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Estimation of approximate activation energy loss and mass transfer coefficient from a polarization curve of a polymer electrolyte fuel cell

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Abstract–A simple electrochemical approach is presented to quantitatively predict activation energy and mass transfer coefficient from a polarization curve of polymer electrolyte fuel cells to examine the membrane-electrode assembly (MEA) performance. It is assumed that the initial voltage drop at open circuit voltage is due to kinetic activation energy and that the current loss at short circuit current is due to mass transfer resistance. Accordingly, voltage drop in the activation polarization is converted into a change in the Gibbs free energy to determine the activation energy requirement. The mass transfer coefficient for current losses is derived from Fick's law, based on the mass transfer limitation of oxygen at the oxygen reduction reaction sites. Case studies from the literature show reasonable correlations to the operating conditions, thereby providing a useful tool for prediction of the preliminary values of the activation energy and mass transfer coefficient for an MEA under various conditions.

Key words: Activation Energy Loss, Mass Transfer Coefficient, Polarization Curve, Membrane-electrode Assembly (MEA), Polymer Electrolyte Fuel Cells (PEFCs)

INTRODUCTION

A polymer electrolyte fuel cell (PEFC) is an electrochemical device that converts chemical energy directly into electrical energy. Its behavior is governed by electrochemical phenomena such as spontaneous catalytic redox reactions and proton transport through a membrane-electrode assembly (MEA). The MEA performance can be globally evaluated via a current-voltage relation, referred to as a polarization curve, which typically takes into account the activation loss, ohmic loss, and mass transfer loss according to the voltage loss characteristics [1]. From an open circuit voltage (OCV) at a net current of zero, voltage loss due to the ohmic resistance of an MEA is unavoidable, which shows a linear curve by ohm's law in the ohmic loss region. In addition to ohmic resistance, kinetic activation losses occur in the activation loss region, primarily due to slow oxygen reduction reaction (ORR). Other losses include concentration polarization losses in the mass transfer loss region either due to rapid consumption of a reactant or water flooding at the cathodic ORR sites [2]. Theoretical approaches for isolating each overpotential have developed empirical fitting models [3-8] based on conventional Butler-Volmer equations as for activation polarization

$$\eta_{act} = \frac{RT}{\alpha nF} \ln\left(\frac{I}{I_0}\right) \quad (1)$$

and for concentration polarization

$$\eta_{conc} = \frac{RT}{nF} \ln\left(\frac{I_L}{I_L - I}\right) \quad (2)$$

Tafel plot analysis for the kinetic activation polarization gives charge transfer coefficient (α) and exchange current density (I_0) from Eq. (1). Also, Eq. (2) analyzes concentration polarization with fitting parameters such as diffusion coefficient of a reactant (D) and distance of diffusion boundary layer (L) for limiting current density (I_L). Beyond the conventional polarization model equations, however, much of the information found in polarization curves has yet to be analyzed quantitatively. The purpose of the present work is to explore a novel electrochemical insight to quantitatively analyze a polarization curve for PEFCs. This approach offers a simple diagnostic tool for predicting the preliminary activation energy and mass transfer coefficient to evaluate an MEA from its practical polarization behaviors of PEFCs. Case studies were performed based on the experimental polarization curves reported in previous studies.

POLARIZATION MODEL AND ASSUMPTIONS

Fig. 1(a) shows a typical polarization curve of a PEFC that takes into account activation loss region, ohmic loss region, and mass transfer loss region. Tangent slopes of the polarization curve indicate the overall resistance according to ohm's law hence, the differentiated voltage from the current indicates the global resistance as illustrated in Fig. 1(b). From the global resistance curve, the two punctual coordinates (i_a, E_a) and (i_m, E_m), clearly divide the three regions. Also, the definite line of the ohmic slope (A) in the polarization curve can be precisely extrapolated such that the slope is the same as the ohmic resistance R_{ohm}. Once the three regions are clearly divided by the differentiated polarization curve, the extrapolated ohmic slope reveals two intercepts denoted as E_O and i_O, respectively. The voltage of E_O indicates the hypothetical voltage output with an assumption of no activation resistance, and the current of i_O is the hypothetical current generation with an assumption of no mass transfer resistance. Further analysis is based on the extrapo-

