Temperature effect on the electrode reactions in a molten carbonate fuel cell

Choong-Gon Lee

Department of Chemical and Biological Engineering, Hanbat National University, 125 Dongseodaero, Yuseong-gu, Daejeon, Republic of Korea

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ABSTRACT

A temperature effect on the electrode reactions was investigated in terms of activation energy of overpotential with 100 cm^2 class molten carbonate fuel cells. The overpotential is attributed to the resistance in the electrochemical reactions on electrodes, thus the activation energy reflects reaction characteristics of the electrodes. The activation energy was measured with electrochemical impedance spectroscopy (EIS) and inert gas step addition (ISA) methods. These methods revealed that the anodic overpotential had positive activation energies showing larger overpotential at higher temperature, whereas the cathodic overpotential had negative activation energies. In particular, the positive activation energy of anodic overpotential is a unique behavior which has not been treated before. The gas phase diffusion resistance in the porous electrode, calling pore diffusion resistance (PDR), would be responsible for the positive activation energy. On the other hand, the temperature dependence of reactant gas dissolution to the carbonate melts and transport through the carbonate film leads to negative activation energy because the cathode is covered by the relatively thick electrolyte film. Insignificant PDR effect is observed at the cathode through the activation energy of gas phase mass transfer resistance at the cathode.

1. Introduction

The molten carbonate fuel cell (MCFC) uses eutectic carbonate melts as electrolyte, so that it has relatively high operation temperature around 923 K. At this temperature, the electrolyte forms thin film on the surface of porous electrodes, which provides large reaction sites made of three-phase boundary of gas-liquid-solid. The film thickness depends on the electrode materials and gas conditions. The anode is supposed to have negligibly thin electrolyte film because it is maintained in the H$_2$ environment with metal electrode and it has large contact angle with carbonate melts [1]. On the other hand, the cathode with very small contact angle is assumed to have relatively thick electrolyte film on the surface [1].

The MCFC runs with gas reactants through the following electrode reactions at the anode (Eq. 1a) and cathode (Eq. 1b).

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \tag{1a}$$

$$1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \tag{1b}$$

The slow processes in the anode and cathode reactions provide overpotential, thus output voltage (V) has following relation with overpotential:

$$V = E_{OCV} - \eta_{IR} - \eta_{an} - \eta_{ca} \tag{2}$$

Because the gas phase reactants are forcedly supplied to the electrode, the MCFC can be considered as a forced-convection system. At a high reaction rate, the gas phase transport of reactant species affect electrode reaction rate. It can be assumed that two cases can affect the reaction rate at both electrodes: (i) gas transport in gas channels, and (ii) gas transport in porous electrodes. A previous work showed an effect of the former process on the electrode reactions using overpotential analysis where the electrode reaction rates are a function of reactant flow rate at both electrodes [2]. When the latter process is assumed to affect the electrode reactions, the electrode reactions have a similarity to the heterogeneous catalyst reactions observed in the porous material. Assuming a chemical reaction in the catalyst, the porous structure of a catalyst provides resistance in the diffusion of reactants inside the catalyst at a high reaction rate, called pore diffusion resistance (PDR) [3–6].

In the MCFC, the effect of PDR on the electrode reaction would be represented in the overpotential [7]. Indeed, the anode reaction is considered to occur inside the pores because the actual surface area of electrode is much larger than geometrical one. When the temperature of the cell rises, reaction rate inside the pores increases. Then the enhanced reaction rate induces larger reactant flux from bulk to pore inside, which yields larger transport resistance in the pores. Simultaneously, severe concentration distribution occurs in the pores and reaction rate decreases by increasing the temperature. Thus it can be expected that overpotential increases by the effect of PDR with increasing temperature. Then the activation energy of overpotential will exhibit the effect of PDR. In particular, the anode reaction accompanies gas production as shown in Eq. (1a), thus more severe effect by the PDR

is expected than the cathode. In a previous work, the effect of PDR on the anode overpotential has been suggested with Thiele modulus ($\phi = L_P \sqrt{\frac{k_o}{D_e r}}$) as Eq. (3) [7].

