. Because GC cannot quantify the water content, only the concentrations of H_2, CO_2, and CO are presented. The gas compositions before CO addition (point (i)) are consistent with the calculated compositions, as shown in Table 2. The gas compositions at the negative voltage shift (point (ii)) show an increase in the CO_2 concentration. This
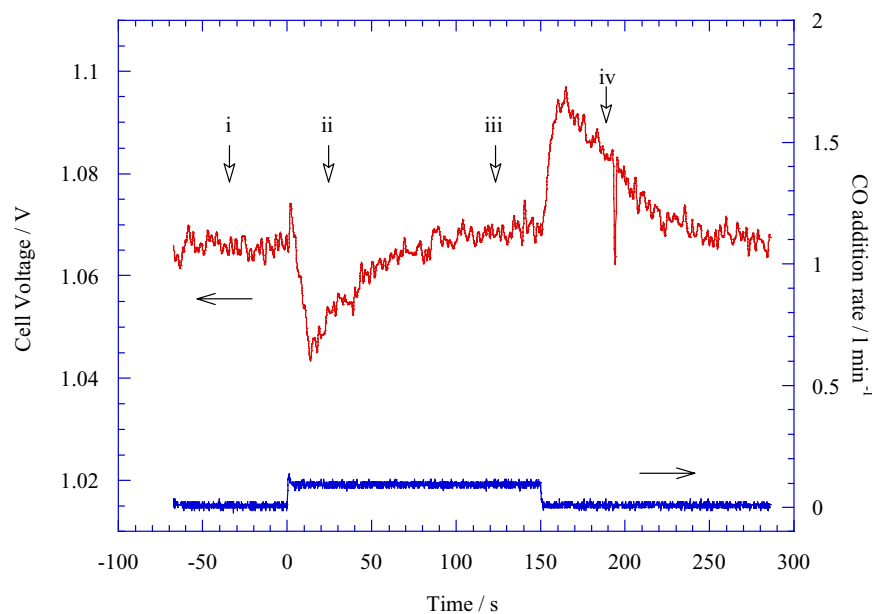

Fig. 3. Effect of CO addition ($0.11 min^{-1}$) on OCV at 923 K, 1 atm. Anode flow rate = $0.253 l min^{-1}$ ($H_2:CO_2:H_2O = 69:17:14 mol\%$). Cathode flow rate = $0.883 l min^{-1}$.
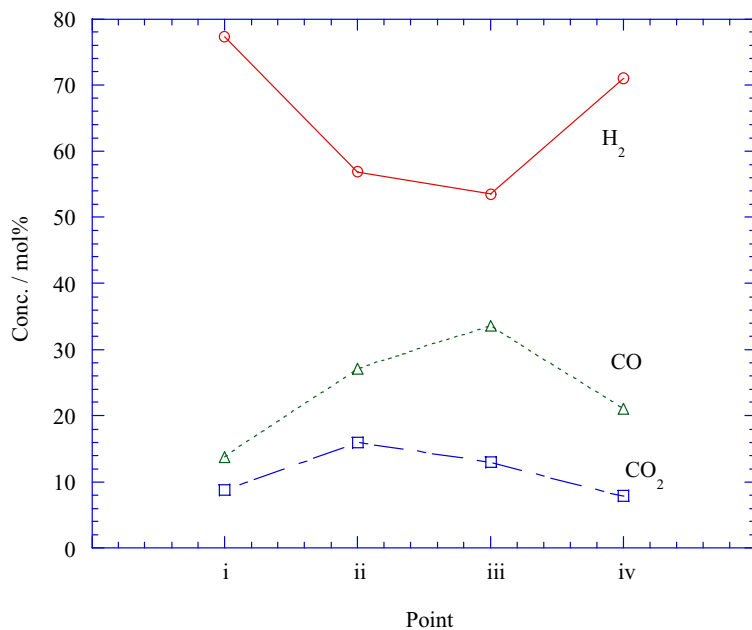
Fig. 4. Gas compositions measured by gas chromatography at given points shown in Fig. 3.

Table 2
Comparison of measured gas composition at anode outlet and calculated compositions at 923 K, 1 atm, open-circuit condition, and inlet condition $H_2:CO_2:H_2O = 0.69:0.17:0.14$ atm

