MECHANISM OF LOW-CO₂ PERFORMANCE OF THE MCFC CATHODE

Yong Hwan Kim and J. Robert Selman
Department of Chemical Engineering
Illinois Institute of Technology
Chicago, IL 60616

ABSTRACT

From data obtained on 3cm² lab-scale Molten Carbonate Fuel Cells (MCFC) at low CO₂ partial pressure of the oxidant, it appears that cathode dissolution decreases and the cell life-time is increased. However, operating MCFCs at very low CO₂ partial pressure (below 0.05 atm) lowers the cell performance; the cell mechanism seems to be changed seriously and performance recovers extremely slowly after returning oxidant composition to normal CO₂ level. The effective cathode polarization for the low-CO₂ range is not fitted by available correlations based on rate control by O₂ and CO₂ diffusion, and it is very high. These effects must be accounted for in the estimation of optimum CO₂ partial pressure for maximum cell life-time and cell performance, and the estimation of optimum electrolyte filling of the cathode.

Key words: cathode polarization, electrolyte filling, AC Impedance

INTRODUCTION

In the last stage before commercialization of the Molten Carbonate Fuel Cell (MCFC), some issues concerning cell life-time such as cathode dissolution, separator plate corrosion, and electrolyte distribution must be satisfactorily resolved. The key to the improvement of long-term MCFC performance seems to be the mechanism of the electrochemical processes which cause the cell performance decay. A correlation of the time-to-short of MCFC cells presented by Kunz and Pandolfo(1) suggests that cell operation at low CO₂ partial pressure lowers cathode dissolution and, therefore, increase cell life-time. In a previous study(2), the effective cathode polarization was expressed as a simple correlation involving P_{O₂}, P_{CO₂} and cell temperature. In Lee and Selman's recent study(3), AC/DC Impedance characteristics of MCFC porous electrodes were analyzed to obtain kinetic and mass transfer information. A mechanism controlled by O₂ and CO₂ was inferred. The overall objectives of the present study are: (a) to observe the cell performance at low CO₂ partial pressure of the oxidant, (b) to understand the relationship between cathode polarization of
MCFC electrodes and current density at low CO₂ partial pressure, (c) to understand the effect of electrolyte filling ratio on cell performance.

EXPERIMENTAL SET UP AND CELL COMPONENTS

The experimental instruments employed in this research included an EG&G Model 173 Potentiostat/Galvanostat with Model 176 compartment for IR compensation, an EG&G Model 273 Potentiostat/Galvanostat, an EG&G Model 175 Universal programmer, a Nicolet Model 206 Digital Oscilloscope, a Fisher Series 5000 recorder, a specially designed current interrupter with very short working time at speed of 2μs, Matheson 600 Series flowmeter, Omega Chromel-Alumel thermocouples, a Simpson digital D.C. millivoltmeter, a Newport digital D.C. milliammeter, and an EG&G Model 5208 Two-Phase Lock-In Analyzer.

3 cm² lab-scale MCFCs were assembled using the configuration which has been previously applied to the 3 cm² lab-scale cells at the Institute of Gas Technology(4), and employed for stationary polarization, AC Impedance, and potential relaxation measurements. The cell consisted of porous electrodes, electrolyte matrix, reference electrodes, and current collectors (Figure 1).

The composition of the oxidant gas supplied to the cathode was a mixture of 30 vol% of CO₂ and 70 vol% of air. Its flow rate was kept constant at 102 ml/min. The analyzed oxidant gas supplied to the cathode was saturated by passing it through a water container which was maintained at a temperature close to room temperature. The composition of the fuel gas supplied to the anode was 75 vol% of H₂ and 25 vol% of CO₂. Its flow rate was kept constant at 102 ml/min. The analyzed fuel gas fed to the anode was saturated by passing it through a water container which was maintained at a constant temperature of 60°C degrees. Flow rate and composition of the anode gas were always maintained at constant values for this research work. The reference gas was a dry mixture of 67 vol% CO₂ and 33 vol% O₂, and its composition was maintained constant during this research work. Its flow-rate was also maintained constant, at 10 ml/min.

The cell temperature was maintained at 650°C degrees, and the cell was usually loaded at 480 mA. The cell was observed by checking the daily performance corresponding to ordinary condition. This explained if the cell is running at steady state. The IR value was also measured using the current interruption method, and to ensure that its value did not vary.
All cell components were supplied by the Institute of Gas Technology. These components were assembled together in a high-purity alumina housing. Porous Ni-10% Cr was used as the anode electrode. Porous lithiated nickel oxide was used as the cathode. Gold wire was used for the reference electrodes. Novamet Ni on the anode side and SS 316 on the cathode side were used as current collectors. Molten carbonate (eutectic mixture of 62 mol% Li₂CO₃ and 38 mol% K₂CO₃) in a ceramic tile (LiAl₂O₃ matrix) was used as the electrolyte layer.

The electrolyte filling ratio (ratio of electrolyte volumes to the void volume of cathode and anode electrodes) was usually 25% at the start of a cell. Sometimes, a lower than 25% of electrolyte filling ratio of both electrodes was applied at the start and the value increased to more than 25% by adding electrolyte.

Cathode gas composition for this research work was varied from 0.9 atm to 0.02 atm of CO₂ and from 0.9 atm to 0.02 atm of O₂. Nitrogen gas was used for balancing all gases. Some experimental data were obtained at higher than standard temperature (698°C) and some at lower than standard temperature (608°C).