$$\eta_{an} \cong \eta_{an,G} = \frac{iR^2 T^2}{n^2 F^2 a p_0}\left(\frac{1}{k_G}\right)\left(L_P \sqrt{\frac{k_o}{D_e r}}\right) = \frac{iR^2 T^2}{n^2 F^2 a p_0}\left(\frac{1}{k_G}\right)\phi = q_{an} u_f^{0.5}$$

(3)

where $q_{an} = 1.51 \frac{R^2 T^2 (i \cdot s \cdot L)^{1/2} \nu^{1/6} \phi}{a \cdot (nF)^{3/2} p_0^{1/2} D_G^{2/3}}$, $u_f \left(= \frac{\nu_C}{\nu_F}\right)$ is the anode gas utilization.

On the other hand, the cathode would have negligible PDR effect because the most rate control process is the mass transfer through the liquid electrolyte. Thus, the following relation has been suggested for the cathode overpotential [2].

$$\eta_{ca} \cong \eta_{ca,L} + \eta_{ca,G} = A \cdot p(O_2)^{-0.75} p(CO_2)^{0.5} + B \cdot p(CO_2)^{-1} + \frac{iR^2 T^2}{n^2 F^2 a p_0}\left(\frac{1}{k_G}\right)$$
$$= A \cdot p(O_2)^{-0.75} p(CO_2)^{0.5} + B \cdot p(CO_2)^{-1} + q_{ca} u_{ox}^{0.5}$$

(4)

Lee et al. reported electrochemical impedance spectroscopy (EIS) [8], inert gas step addition (ISA) [2], and reactant gas addition (RA) [9] methods to investigate reaction characteristics in the MCFC. The methods provide reaction overpotential due to the mass-transfer resistance at an electrode. Analyzing the overpotential with respect to the reactant flow rate as well as partial pressure clearly represented reaction characteristics at the electrodes: the anode is mainly mass-transfer control process in the gas phase, while the cathode is most mass-transfer control process in the liquid phase. Furthermore, they gave quantitative information about the overpotential at both electrodes.

As a temperature effect at the cell, Yuh and Selman reported following overpotential relations at the anode and cathode [10].

$$\eta_{an} = 2.27 \times 10^{-5} p(H_2)^{-0.42} p(CO_2)^{-0.17} p(H_2O)^{-1.0} \exp\left(\frac{53,500}{RT}\right) \cdot i$$

(5a)

$$\eta_{ca} = 7.505 \times 10^{-6} p(O_2)^{-0.43} p(CO_2)^{-0.09} \exp\left(\frac{77,300}{RT}\right) \cdot i$$

(5b)

Above equations show that both electrodes have negative exponents to the anode and cathode gases and have negative activation energies. It implies that overpotential at the electrodes decreases with increasing temperature and gas partial pressures. However the research was carried out with 3 cm^2 coin cell and gas utilizations of H_2 and O_2 were kept below 15% to neglect gas-phase mass-transfer effect. The cell condition was far from real condition where the anode gas utilization is close to 75%, and they excluded gas-phase mass-transfer effect. CRIEPI in Japan has reported following anodic overpotential relation with 100 cm^2 class single cells [11,12].

$$\eta_{an} = A_{f,an} \exp\left(\frac{-\Delta H_{an}}{RT}\right) p(H_2)^{-0.5} \cdot i$$

(6a)

$$\eta_{ca} = \left\{ A_{f,ca,1} \exp\left(\frac{-\Delta H_{ca,1}}{RT}\right) p(O_2)^{-0.75} p(CO_2)^{0.5} \right.$$
$$\left. + A_{f,ca,2} \exp\left(\frac{-\Delta H_{ca,2}}{RT}\right) p(CO_2)^{-1.0} \right\} \cdot i$$

(6b)

The activation energy of ΔH_{an} was in the range from -65 kJ mol^{-1} to -139 kJ mol^{-1} [11]. The relation shows that anodic overpotential has a negative exponent for H_2 partial pressure and negative activation energy. The values of $\Delta H_{ca,1}$ and $\Delta H_{ca,2}$ are ca. -80 and -20 kJ mol^{-1}, respectively [12]. However, Eq. (5a) is different from Eq. (6a) where the effect of CO_2 and H_2O on the overpotential is neglected, and Eqs. (6a) and (6b) also do not contain flow rate effect at both electrodes.