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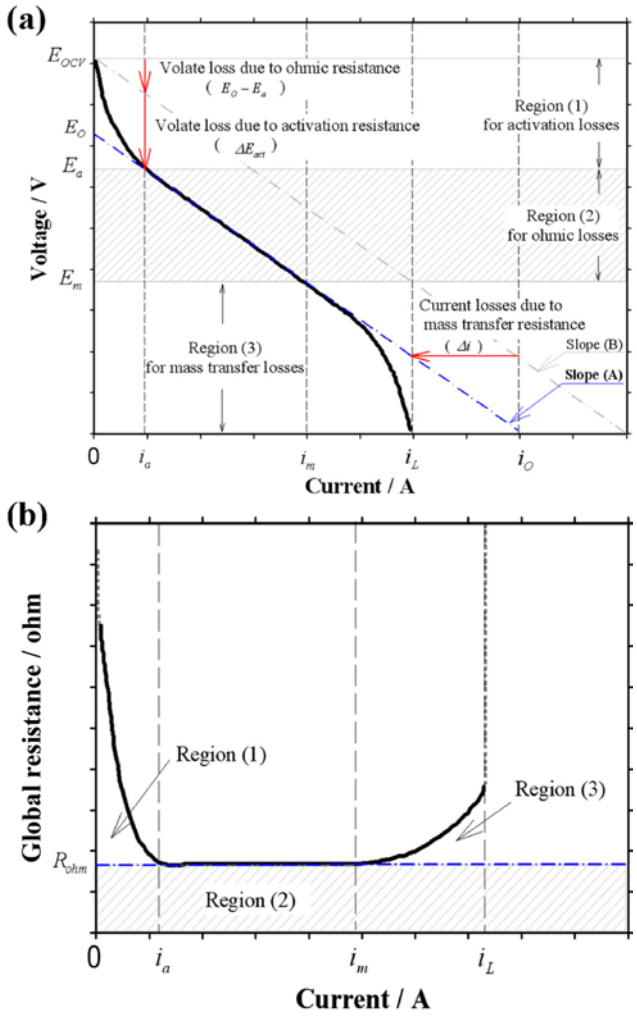

Fig. 1. (a) Typical polarization curve of a PEFC schematically from OCV (E_{OCV}) to limit current (i_L) taking into account region (1) for activation loss, region (2) for ohmic loss, and region (3) for mass transfer loss, and (b) its differential form for global resistance versus current; the dash-dot slope (A) is precisely extrapolated within the two punctual coordinates (i_a, E_a) and (i_m, E_m) to obtain the y-intercept (E_O) and x-intercept (i_O). Slope (B) is a hypothetical polarization curve without activation energy and mass transfer losses, and further activation and mass transfer polarization models are based on the slopes and intercepts.

lated slope (A) of the ohmic resistance.

1. Model for the Overall Activation Energy Loss

Consider an R_{ohm} without kinetic losses at activation loss region in this case, a polarization behaves ideally as in the slope (B) from E_{OCV} (see Fig. 1(a)). In practice, lowering the cell potential mainly due to kinetic activation with ohmic resistance causes a dramatic voltage loss, hereafter denoted as activation voltage loss ΔE_{act}. This energy loss is readily obtained by the y-intercept, E_O of the slope (A) and practical E_{OCV}, based on the equation

$$\Delta E_{act} = E_O - E_{OCV} \tag{3}$$

The activation voltage loss is referred to as electrical work loss due to activation resistance, and can be converted into the change in Gibbs free energy by

$$\Delta G_{act} = -nF\Delta E_{act}, \text{ (kJ mol}^{-1}\text{)} \tag{4}$$

Eq. (4) describes the activation energy at activation loss region, where n is the number of electrons per mole of the fuel (here, n is two for hydrogen oxidation) and F is Faraday's constant. ΔG_{act} involves the kinetic activation dominantly due to slow ORR over the activation energy requirements for proton migration of around 7 to 10 kJ mol^{-1} in both cases for Nafion® membranes [9-11] and aqueous solution [12]. Thus, the energy loss defined at Eq. (4) comprehensively describes the overall activation energy loss of an MEA, which is defined as being negative in a PEFC.

2. Model for the Mass Transfer Coefficient

Consider R_{ohm} without mass transfer resistance at mass transfer loss region. Then, a hypothetical polarization behaves as for slope (A) from (i_m, E_m) to (i_O, 0) as schematically shown in Fig. 1(a). The hypothetical current of i_O coincides with the maximum current flow of a PEFC when the mass transfer resistance is zero. Therefore, at i_O the partial oxidant pressure $P_{cathode}|_{i_O}$, is the same as the bulk pressure P_{bulk}. The mass transfer limitation, however, commonly incurs additional voltage losses due to the limited oxidant pressure at the ORR sites, predominantly by water flooding [2]. Thus, the current is limited to i_L, and here we assume that $P_{cathode}|_{i_L}$ is zero. Accordingly, the difference in the current between i_L and i_O describes the limited oxygen diffusion to the ORR sites. Therefore, the following boundary conditions apply:

