A NOVEL METHOD FOR THE PERFORMANCE ANALYSIS OF A MOLTEN CARBONATE FUEL CELL

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Abstract. This work has been focused on the behavior of overpotential increase by utilization rise in a molten carbonate fuel cell. The behavior is generally explained by Nernst loss, which is a kind of voltage loss due to the thermodynamic potential gradients at a polarization state by the concentration distribution of reactant species through the gas flow direction. The evaluation of Nernst loss was carried out with traditional experimental way of constant gas utilization (CU). On the other hand, overvoltage due to the gas-phase mass-transport resistance at the anode and cathode showed dependence on the utilization which was measured with the inert gas step addition (ISA) method. Since the Nernst loss was assumed by the thermodynamic reasons, the voltage loss can be calculated by the Nernst equation, calling simple calculation (SC) in this work. The three values of voltage loss by CU, ISA, and SC were compared, showing these values rise with utilization increase within acceptable deviations. When we consider that the anode and cathode reactions are significantly affected by the gas-phase mass transfer, the behavior strongly implies that the voltage loss is attributed not to the thermodynamic reasons, i.e, Nernst loss, but to the kinetic reason of mass-transfer resistance in the gas phase.

Keywords: MCFC; overpotential; mass transfer; Nernst loss

1. Introduction

Understanding of the reaction kinetics in the molten carbonate fuel cell (MCFC) is required for its practical development because the performance is determined by the reaction kinetics at the electrodes. Since the electrode kinetics determines performance via overpotential at the anode and cathode, the correct evaluation of overpotential provides clues for the analysis of reaction characteristics. Voltage loss in the MCFC generally comprises of ohmic loss (η_{IR}) and reaction overpotential at the anode (η_{an}) and cathode (η_{ca}); ohmic resistance is due to the electrical resistance among the cell components and reaction overpotential is ascribed to the resistance in the electrochemical reactions at both electrodes. Thus, output voltage (V) can be expressed as follows;

$$V = E_{OCV} - \eta_{IR} - (\eta_{an} + \eta_{ca}) \tag{1}$$

where, $E_{OCV} = E_0 + \dfrac{RT}{2F} \ln\left(\dfrac{[H_2]}{[H_2O][CO_2]_{an}} [O_2]^{0.5}[CO_2]_{ca} \right)$, and E_0 is the standard potential.

Subscripts an and ca represent anode and cathode, respectively. Other symbols have their own meanings.

The MCFC, normally running around 650°C with carbonate electrolyte, has relatively severe operating conditions; 1) it uses porous electrode with corrosive carbonate electrolytes melting around 500°C, 2) combination of cell components such as electrodes, electrolyte, and matrices may have deviations by the cells, 3) the cell is assembled with thinner and lighter components, not allowing stable installation of reference electrode to analyze overpotential at the electrodes. The complete analysis of the overpotential and reaction kinetics has been obstructed by the reasons.

In the previous papers, the reaction characteristics have been illuminated in the MCFC with several experimental ways; inert gas step addition (ISA) method [Lee et al. 2003], reactant gas addition (RA) method [Lee et al. 2003] and water head (WH) measurements [Lee et al. 2004]. They mostly treated gas flow effects on the overpotential, indicating consistently that the anode is principally mass-transfer controlling process in the gas phase, whereas the cathode is mixed mass-transfer controlling processes in the gas and liquid phases.

As a voltage loss in the MCFC, Nernst loss has been suggested [Sampath et al. 1980]. It is based on the assumption that concentration distribution occurs along the gas flow way at a polarization state, and it induces potential gradient in the cell according to the Nernst equation. Then, the potential difference between gas inlet and outlet behaves as overvoltage, called Nernst loss. However, the thermodynamic relation of Nernst equation is based on the equilibrium state which the concentrations of reactants are the same everywhere in the cell. It has been reported that MCFC in a polarization state has concentration distribution vertically from the gas phase to the electrode surface [Lee et al. 2003]. Then it is questionable that the potential calculated from the bulk concentration can represent electrode potential while the concentration on the electrode surface may have different value from the bulk due to the concentration gradient at polarization state.

The dependence of overpotential on the utilization at both electrodes was illuminated by comparing the Nernst loss from the traditional ways with overpotential from a novel experimental way. As the conventional ways, the constant gas utilization (CU) method and simple calculation (SC) were employed. Those are considered as experimental and theoretical methods to obtain the Nernst loss. As a novel way, inert gas step addition (ISA) method was used. Voltage losses were obtained from CU, SC, and ISA and compared among them at various anode and cathode utilizations.