The activation energies should contain the temperature effects of reaction rate and mass transfer processes including dissolution into the electrolytes. In this work, the effect of temperature on the electrode

reactions has been investigated through the activation energy. In addition, the PDR has been clarified by the analysis of the activation energy obtained from EIS and ISA data at 100 cm^2 class MCFC single cells.

2. Experimentals

The 100 cm^2 class MCFC single cells used in this work were provided by Korea Electric Power Research Institute (KEPRI). They were fabricated with Ni-Al alloy anode, in-situ oxidized NiO cathode, ceramic matrix made of LiAlO$_2$ with alumina fiber, and eutectic carbonate melts of $(62 + 38)$mol% $(Li + K)_2CO_3$. More details about the cell fabrication and operation are described in a previous work [2].

A mixture of 80 mol% H_2 and 20 mol% CO_2 was humidified with 53 °C water and supplied to the anode. A mixture of 70 mol% air and 30 mol% CO_2 was served as cathode gas. Temperature was controlled in the range of 823 K to 973 K, and the cells were operated under atmospheric condition.

EIS was measured with PAR 273 and Solartron 1250 FRA in the frequency range from 1 kHz to 0.01 Hz at open circuit state. The AC signal was 5 mV rms.

3. Results and discussion

3.1. Activation energy

In general, temperature dependence of an overpotential (η) can be expressed as an Arrhenius type function because it is caused by the kinetic and mass transfer processes.

$$\eta = A_f \exp\left(-\frac{\Delta H}{RT}\right)$$

(7)

Table 1 compares the activation energies of the overpotential reported so far. In the Li-K carbonate melts, the activation energy of anode reaction has relatively consistent, which has ca. 50 kJ mol^{-1}, but that of the cathode has quite significant deviation among the methods and temperatures. The clear dependence of activation energy on the temperature at the oxygen reduction has been reported by Uchida et al. [19] that activation energy was changed at 973 K and higher value was obtained above the temperature. However, the resistance measured in the table would contain not only reaction rate but also mass transfer processes in the liquid phases. Uchida et al. has suggested that the activation energy of reaction rate (ΔH_{io}) of 25 kJ mol^{-1} at the oxygen reduction be caused by the dissolution process into the carbonate melts [19]. The ΔH_{io} of 77 kJ mol^{-1} from Yuh and Selman [10] would also contain dissolution and diffusion processes because they measured cathodic overpotential with steady state polarization with 3 cm^2 class cell. Morita et al. reported the value of 80 kJ mol^{-1} which contained dissolution and diffusion processes at steady state [12].

Most of the measurements had very high gas flow rate where the utilization was below 10%, thus the gas-phase mass-transfer resistance could be neglected. Consequently, ΔH_{io} around 50 kJ mol^{-1} at the anode and about 30 kJ mol^{-1} at the cathode in Table 1 indicate that those reactions are mass transfer control processes because the mass transfer process generally are below 40 kJ mol^{-1} of activation energy [10]. Table 2 also compares activation energy of the gas dissolution into the carbonate melts (ΔH_C), the diffusivity in the melts (ΔH_{D_L}) and in the gas phase (ΔH_{D_G}). The ΔH_C of O_2 species into Li-K carbonate melts is around 50 kJ mol^{-1} while CO_2 and H_2O are about 20 kJ mol^{-1}. The solubility of CO_2 and H_2 is one order higher than that of O_2, thus the difference of activation energy is plausible. However, the ΔH_{D_L} of superoxide ion (O_2^-) is 97 kJ mol^{-1}. Comparing the general ΔH_{D_L} of ionic species in the carbonate melts is about 50 kJ mol^{-1} [20], the 97 kJ mol^{-1} of ΔH_{D_L} of superoxide ion (O_2^-) is quite large value. On the other hand, ΔH_{D_L} of CO_2 is only 17 kJ mol^{-1}. This is also much