1. The partial pressure of oxidant at the i_O where V=0 due to ohmic resistance only:

$$P_{cathode}|_{i_O} = P_{bulk} \tag{5}$$

2. The partial pressure of oxidant at the i_L where V=0 due to ohmic resistance and mass transfer resistance:

$$i_L: P_{cathode}|_{i_L} = 0 \tag{6}$$

where P_{bulk} is the partial pressure of the cathodic oxidant at bulk and $P_{cathode}$ is the partial pressure at ORR sites. This mass transfer limitation is often described by Fick's linear diffusion [13], and the mass transfer coefficient, k is derived as provided in the Appendix:

$$k = \frac{RT\Delta j}{nF\Delta P}, \text{ (cm sec}^{-1}\text{)} \tag{7}$$

where T is the operating temperature, Δj is the current loss due to the mass transfer resistance, and ΔP is the partial pressure difference of cathodic substrate, which is the same as for P_{bulk}.

CASE STUDIES

Although a large number of polarization curves for PEFC have been presented in literature, many have not presented a practical i_L at mass transfer loss region in their curves. To predict the activation energy and mass transfer coefficient of PEFCs, the polarization curves in literature [8,14-17] are examined here. The curves were extrapolated to determine the empirical E_{OCV} and i_L, in addition to the hypothetical E_O and i_O. Subsequently, the activation energy ΔG_{act} and mass transfer coefficient k were calculated according to Eq. (4) and (7). The summarized results are given in Table 1, including experimental conditions.

Table 1. Summary of case studies for the predicted overall activation energy loss and mass transfer coefficient

Remark[ref]	Membrane contribution			Catalyst contribution			Cell		Fuel gases		ΔE_{act}			Δj			Ohmic resistance	Activation energy	Mass transfer coefficient
				Pt catalyst		Binder			H_2	O_2(Air)									
	Type	d	σ	Anode	Cathode	Nafion	RH	T	P_{anode}	$P_{cathode}$	E_{OCV}	E_O	i_L	i_O	A		ASR of R_{ohm}	ΔG_{act}	k
	Nafion	μm	S cm^{-1}	mg cm^{-2}			%	°C	atm	atm	V	V	A	A	cm^2		Ω cm^2	kJ mole^{-1}	cm sec^{-1}
Case 1.[8]									1	1	0.976	0.847	65.5	85.8			0.494	24.9	0.0113
O_2 pressure increase	115	127	NA[a]	0.30	0.30	0.60	100	50	3	3	1.010	0.880	70.0	101.6	50		0.433	25.0	0.0059
									5	5	1.027	0.897	73.3	109.9			0.408	25.1	0.0041
Case 2.[8]									1	(1)	0.943	0.826	39.4	92.6			0.446	22.5	0.0314
Air pressure increase	115	127	NA[a]	0.30	0.30	0.60	100	70	3	(3)	0.992	0.868	54.9	104.1	50		0.417	23.9	0.0097
									5	(5)	1.000	0.873	62.5	114.8			0.380	24.6	0.0062
Case 3.[14]								50			0.894	0.794		26.7			0.750	19.3	
T increase	115	127	NA[a]	0.20	0.20	NA[a]	100	70	0.987	(0.987)	0.905	0.821	NA[a]	28.1	25		0.730	16.3	NA[a]
								80			0.900	0.834		28.7			0.727	12.8	
Case 4.[14]									0.987	(0.987)	0.894	0.794		26.7			0.750	19.3	
Air pressure increase	115	127	NA[a]	0.20	0.20	NA[a]	100	50	1.480	(1.480)	0.904	0.798	NA[a]	29.7	25		0.672	20.5	NA[a]
									1.974	(1.974)	0.912	0.798		40.2			0.496	22.0	
Case 5.[15]								30			1.025	0.894		76.0			0.294	25.2	
T increase	115	127	NA[a]	4.00	4.00	NA[a]	0.00	50	3	3	1.017	0.904	NA[a]	100.4	25		0.225	21.9	NA[a]
								70			1.016	0.912		114.4			0.199	20.0	
Case 6.[16]	115	127	NA[a]	0.40	0.40	NA[a]	100	80	0.680	0.817	0.898	0.709	NA[a]	5.3	5		0.665	36.5	NA[a]
T increase							67.4	90			0.953	0.724		8.4			0.430	44.2	
Case 7.[17]						0.00[b]					0.970	0.844		8.0			0.528	24.4	
Binder increase	212	58	0.07	0.40	0.40	0.15[b]	100	60	1	1	0.970	0.854	NA[a]	16.8	5		0.254	22.3	NA[a]
						0.30[b]					1.000	0.841		24.6			0.171	30.7	
						0.60[b]					1.000	0.838		22.6			0.186	31.2	

