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Short communication

An alternative way of estimating anodic and cathodic transfer coefficients from PEMFC polarization curves

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ABSTRACT

This study presents a new technique for estimating cathodic and anodic charge transfer coefficients from fuel cell voltage–current curves. In contrast to conventional approach, the new technique allows estimation of anodic and cathodic charge transfer coefficients simultaneously from integral characteristics of voltage–current curves. Case studies illustrate the parameter estimation from PEMFC polarization curves. The new technique is compatible with available parameter estimation methods.

1. Introduction

PEMFC operates at low temperature and delivers high power density with low weight and cost. The performance of the fuel cell is characterized by current–voltage curves. Charge transfer coefficients are important parameters that relate to anode and cathode electrochemical reactions. Conventional way of estimating the charge transfer coefficient is based on fitting an empirical equation to experimental current–voltage curves [1–4]. A limitation of available parameter estimation methods is that only cathodic charge transfer coefficient can be estimated from experimental curves. This paper deals with the development of a new technique for estimating anodic and cathodic charge transfer coefficients from integral characteristics of experimental current–voltage curves.

2. Alternative technique for transfer coefficients

The actual cell voltage is lower than the theoretical open circuit voltage. The cell voltage includes the contribution of the anode and cathode potentials and ohmic polarizations as shown below:

$$V_{cell} = V_{oc} - \eta_{act}^{A} - \eta_{act}^{C} - |\eta_{conc}^{A}| - |\eta_{conc}^{C}| - \eta_{Ohmic} \tag{1}$$

The open circuit voltage V_{oc} is calculated from Nernst equation [5]. Activation overpotential is related to the rates of electrochemical reactions:

$$\eta_{act}^{A} = \frac{RT}{\alpha_A F} \ln\left(\frac{I}{I_A}\right) \tag{2}$$

$$\eta_{act}^{C} = \frac{RT}{\alpha_C F} \ln\left(\frac{I}{I_C}\right) \tag{3}$$

Concentration overpotential includes a loss of potential due to concentration change at the electrode:

$$\eta_{conc}^{A} = \frac{RT}{z_A F} \ln\left(1 - \frac{I}{I_{\lim,A}}\right) \tag{4}$$

$$\eta_{conc}^{C} = \frac{RT}{z_C F} \ln\left(1 - \frac{I}{I_{\lim,C}}\right) \tag{5}$$

Ohmic polarization characterizes the resistance of electrolyte and electrode materials

$$\eta_{Ohmic} = R_{Ohmic} I \tag{6}$$

where R_{Ohmic} is total cell resistance including electronic and ionic resistances.

Fig. 1 shows a typical current–voltage curve. New technique for estimating anodic and cathodic transfer coefficients is based on integral characteristics of fuel cell polarization curve. We define the next ratio from an experimental polarization curve

$$\gamma = \frac{S_2}{S_1} \tag{7}$$

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Nomenclature

C	constant
I	current density (A/m^2)
I_C	cathode exchange current density (A/m^2)
I_A	anode exchange current density (A/m^2)
F	Faraday's constant ($C\,mol^{-1}$)
R	ideal gas constant ($J\,mol^{-1}\,K^{-1}$)
R_{Ohmic}	Ohmic resistance ($\Omega\,m^2$)
S	area (m^2)
T	temperature (K)
V_{cell}	cell voltage (V)
V_{oc}	open circuit voltage (V)

Greek symbols

α_A	anode charge transfer coefficient
α_C	cathode charge transfer coefficient
γ	coefficient
η	overpotential (V)

The area under the polarization curve S_1 is calculated as an integral with respect to I from I_1 to I_2:

$$S_1 = \int_{I_1}^{I_2} (V_{oc} - \eta_{act}^A - \eta_{act}^C - |\eta_{conc}^A| - |\eta_{conc}^C| - \eta_{Ohmic})\,dI \qquad (8)$$

The total area S is given by

$$S = \int_{I_1}^{I_2} V_{oc}\,dI = V_{oc}(I_2 - I_1) \qquad (9)$$

and the area S_2 is

$$S_2 = S - S_1$$

or

$$S_2 = \int_{I_1}^{I_2} (\eta_{act}^A + \eta_{act}^C + |\eta_{conc}^A| + |\eta_{conc}^C| + \eta_{Ohmic})\,dI \qquad (10)$$

Considering the ratio of integrals S_2 and S_1, as shown in Fig. 1, we get a new relationship for the charge transfer coefficients. Substituting