2. Experimental

The MCFC used in this work had about 100 cm^2 of geometrical surface area of electrode. Anode was a porous slab of Ni-Al alloy while the cathode was a porous Ni slab. Matrix was fiber reinforced LiAlO$_2$, and the electrolyte was (62+38)mol% (Li+K)$_2$CO$_3$ eutectics. The single cell was operated at an atmospheric condition, and temperature was kept at 923K.

More details of the cell components and cell operation were described in a previous work [Lee et al. 2003].

Mixtures of 80 mol% H_2 and 20 mol% CO_2 through the 53°C water bubbler was supplied to the anode, whereas mixtures of 70 mol% air and 30 mol% CO_2 was fed to the cathode. Utilization, a ratio of consumed gas amount to feed amount, of anode (u_f) and cathode (u_{ox}) ranged from 0.2 to 0.6 at 15 A. The gas flows were controlled by several MFCs (Mass Flow Controllers).

Steady state polarization has been carried out to obtain the effect of utilization change on the overvoltage. The current was raised from 0 to 15 A with a galvanostat at a fixed reactant flow rate. Then, we could obtain total overvoltage with respect to the utilization.

As a conventional way to measure Nernst loss, constant gas utilization (CU) has been employed. Figure 1 shows how to measure the Nernst loss at the anode ($\Delta V_{u,an}$) and cathode ($\Delta V_{u,ca}$) with CU method. Since the Nernst loss is a function of utilization, a difference between OCV(E_{OCV}) and an extrapolated voltage to 0 current from the current-voltage line of constant utilization is regarded as Nernst loss at the utilization.
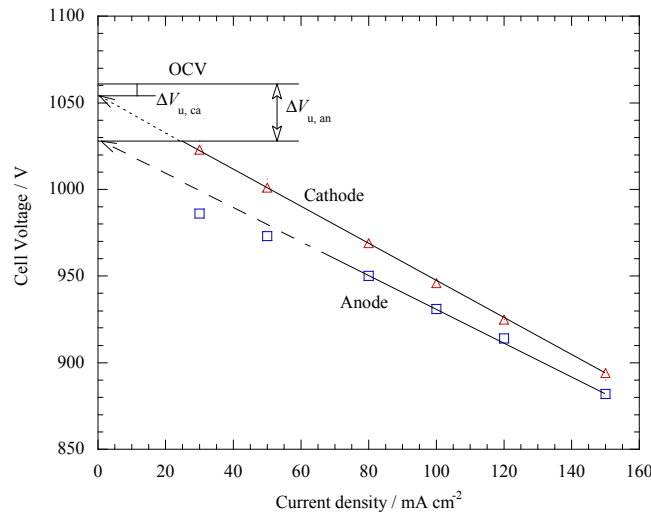

Fig. 1 Estimation of voltage loss with constant gas utilization (CU) method at the anode (u_f=0.2) and cathode (u_{ox}=0.4), 923K, 1 atm.

$$\Delta V_u = E_{OCV} - V(u, i\rightarrow 0) \tag{2}$$

The constant utilization was kept by controlling the gas flow rate according to the applied currents; thus the gas flow rates were proportionally reduced to the applied currents. The value of $\Delta V_{u,an}$ is much larger than $\Delta V_{u,ca}$ as shown in Fig.1. Thus it is known that anode has much larger Nernst loss than cathode.

As a novel method, inert gas step addition (ISA) method was employed in this work. ISA adds certain flow rate of inert gas to the cell. The added inert gas raises reactant gas flow rate

without changing gas composition while the inert gas arrives at the cell. Then, overvoltage change by the flow rate shift can be obtained by measuring voltage shift. Thus, ISA can provide overvoltage with respect to the reactant flow rate and utilization. Nitrogen gas was used as an inert gas to the anode and cathode, and its flow rate ranged from 0.1 to 1.0 L min^{-1}. Addition port for N_2 was installed about 4 m before the anode and about 1.5 m ahead of the cathode. All the gas tubes are 1/4 inches of outer diameter with stainless steel. More detailed characteristics of ISA method were described in a previous paper [Lee et al. 2003].