[a]Not available from the polarization curve and the experimental information

[b]Outer Nafion binder content in addition to a constant electrode binder content of 0.035 mg cm^{-2}

RESULTS AND DISCUSSION

1. Activation Energy

The activation energy, ΔG_{act} is a positive value due to the negative entropy change of energy losses against the spontaneity. Accordingly, a lower ΔG_{act} indicates a lower activation energy requirement. Therefore, lowering ΔG_{act} as simply defined in Eq. (4) without cur- rent function is a quantitative merit of MEAs in terms of energy conversion efficiency for comprehensive conditions related to the catalysts, membranes, gas diffusion layer, interfaces, temperature, humidity, and so on.

The predicted activation energy decreased with increasing temperature (see Cases 3 and 5 in Table 1). An increase in temperature reduces the overall Gibbs free energy during the reactions, though increases cell performances, due to the positive effects on the reaction kinetics such as for ORR and hydrogen oxidation reaction (HOR) [18]. Also, proton transport is enhanced with increasing temperature [12] as it lowers the internal resistance in terms of R_{ohm}, thereby decreasing the predicted activation energy. In spite of these benefits, high temperature and low humidity in Nafion® membranes generally decrease fuel cell performance due to the prohibition of proton transport through the readily dehydrated membrane. Thus, the overall activation energy loss of Case 6 was much greater than in the other cases.

The activation energy loss increased with the increasing partial pressure of oxygen (see Case 1) and air (see Cases 2 and 4). A high partial pressure increases the E_{OCV} governed by the Nernst equation and simultaneously decreases R_{ohm}, so the difference between E_{OCV} and E_O tends to be significant as defined in Eqs. (3) and (4). Otherwise, it may seem to be a thermodynamically odd phenomenon under the consideration only for the half-cell catalytic reaction kinetic of HOR and ORR. Since, the activation energy losses defined in this study are obtained from a comprehensive polarization curve during the MEA operation, it is different with pure catalytic reaction kinetic. In other words, it comprehensively predicts energy requirements for an MEA activation including catalytic activation energy for HOR and ORR, and phenomenological proton migration. Therefore, the partial pressure enhancement can positively affect the open circuit voltage and ohmic resistance, though it was found to be not significantly positive to reduce overall activation energy loss, whereas high temperature readily decreased the activation energy.

Case 7 shows the effect of binder contents to the activation energy losses particularly for outer binder additions in an MEA [17]. With the increase of binder content from 0 to 0.30 mg cm^{-2}, the in-

ternal losses were decreased as predicted from their polarization curves by R_{ohm}. With the excess amount of binder, however, R_{ohm} was increased and these results are well matched with their impedance data. Otherwise, the predicted activation energy losses showed different pattern with the R_{ohm}. The minimum activation energy loss was found at the binder content of 0.15 mg cm^{-2} whereas the minimum internal resistance, R_{ohm} was shown at 0.30 mg cm^{-2}. It implies that the binder content can reduce R_{ohm} by advancing interfacial contact resistant in an MEA, and it can prohibit reaction kinetics independent to the minimized R_{ohm} at a certain content of binder. This information from the practical polarization curves suggests that even though the activation energy losses do not significantly affect the maximum power generation, the overall activation energy losses should be quantitatively compared in conflict with the internal resistance to evaluate the efficiency of an MEA.

2. Mass Transfer Coefficient

Many efforts to solve water flooding in PEFCs have focused on controlling operation conditions and evaluating the polarization curves (see Ref. 2 and the literature cited therein) however, no comprehensive study has been reported on the quantitative information found in the polarization curves. By the definition of Eq. (7), a low mass transfer coefficient k indicates a lower mass transfer resistance. Obviously, this coefficient can then be used to quantitatively describe how close i_L is to i_O by reducing the mass transfer limitations such for either water flooding or reactant deficient problems. Moreover, k should also be the same for an MEA under the same operating conditions; k readily changes according to operating conditions, most notably due to changes in temperature and gas pressure. Thus, it can be used to quantitatively evaluate the mass transfer performance by an MEA.

