

## Performance Analysis of NiO Cathode Using a Molten Carbonate Fuel Cell with Gas Recycle

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**Abstract**—The effect of oxidant gas composition on the polarization of NiO cathode has been investigated in a bench-scale molten carbonate fuel cell operating at 650 °C. Cathode gas recycling has been applied to minimize the gradient of oxidant gas composition within the cell. The performance of NiO cathode was analyzed at a number of gas recycling ratios and a variety of inlet gas compositions to investigate the relation between cathode polarization and partial pressure of oxidant gas. It was found that the correlation equation based on superoxide mechanism could be used to estimate the cathode performance in a broad partial pressure range of oxidant gas.

Key words: MCFC, Cathode, Recycle, Performance, Correlation

### INTRODUCTION

The performance of a molten carbonate fuel cell (MCFC) operating under isothermal and isobaric conditions depends on the gas composition. The cell voltage  $V$  is related to the reversible cell potential  $V_o$  and total cell polarization  $\eta$  by the following potential balance:

$$V = V_o - \eta. \quad (1)$$

The reversible cell potential  $V_o$  can be obtained from the Nernst equation using partial pressures of gases,  $P_j$ , within the cell:

$$V_o = E_o + (RT/2F) \ln (P_{H_2} P_{CO_2,c} P_{O_2}^{0.5} / P_{H_2O} P_{CO_2,a}) \quad (2)$$

where the subscripts a and c denote the anode and cathode gas, respectively. The total polarization of the cell is also a function of  $P_j$ :

$$\eta = \eta (P_j) \quad (3)$$

Therefore, if we know the exact gas composition in the cell during the experiment, we can then get information on  $\eta (P_j)$  from Eq. (1). A laboratory-scale cell of about 3 cm<sup>2</sup> electrode area has been commonly used at negligible gas utilization to quantify the polarization [Selman, 1993]. But, according to our experience, reliable operation of this small cell is more difficult than that of a bench-scale cell because the performance of a small cell is very sensitive to artifacts in cell construction. In this study, we use a bench-scale cell of 100 cm<sup>2</sup> electrode area to obtain polarization data of MCFC cathode.

The exact gas composition inside a bench-scale cell, however, is hard to define since there exists a concentration gradient along the gas flowing direction as fuel and oxidant are consumed by electrochemical reaction. For practical purposes, average gas composition has been used to get performance correlation equations,

but the average composition is not suitable to represent the exact gas composition inside the cell, especially when gas utilization is high. Furthermore, depending on the configuration of the gas channel, there may be micromixing or channeling of gases inside the cell, which makes the performance analysis very difficult. Therefore, in order to obtain reliable polarization data using a bench-scale cell, it is important to carry out experiments in such a way that the gradient of reactant composition within the cell can be minimized. One way of achieving such a condition is to decrease the gas utilization. As the gas utilization decreases, the outlet composition becomes close to the inlet composition, and only in this experimental condition, we can approximately regard the arithmetic mean of inlet and outlet gas composition as the gas composition within the cell. This condition is usually realized in laboratory-scale cell experiments. Another way of achieving relatively uniform distribution of gas composition within the cell is to carry out gas recycling. In this case, the inlet composition approaches to outlet composition as gas recycling ratio increases.

In this study we applied the gas recycling method to minimize the gradient of oxidant gas composition within the cell. The effect of gas recycling on gas composition and polarization of NiO cathode was investigated. In addition, a relatively simple material balance was established to estimate the gas composition within the cell.

### EXPERIMENTAL

#### 1. Cell Components

A cell with effective electrode area of 100 cm<sup>2</sup> was prepared using Ni-10 wt%Cr anode, lithiated NiO cathode,  $\gamma$ -LiAlO<sub>2</sub> matrix, and  $(Li/K)_2CO_3$  electrolyte of Li/K=70/30 mole ratio. All the cell components were fabricated by tape casting technique. Green sheets of anode and cathode were sintered under 10% H<sub>2</sub> in Ar atmosphere at temperatures between 800 and 1,000 °C. The green layers of matrix and electrolyte were laminated to produce an elec-

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trolyte matrix tape which was used in the cell without further treatment. The perforated sheets of Ni and SUS316L were used as current collectors at the anode side and cathode side, respectively. The cell frame was made of SUS316L. The details of component fabrication are described elsewhere [Hong et al., 1997].