EXPERIMENTAL RESULTS AND DISCUSSION

1. Stationary polarization

The correlation between the cathode polarization and current density is linear at high CO₂ partial pressure (above 0.1 atm). As CO₂ partial pressure decreases, the relationship becomes non-linear (Figure 2). As Fig. 2 shows, at or below 0.02 atm CO₂ partial pressure, the polarization becomes very large, and cell performance extremely poor.

The correlation between the cathode polarization and current density is also linear at high O₂ partial pressure (above 0.1 atm). As in the case of CO₂, as O₂ partial pressure decreases, the relationship becomes non-linear. However, the effect of O₂ on the relationship between the cathode polarization and current density seems to be less significant than that of CO₂.

Cathode polarization is also affected by electrolyte filling. Minima in cathode polarization were observed in the range of 20% - 30% electrolyte filling ratio (Figure 3). As current density increases, the deviation from linearity becomes obvious. In the low range of current density, the
correlation between cathode polarization and current density is clearly linear.

2. AC/DC Impedance

AC/DC impedance data were obtained under various conditions. At constant O₂ partial pressure (0.3 and 0.1 atm) of oxidant, a weak effect of CO₂ on the charge transfer resistance and a strong effect of CO₂ on the mass transfer resistance were observed. Two semi-circles (kinetic loop and diffusion loop) were clearly observed as the CO₂ concentration was decreased. At constant CO₂ partial pressure (0.3, 0.1, and 0.02 atm) of oxidant, strong effect of O₂ on mass transfer resistance were observed. Also, two distinct semi-circles (kinetic loop and diffusion loop) were observed at high O₂.

At very low CO₂ pressure (e.g. 0.02 atm), results under current load and under OCV were significantly different. Under these conditions, AC/DC Impedance data for different electrolyte filling ratios were also significantly different. The mechanism of oxygen reduction under low CO₂ conditions is changed by current load much more than under standard gas conditions. Therefore, kinetic information obtained from AC/DC impedance measurements at OCV may not be applicable to operation under load.

3. Potential Relaxation

The potential relaxation upon switching the oxidant gas from one concentration to another was systematically measured at 650°C. The time required to reach steady state upon switching to lower CO₂ oxidant was longer than that to higher CO₂ oxidant. Especially, switching to 0.02 atm CO₂ oxidant showed significantly slower transition. Under load condition, steady state seemed to be reached within 1 hour after switching gas. However, cathode polarization still increased significantly after about 2 hours (Figure 4). Cell performance hardly recovered, even if gas was switched to at, or above, normal CO₂ levels.

DISCUSSION AND CONCLUSION

Operating a MCFC using very-low-CO₂ oxidant lowers the cell performance drastically. The cell mechanism seems to be changed seriously and to be more complex than the mechanism at or above 0.1 atm of CO₂ partial pressure. The cell performance recovers extremely slowly after return to normal CO₂ levels (e.g. 0.147 atm). The effective cathode polarization for this
The low range of CO₂ was not predicted correctly by correlations such as those of Yuh (Figure 5).

The present study is helpful in estimating optimum CO₂ partial pressure for maximum cell life-time and cell performance. It is also relevant for the estimation of optimum electrolyte filling. Even though AC/DC Impedance has been considered a useful tool for electrochemical application, a more accurate technique and less external noise in AC Impedance measurements seems to be required to provide sufficiently accurate information for the kinetics and mass transfer resistance of the cell in the low-CO₂ range.

ACKNOWLEDGEMENTS

This work has been carried out at the Institute of Gas Technology. We acknowledge technical assistance of the staff at Institute of Gas Technology to obtain experimental evidence.

REFERENCES

1. H.R. Kunz and J.W. Pandolfo, J. Electrochem. Soc., 139, 1549 (1992)
2. a). C.Y. Yuh and J.R. Selman, J. Electrochem. Soc., 138, 3642 (1991)
   b). C.Y. Yuh and J.R. Selman, J. Electrochem. Soc., 138, 3649 (1991)
3. G.L. Lee, Ph.D. Dissertation, IIT, Chicago, IL (1992)
4. E.S. Argano and J. Levitan, J. Electrochem. Soc., 116, 153 (1969)

Fig. 1. Schematic of 3 cm² lab-scale cell
Cathodic Polarization at 25.2% Filling
constant \(\text{O}_2\) partial pressure, 650°C

![Diagram showing cathodic polarization vs current density as \(\text{CO}_2\) varies.](image)

**Fig. 2.** Cathode polarization vs current density as \(\text{CO}_2\) varies.

Polarization at Various Fillings
STD Gas(30%:14.7%), 650°C

![Diagram showing polarization at various fillings.](image)

**Fig. 3.** Cathode polarization vs electrolyte filling (Symbols indicate current density in mA/cm². U indicates utilization of oxidant in %.)
Cathodic Polarization change w/ Time

2% CO2 / 30% O2

\[ \text{Polarization(mV)} \]

\[ \text{Time(min)} \]

\[ -700 \]

\[ -600 \]

\[ -500 \]

\[ -400 \]

\[ -300 \]

\[ -200 \]

\[ -100 \]

0

0 20 40 60 80 100 120

Fig. 4. Cathodic polarization vs time for very low CO2 gas

Effective resistance, Z(CR2), 650°C, +++

10% O2, 33.9% filling, IR free

Fig. 5. Cathodic polarization from experimental data and Yuh's correlation