	Gas composition (mol%)		
	H_2	CO_2	CO
Calculated	77.3	8.9	13.8
Measured with GC	77.4	9.8	12.8

indicates that the Boudouard reaction is responsible for the negative voltage shift. A decrease in CO_2 concentration is observed at point (iii), because the increased CO_2 concentration due to the Boudouard reaction is reduced again by the wgs reaction. This interpretation of the results is supported by the decreased H_2 and increased CO concentrations at point (iii) compared with those at point (ii). The CO_2 concentration at point (iv) is lower than that before the CO addition (at point (i)), which implies that the reverse reaction
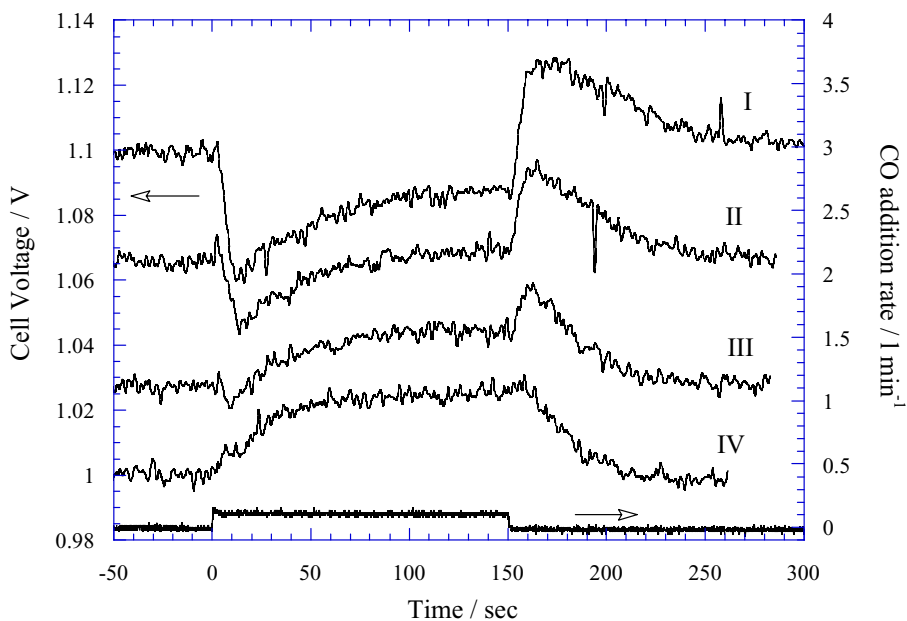

Fig. 5. Effect of CO addition on OCV with various $H_2:CO_2$ ratios at 923 K, 1 atm. Cathode flow rate $= 0.883\,l\,min^{-1}$. (I): $H_2:CO_2 = 90:10$ mol%, (II) 80:20 mol%, (III) 70:30 mol%, (IV) 60:40 mol% ($0.253\,l\,min^{-1}$ of total anode flow).
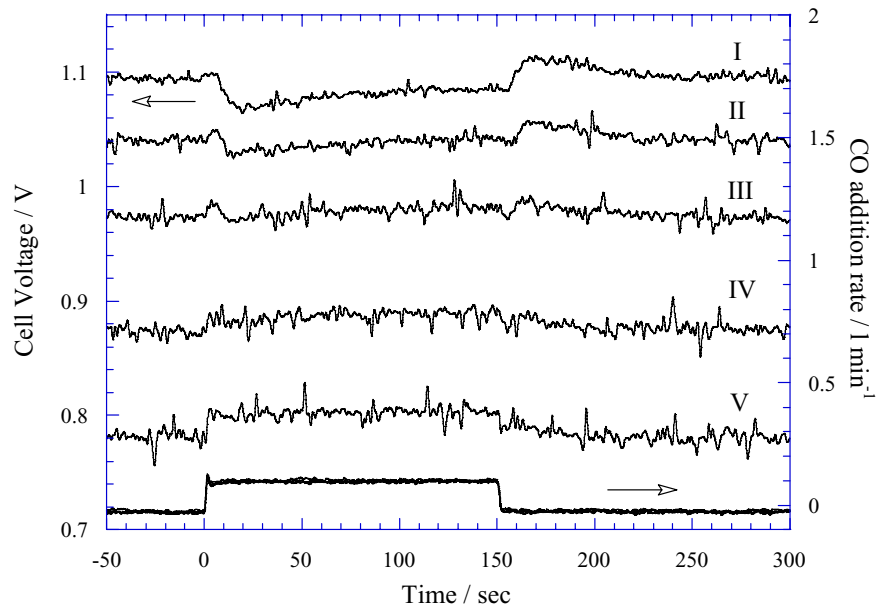
Fig. 6. Effect of CO addition on cell voltage at $H_2:CO_2 = 90:10$ mol% ($0.253 \, l \, min^{-1}$ of total anode flow). Cathode flow rate $= 0.883 \, l \, min^{-1}$, 923 K, 1 atm. (I) Current density $= 0 \, mA \, cm^{-2}$, (II) $20 \, mA \, cm^{-2}$, (III) $50 \, mA \, cm^{-2}$, (IV) $100 \, mA \, cm^{-2}$, (V) $150 \, mA \, cm^{-2}$.

of the Boudouard reaction occurs on CO interruption. The OCV finally relaxes to a steady value, which is determined by the wgs reaction.