3. Results and discussions

Figure 2 shows results of steady state polarization (SSP) with respect to the anode (a) and cathode utilization (b). Since the utilization is a ratio of consumed reactant amounts to fed amount at a fixed current load, higher utilization means lower flow rate of reactant gases. The clear dependence of voltage on the utilization and flow rate is observed. The SSP represents total overvoltage by the difference between output voltage (V) and open circuit voltage (E_{OCV}), then it is obvious that higher utilization has larger overvoltage. In addition, the distinguishable change of the slope at the anode indicates that the anodic overpotential more strongly depends on the flow rate than the cathodic one. The electric conductivity of carbonate electrolyte is generally seldom dependent on the flow rates, thus the flow rate change is wholly responsible for the overpotential variation.
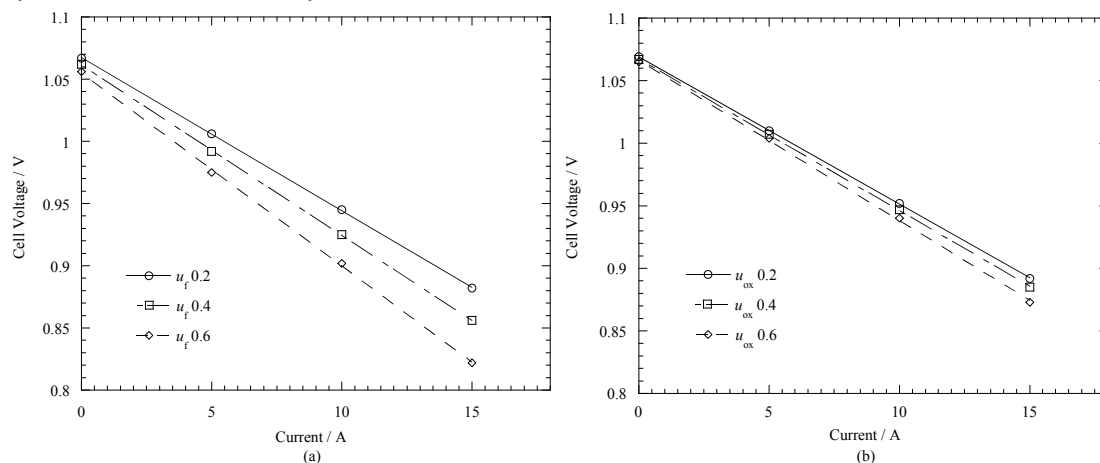

Fig. 2. Results of steady state polarization (a) at anode of u_{ox}=0.4 (15A), (b) at cathode of u_f=0.2 (15A), 923K, 1atm.

In a previous work of Sampath et al. [Sampath et al. 1980], the behavior has been interpreted thermodynamically. Since the cell consumes a certain amount of gas at a fixed current load, flow rate change leads to various concentration distributions along the gas flow way. More severe concentration distribution is expected at lower flow rate. From a theoretical view point [Bard et al., 2001], potential of a reversible system is determined by the concentration of reactant and product species. Thus the concentration distribution gives rise to potential gradient along the gas flow way. Steeper potential gradient occurs at lower gas flow rate and higher utilization at a fixed current. They suggested that the potential gradient behaves as a voltage loss, called Nernst loss. Thus larger Nernst loss is suggested at higher utilization and lower flow rate. According to their suggestion, the large overvoltage at a high utilization is due to the significant amount of Nernst loss.

However, Lee et al. [Lee et al. 2003] has suggested that MCFC has significantly high reaction rate at the anode and cathode, thus the reactions at the anode are mass-transfer controlling processes in the gas phase while the cathode reaction is mixed mass-transfer limiting processes in the gas and liquid phases from the ISA method. They also reported that the anode overpotential is mostly attributed to the mass-transfer resistance of CO_2 and H_2O at a normal operating condition (H_2:CO_2:H_2O=0.69:0.17:0.14 atm) [Lee et al. 2005].

Figure 3 shows results of ISA measurement with addition of 0.3 L min^{-1} N_2 to the anode (a) and cathode (b). As reported in a previous work [Lee et al. 2003], N_2 addition to the anode immediately raises voltage because the addition enhances reactant flow rate without changing composition. Thus the voltage gain ($\Delta V_{l,an}$) is obtained by the overvoltage shift due to the flow rate variation. Since the overpotential induced by the gas-phase transport is a function of flow velocity and the flow rate at a fixed current is a function of utilization, the voltage gain can be expressed as follows [Lee et al. 2003];