## 2. Gas Recycling Operation

A schematic diagram of a cell with cathode gas recycle is shown in Fig. 1. In the cathode side, a gas mixture of  $O_2$ ,  $CO_2$  and  $N_2$  was introduced to the cell, and a part of the cathode exhaust was recycled back to the cathode inlet by a recycling pump. The cathode gas recycling ratio was controlled by adjusting the pumping speed. In the anode side, a gas mixture of 80%  $H_2$  and 20%  $CO_2$  was fed to the humidifier at a flow rate of  $350 \text{ cm}^3(\text{STP})/\text{min}$  and introduced to the anode. The temperature of the humidifier was adjusted in such a way that the mole fraction of water vapor in the anode gas was 10%. The cell performance was measured at a current density of  $150 \text{ mA/cm}^2$  and at  $650^\circ\text{C}$ . The total pressure of the cell was varied between 1 atm and 5 atm. The gas composition at the cathode inlet and outlet was measured by a mass spectrometer (Balzers QMS200).

## MATERIAL BALANCE

The steady-state material balance was applied in a cell depicted in Fig. 1 to estimate the gas composition at the cathode inlet and outlet. The estimation of the gas composition allows us to calculate the effective reversible potential within the cell. Consider the following reaction,



taking place at the cathode with average reaction rate  $r$  ( $\text{mol}/\text{cm}^2 \cdot \text{s}$ ). The overall material balance can be described as:

$$y_{0j} Q_{c0} - y_{3j} Q_{c3} + v_j A r = 0 \quad (5)$$

where  $y_j$  denotes the mole fraction of species  $j$ ,  $Q$  denotes the molar flow rate ( $\text{mol/s}$ ),  $v_j$  denotes stoichiometric coefficient of species  $j$  in reaction (4) and  $A$  denotes electrode area. If the cell is operated under constant current mode, average reaction rate can be described by:

$$r = i/2F \quad (6)$$

where  $i$  is average current density and  $F$  is Faraday constant. Gas utilization  $u_e$  is defined such that

$$u_e = (iA/2F)/Q_{co} = 2 u_{O2} y_{O2,02} = u_{CO2} y_{CO2,02} \quad (7)$$

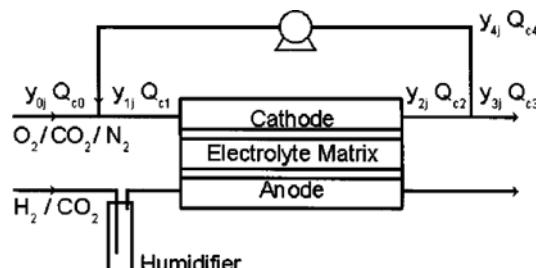


Fig. 1. Schematic diagram of an MCFC with cathode gas recycle.

where  $u_{O2}$  and  $u_{CO2}$  refer to the  $O_2$  utilization and  $CO_2$  utilization, respectively. Then mole fraction of  $j$  at the cathode outlet becomes:

$$y_3 = y_2 = y_4 = (y_0 + v_j u_e) / (1 - 1.5 u_e) \quad (8)$$

The cathode gas recycling ratio  $\alpha_e$  is given by:

$$\alpha_e = Q_{c4} / Q_{c2} \quad (9)$$

and  $Q_{c2}$  can be calculated as:

$$Q_{c2} = Q_{c0} (1 - 1.5 u_e) / (1 - \alpha_e) \quad (10)$$

At the cathode inlet, the recycling stream is mixed with the feed stream and introduced to the cathode. From the material balance at the cathode inlet:

$$y_{0j} Q_{c1} = y_{0j} Q_{c0} + y_4 Q_{c4} \quad (11)$$

the mole fraction of  $j$  at the cathode inlet becomes:

$$y_{0j} = (y_0 + \alpha_e v_j u_e) / (1 - 1.5 \alpha_e u_e) \quad (12)$$

As can be seen from Eqs. (8) and (12),  $y_{0j}$  becomes close to  $y_{2j}$  with increasing cathode gas recycling ratio  $\alpha_e$ .