As a further attempt to investigate the reactions at the voltage shifts, OCV patterns resulting from CO addition were measured at various $H_2:CO_2$ ratios (Fig. 5). Significant negative and positive voltage shifts are observed at a ratio of $H_2:CO_2 = 90:10$ mol%. The heights of the voltage peaks are reduced, however, with increasing CO_2 concentration.

The voltage peaks disappear and the OCV increases on CO addition over a CO_2 concentration of 30 mol%. This can be explained as follows. When the CO_2 concentration is lower than 30 mol%, the Boudouard reaction prevails on CO addition and the increased level CO_2 caused by the Boudouard reaction reduces the OCV according to the Nernst equation. On the other hand, the wgs reaction appears to be more dominant than the Boudouard reaction at CO_2 concentrations higher than 30 mol%. Thus, CO addition increases the

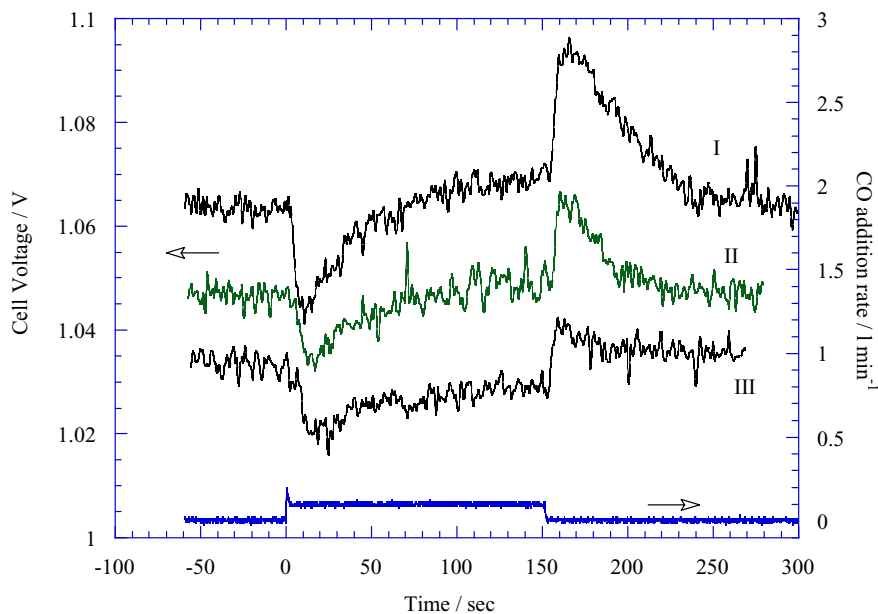Fig. 7. Effect of CO addition on OCV with various H_2O concentrations at fixed H_2 and CO_2 flow rates ($0.217 \, l \, min^{-1}$ of total, $H_2:CO_2 = 80:20$ mol%), 923 K, 1 atm. Cathode flow rate $= 0.883 \, l \, min^{-1}$. H_2O concentration $=$ (I) 20 mol%, (II) 30 mol%, (III) 40 mol%.

H_2 concentration and reduces the H_2O concentration, which results in a positive shift in the OCV.

The above interpretation of the results is validated by the current changes shown in Fig. 6. At open circuit, clear negative and positive voltage shifts are observed at the moment of CO addition and interruption, respectively. At higher currents, however, only positive voltage shifts with the CO addition are observed. This is apparently the result of the dominance of the wgs reaction at the polarization state, even at a low CO_2 concentration, i.e. $H_2:CO_2 = 90:10$ mol% due to the CO_2 produced from the anode reaction by the applied current.

To investigate the CO hydrogenation effect (Eq. (4)), the OCV is recorded at various H_2O concentrations with CO addition (Fig. 7). A decrease in the OCV is observed with increasing H_2O concentration, according to the Nernst equation. If the CO hydrogenation reaction is appreciable on CO addition, the voltage peak is affected. Similar voltage shifts are obtained at various H_2O concentrations, except the voltage peaks are smaller at higher H_2O concentrations. The same amount of CO addition results in smaller changes in gas concentration at higher H_2O concentrations due to the enlarged anode gas flow. Thus, smaller voltage peaks are obtained at higher H_2O concentration. This similarity in the voltage peaks indicates that the CO hydrogenation reaction might not be effective at the anode.

4. Conclusions

From an analysis of the gas-phase chemical reactions at the anode of a molten carbonate fuel cell on the addition of CO and CO_2, the following conclusions are obtained:

(i) The dominant gas-phase reactions on CO addition depend on the CO_2 concentration.
(ii) At CO_2 concentrations below $H_2:CO_2 = 70:30$ mol%, the Boudouard reaction prevails.
(iii) At CO_2 concentrations above 30 mol%, the wgs reaction is dominant.
(iv) In a polarization state, the wgs reaction prevails even at low CO_2 concentration, i.e. $H_2:CO_2 = 90:10$ mol% due to the enhanced partial pressure of CO_2 produced by the anodic reaction.

References

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