$$\Delta V_l = \eta_{G,1} - \eta_{G,2} = q(u_1^{0.5} - u_2^{0.5}) \tag{3}$$

where η_G is the overvoltage due to the gas-phase mass transfer effect, q is the slope of the voltage gain vs. square root of utilization, u is the utilization, and subscripts 1 and 2 denote before and after N_2 addition, respectively. On the other hand, the voltage gain at the cathode ($\Delta V_{l,ca}$) is relatively small compared with $\Delta V_{l,an}$ as shown in Fig. 3(a). This means that the cathode has smaller mass-transfer resistance in the gas phase than anode because the cathode has only deficiency of O_2 species and more sluggish diffusion process through the liquid electrolyte film prevails [Lee et al. 2005].
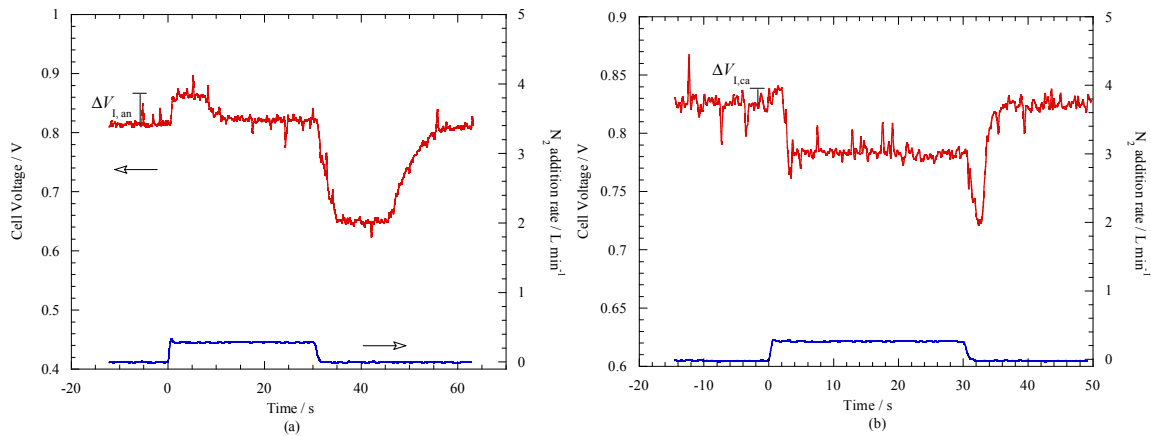

Fig. 3 Voltage patterns by the addition of 0.3 L min^{-1} N_2 to the anode of total flow rate of 0.253 L min^{-1} (a) and cathode of total flow rate of 0.883 L min^{-1} (b) at 923K, 1 atm.

When we assume that the utilization before the N_2 addition is a constant, then the following equation is available from Eq.(3) [Lee et al. 2003];

$$\Delta V_l = m - qu_2^{0.5} \tag{4}$$

Figure 4 shows the relation of Eq.(4). Since the anode gas flow rate (total 0.253 L min^{-1} at u_f=0.6) is much smaller than that of cathode (total 0.883 L min^{-1} at u_{ox}=0.4), the same amount of flow rate increase by the addition of N_2 (0.1 to 1.0 L min^{-1}) reduces the anode utilization to much lower value than the cathode utilization. We can obtain q values from the slopes; the anodic value of q (q_{an}) is 160.0 mV and the cathodic one (q_{ca}) is 29.5 mV. In addition, the overpotential due to the gas-phase transport (η_G) can be expressed as Eq.(5) from the Eq.(3).
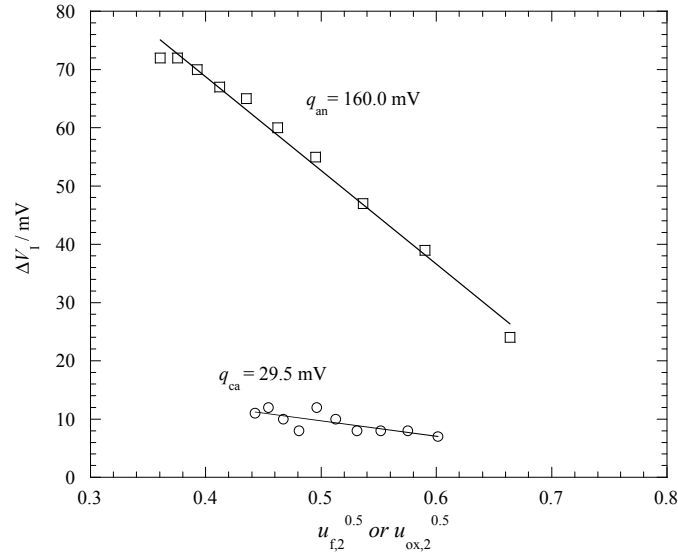

Fig. 4 Relations of Eq. (4) at the anode and cathode with ΔV_l obtained from Fig. 3.

$$\eta_G = qu^{0.5} \tag{5}$$

With Eq.(5) we can obtain the overpotential due to the gas-phase transport at various utilization.