## RESULTS AND DISCUSSION

### 1. Effect of Cathode Gas Recycling on Cell Performance

Fig. 2 shows the effect of cathode gas recycling on  $CO_2$  partial pressure at the cathode inlet and outlet. The  $CO_2$  partial pressure at the cathode inlet decreases with increasing the recycling ratio while the partial pressure at the cathode outlet is nearly constant. The solid line in Fig. 2 represents the result estimated from the material balance indicating that the  $CO_2$  partial pressure calculated from Eqs. (8) and (12) is in good agreement with experimental data. Since the difference in partial pressure of oxidant gas at the cathode inlet and outlet decreases with increasing gas recycling ratio, the partial pressure of oxidant gas within the cell can be more reliably represented by the average partial pressure of oxidant gas

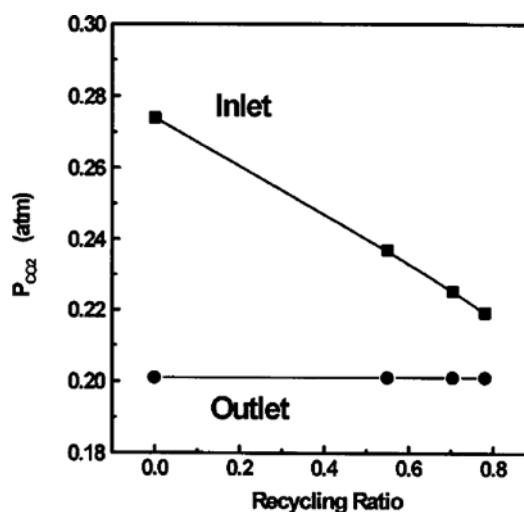


Fig. 2. Effect of cathode gas recycling ratio on  $CO_2$  partial pressure at the cell inlet and outlet (Operating condition: feed  $y_{O2}=0.147$ ,  $y_{CO2}=0.3$ ; overall utilization: 0.59,  $i=150 \text{ mA/cm}^2$ ).

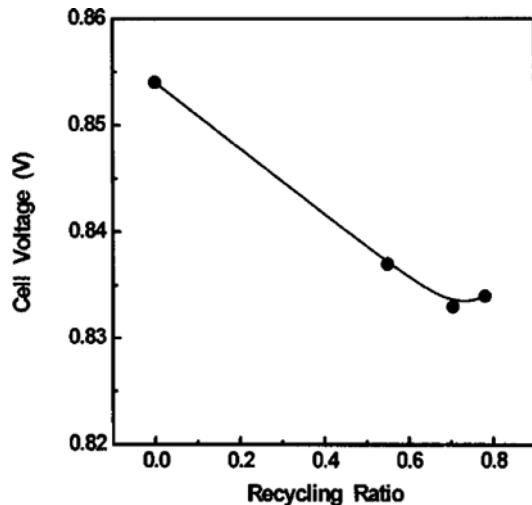


Fig. 3. Effect of cathode gas recycling ratio on the cell voltage at 150 mA/cm<sup>2</sup>.

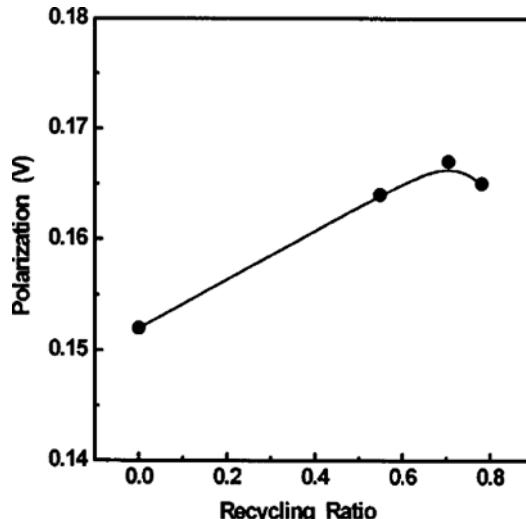


Fig. 5. Effect of O<sub>2</sub> and CO<sub>2</sub> partial pressures on the IR-free electrode polarization of the cell at 150 mA/cm<sup>2</sup>.