As expected by Eq. (7), k decreased with increases in the cathodic partial pressure of oxygen (Case 1) and air (Case 2). Since high pressure extrudes the accumulated water in the cathode at a high current, the mass transfer resistance due to water flooding was reduced. Accordingly, a low k was predicted according to the increasing partial pressure. Also, the influence of temperature was shown by Case 1 versus Case 2. Since concentrated cathodic water at high current could evaporate at high temperature resulting in a reduction of mass transfer resistance, it is expected that k will decrease with the elevated temperature for the low temperature PEFCs in spite of proportional form to the temperature in Eq. (7). However, the predicted values are showing an increase of k in spite of temperature elevation because the cathodic reactant of Case 2 was air. This result implies that a low concentration of oxidant induces a relatively high mass transfer resistance caused by the usual water flooding at mass transfer loss region, due to limited oxygen diffusion through the air. Therefore, it could be confirmed the mass transfer coefficient was reasonably predicted for an MEA, in terms of mass transfer resistance and water management.

CONCLUSIONS

We have demonstrated a novel method for predicting the approximate activation energy loss and mass transfer coefficient from the polarization curve of a PEFC. These empirical parameters show reasonable correlations with operating conditions. The approach may enable researchers to simply predict approximate values of the activation energy and mass transfer coefficient for an MEA, and to evaluate the overall performance of an MEA in light of reaction and mass transfer kinetics. Further analyses of additional polarization curves obtained from experimental data and their archives using this approach will provide useful references for MEA design and operation.

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NOMENCLATURE

i_a : boundary current for activation loss region [A]
E_a : boundary voltage for activation loss region [V]
i_m : boundary current for mass transfer loss region [A]
E_m : boundary voltage for mass transfer loss region [V]
E_{OCV} : open circuit voltage [V]
i_L : practical limiting current [A]
E_O : hypothetical voltage without activation resistance [V]
i_O : hypothetical current without mass transfer resistance [A]
R_{ohm} : ohmic resistance [ohm]
A : area of electrode [cm^2]
d : thickness of a membrane [μm]
σ : proton conductivity of a membrane [S cm^{-1}]
Δj : difference of limiting current density [A cm^{-2}]
ΔE_{act} : activation voltage loss [V]
D : diffusion coefficient of oxygen [cm^2 s^{-2}]
L : thickness of boundary layer [cm]
F : faraday constant [96485 Coulomb mol^{-1}]
R : gas constant [0.0821 L atm K^{-1} mol^{-1}]
T : operating temperature [K]
RH : relative humidity [%]
C : concentration of oxygen [mol L^{-1}]
P_{bulk} : partial pressure of cathodic substrate at x=0 [atm]
$P_{cathode}$: partial pressure of cathodic substrate at ORR sites at x=L [atm]
ΔG_{act} : activation energy [kJ mol^{-1}]
k : mass transfer coefficient [cm sec^{-1}]

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APPENDIX

A. Derivation of Mass Transfer Coefficient by Fick's Diffusion Law

Fick's linear diffusion under steady-state has a flux form

$$J = -D\frac{dC}{dx} \tag{A.1}$$

where J is the local flux of the cathodic substrate, and it is proportional to the concentration gradient of the substrate dC/dx and its diffusion coefficient D. Let the local distance for diffusion of the substrate be L, that of the thickness of boundary diffusion layer. Then, the flux difference between i_L and i_O at the voltage of zero and the distance of L, as illustrated in Fig. 1(a), is

$$\Delta J = -\frac{D}{L}\Delta C \tag{A.2}$$

Here, the molality difference between i_L and i_O is described by the ideal gas law as

$$\Delta C = \frac{\Delta P}{RT} \tag{A.3}$$

where, R is the gas constant and T is the operating temperature of a PEFC. Here, the partial pressure difference between i_L and i_O is defined as

$$\Delta P = P_{cathode}|_{i_O} - P_{cathode}|_{i_L},\ \ P_{cathode}|_{i_L} = 0 \tag{A.4}$$

by the boundary conditions thus ΔP is the same as ΔP_{bulk}, which is the gas pressure of an oxidant. Substituting Eq. (A.3) into Eq. (A.2), we then get the equation

$$\Delta J = -\frac{D}{L}\frac{\Delta P}{RT} \tag{A.5}$$

The flux of the reduced substrate at ORR sites is converted into the difference of current density,

$$\Delta J = \frac{\Delta N}{tA} = \frac{\Delta j}{nF} \tag{A.6}$$

where, N is moles of reduced substrate, A is the electrode area, n is the stoichiometric number of electrons consumed for ORR, and t is the time for diffusion at V=0. Therefore, expressing Eq. (A.5) by substituting into Eq. (A.6), and letting (−D/L) be k is as follows:

$$\Delta j = k\frac{nF\Delta P}{RT} \tag{A.7}$$

Therefore, k can be calculated from the polarization curve at Region (3) as in Fig. 1(a), and is denoted as the mass transfer coefficient.