The overpotential due to the gas-phase transport (η_G) was compared with the Nernst loss obtained by experimental way and calculation. As a experimental way for the Nernst loss, the constant gas utilization (CU) method was employed. An arithmetic mean of potential difference between the gas inlet and outlet (*Nst*) was calculated for the Nernst loss as a simple calculation (SC) method. Since the open circuit voltage is a function of temperature and gas compositions (Eq.(1)), the different gas compositions at the gas inlet and outlet at a current load gives potential gap.

$$Nst = (E_{in} - E_{out})/2 \tag{6}$$

Figure 5 compares the overpotential at the anode ($\eta_{an,G}$) and the cathode ($\eta_{ca,G}$) with Nernst loss with CU method ($\Delta V_{u,an}$ at the anode and $\Delta V_{u,ca}$ at the cathode) and SC method (*Nst*$_{an}$ at the anode and *Nst*$_{ca}$ at the cathode). Although the values at the anode have some of deviation, they show consistency of rising with utilization at a similar slope. The values among them show more close each other at the cathode. As mentioned above, the result of ISA indicates that MCFC has overpotential due to the slow gas-phase mass transfer process. This

implies that the concentration gradient from the gas phase reactant to the electrode surface exists and the compositions of reactants in the bulk gas are different from those of electrode surface. However, the Nernst loss was suggested on the assumption of the equality of bulk gas composition to the electrode surface. When we consider the discrepancy between Nernst loss and the experimental results, the overpotential variation by utilization change is ascribed to the kinetic reasons of mass transfer in the gas phase.
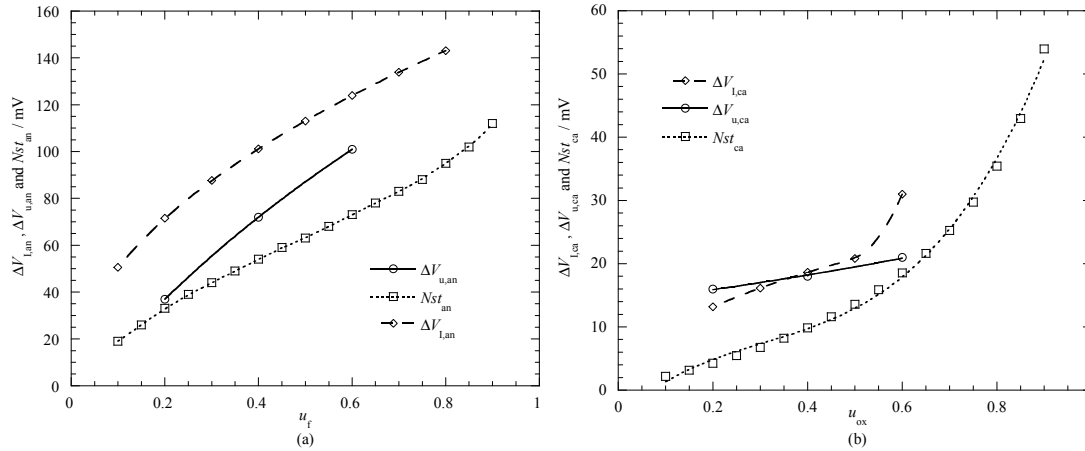

Fig. 5 Comparisons of overpotential measured by ISA method (ΔV_I) with Nernst loss obtained by CU method (ΔV_u) and calculation (*Nst*) at the anode (a) and cathode (b) at 923K, 1 atm.

4. Conclusion

The overpotential, showing larger value at higher utilization, was investigated by comparison of overpotential due to the gas-phase mass-transfer resistance with Nernst loss, a hypothetic voltage loss with thermodynamic backgrounds. The overpotential induced by the mass transfer effect was measured with inert gas step addition (ISA) method, whereas the Nernst loss was obtained by a calculation (simple calculation, SC) method and an experimental way (constant gas utilization, CU). Measured overpotential with ISA showed similar behavior against utilization with values of Nernst loss obtained by SC and CU methods. The Nernst loss, based on the assumption that the cell potential is determined by the bulk gas composition, is a kind of hypothetic value and discord with an experimental result that the bulk gas composition may be different from that of the electrode surface. When we consider the theoretical vulnerability of Nernst loss, the overvoltage is ascribed to the kinetic reason of mass transfer effect through the gas phase.

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