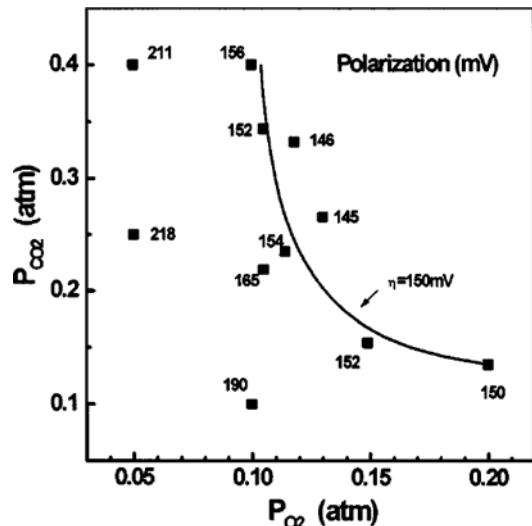


Fig. 4. Effect of cathode gas recycling ratio on the polarization of the cell at 150 mA/cm<sup>2</sup>. Calculation of the polarization was based on arithmetic mean of partial pressure at the cell inlet and outlet.

at higher gas recycling ratio.

Fig. 3 shows the effect of the recycling ratio on cell voltage. As the recycling ratio increases, average partial pressure of oxidant in the cell reduces, resulting in the decrease of cell voltage. The total cell polarization was calculated as a function of the recycling ratio and the result is shown in Fig. 4. The polarization of the cell increases with increasing the recycling ratio. This is due to the fact that average concentration of O<sub>2</sub> and CO<sub>2</sub> in the cell decrease with increasing the recycling ratio. When recycling ratio is higher than 0.7, however, the polarization becomes nearly constant. In view of Fig. 4, it can be said that the polarization of the cell is about 165 mV at P<sub>CO₂</sub>=0.21 atm and P<sub>O₂</sub>=0.105 atm. Ohmic polarization was found to be 63 mV from a current interruption experiment. So, IR-free electrode polarization corresponds to 102 mV.

## 2. Effect of Cathode Gas Composition on Polarization

A number of gas recycling experiments were carried out to ac-

cumulate polarization data at various sets of P<sub>CO₂</sub> and P<sub>O₂</sub>, and the result obtained at total pressure of 1 atm is shown in Fig. 5. The IR-free electrode polarization increases with decreasing P<sub>CO₂</sub> or P<sub>O₂</sub>. The locus of constant polarization of 150 mV shown in Fig. 5 indicates that increasing the operating pressure could reduce the cathode polarization. A variety of equations have been previously suggested to correlate cathode polarization and partial pressures of O<sub>2</sub> and CO<sub>2</sub>. Some of them are [Selman and Lee, 1993; Morita et al., 1995]:

$$\eta_{cathode} = A P_{O_2}^{-0.63} P_{CO_2}^{0.04} \quad (13)$$

$$\eta_{cathode} = A P_{O_2}^{-0.75} P_{CO_2}^{0.50} + B P_{CO_2}^{-1} \quad (14)$$

$$\eta_{cathode} = A P_{O_2}^{0.50} P_{CO_2}^{1.00} + B P_{CO_2}^{-1} \quad (15)$$

and these correlations can be expressed in the form of:

$$\eta_{cathode} P_{CO_2} = A P_{O_2}^a P_{CO_2}^b + B. \quad (16)$$

The polarization data obtained at a total pressure of 1 atm were rearranged according to Eq. (16) considering that the anode polariza-

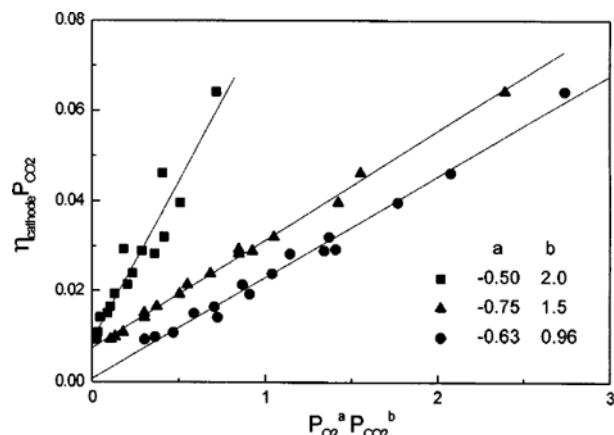
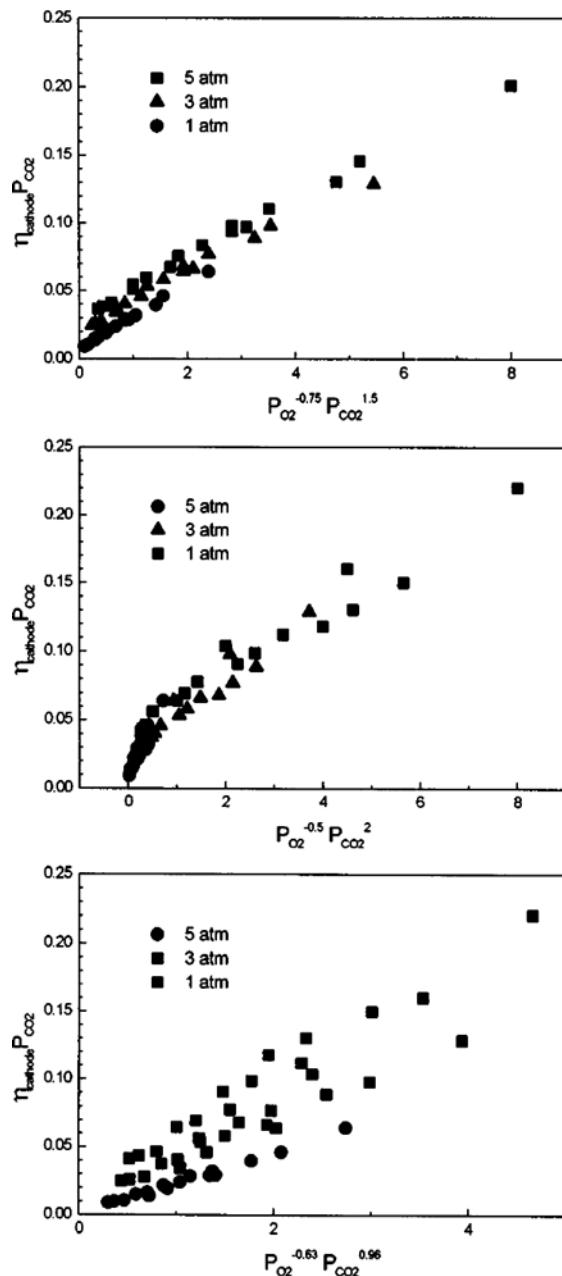


Fig. 6. Comparison of various correlation equations between IR-free electrode polarization and partial pressure of cathode gas at a total pressure of 1 atm.



**Fig. 7. Comparison of various correlation equations between IR-free electrode polarization and partial pressure of cathode gas at total pressure of the cell up to 5 atm.**

zation was about 10 mV under the experimental conditions employed in this study. It's clear from Fig. 6 that all the above correlation equations show proportionality between  $\eta_{cathode} P_{CO_2}$  and  $P_{CO_2}^b P_{CO_2}^a$ . This means that at a total pressure of 1 atm, any one of the above correlation equations can be used to estimate the performance of the NiO cathode. On the other hand, if the total pressure of the cell increased up to 5 atm, then only the correlation Eq. (14) shows the linear relationship between  $\eta_{cathode} P_{CO_2}$  and  $P_{CO_2}^b$ .

$P_{CO_2}^b$  as shown in Fig. 7. The Eq. (14) was derived based on the assumption that superoxide mechanism controlled the polarization of the cathode [Morita et al., 1995]. So it can be concluded that superoxide mechanism dominates the cathode reaction in our MCFC, and the correlation equation based on the superoxide mechanism can be used to estimate the polarization of NiO cathode under the oxidant gas partial pressure range employed in this study. The above conclusion, however, was drawn under the assumption that the anode polarization corresponds to 10 mV irrespective of the total cell pressure. In fact, the anode polarization decreases with increasing total pressure [Hirschenhofer et al., 1994] and more work is needed to clarify the effect of the total pressure on the cell polarization.

## SUMMARY

In order to quantify the cathode polarization of MCFC, experiments were performed in a bench-scale cell with cathode gas recycling. The gas recycling reduced the average partial pressure of oxidant within the cell, leading to the decrease in cell performance. The reactant distribution, however, becomes more uniform as the recycling ratio increases and reliable polarization data can be obtained at high recycling ratios. Analysis of the cathode polarization data indicates that the correlation equation,  $\eta_{cathode} = A P_{CO_2}^{-0.75} P_{CO_2}^{0.5} + B P_{CO_2}^{-1}$ , can be used to estimate our bench-scale cell performance. A material balance was applied to the cell to predict the gas composition at the cathode inlet and outlet. The gas composition measured in the experiment was in good agreement with the composition calculated from the material balance.

## ACKNOWLEDGEMENT

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