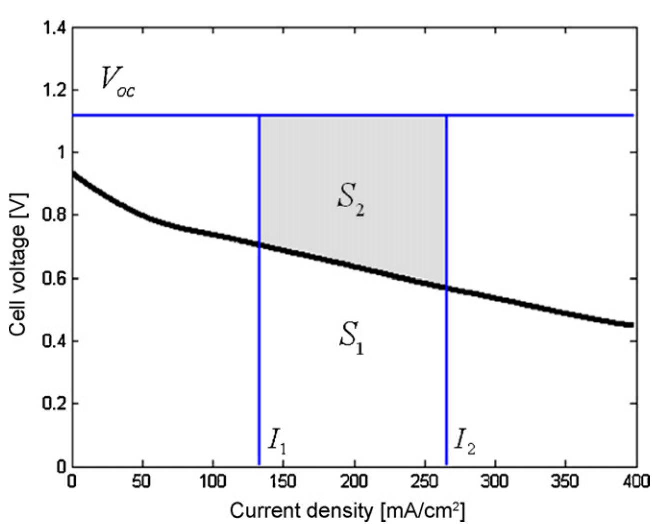

Fig. 1. Illustration for an alternative way of estimating charge transfer coefficient using integral characteristics of PEMFC polarization curves. $\gamma = S_2/S_1$, $S_1 + S_2 = V_{oc}(I_2 - I_1)$.

Eqs. (8) and (10) into Eq. (7) gives

$$\gamma = \frac{\int_{I_1}^{I_2} (\eta_{act}^A + \eta_{act}^C + |\eta_{conc}^A| + |\eta_{conc}^C| + \eta_{Ohmic})\,dI}{\int_{I_1}^{I_2} (V_{oc} - \eta_{act}^A - \eta_{act}^C - |\eta_{conc}^A| - |\eta_{conc}^C| - \eta_{Ohmic})\,dI} \qquad (11)$$

The next step is to find the analytical expressions for component part integrals. Transformation of activation overpotentials integrals is given below:

$$\int_{I_1}^{I_2} (\eta_{act}^A + \eta_{act}^C)dI = (B_A + B_C)\int_{I_1}^{I_2} \ln(I)dI - (B_A\ln(I_A) + B_C\ln(I_C))\int_{I_1}^{I_2} dI \qquad (12)$$

where $B_C = RT/\alpha_C F$, $B_A = RT/\alpha_A F$ are constants with charge transfer coefficients.

Integral of voltage drop due to the ohmic resistance with respect to I from I_1 to I_2 is

$$\int_{I_1}^{I_2} \eta_{Ohmic}\,dI = R_{Ohmic}\int_{I_1}^{I_2} I\,dI = R_{Ohmic}\frac{I_2^2 - I_1^2}{2} \qquad (13)$$

Using a power series, integral of concentration overpotential with respect to I from I_1 to I_2 is approximated as follows:

$$\int_{I_1}^{I_2} (|\eta_{conc}^A| + |\eta_{conc}^C|)\,dI \approx \frac{I_2^2 - I_1^2}{2}\frac{RT}{F}\left(\frac{1}{z_A I_{\lim,A}} + \frac{1}{z_C I_{\lim,C}}\right) \qquad (14)$$

Rearrangement of Eq. (11) with Eqs. (12)–(14) gives

$$A_1C_1 + A_2C_2 + A_3C_3 = V_{oc} \qquad (15)$$

where $A_1 = ((1+\gamma)/\gamma)\left(\left(\int_{I_1}^{I_2}\ln(I)dI\right)/(I_2 - I_1)\right)$; $A_2 = -(1+\gamma)/\gamma$ and $A_3 = ((1+\gamma)/2\gamma)((I_2^2 - I_1^2)/(I_2 - I_1))$.

The parameters of analytical polarization curve are grouped together into new constants:

$$C_1 = B_A + B_C \qquad (16)$$

$$C_2 = B_A\ln(I_A) + B_C\ln(I_C) \qquad (17)$$

$$C_3 = R_{Ohmic} + \frac{RT}{F}\left(\frac{1}{z_A I_{\lim,A}} + \frac{1}{z_C I_{\lim,C}}\right) \qquad (18)$$

The integral of natural logarithm with respect to I from I_1 to I_2 is

$$\int_{I_1}^{I_2} \ln(I)\,dI = I_2\ln(I_2) - I_1\ln(I_1) - (I_2 - I_1) \qquad (19)$$

It should be noted that application of the ratio of integrals Eq. (7) allows us to transfer from Eq. (1) with seven parameters (α_A^A, α_C^C, I_A, I_C, R_{Ohmic}, $I_{\lim,A}$ and $I_{\lim,C}$) to Eq. (15) with three new combined parameters (C_1, C_2 and C_3). Thus, dividing the experimental polarization curve into three parts and applying new Eq. (15) to each part as shown in Appendix A, we get the next set of linear algebraic equations with respect to the new three parameters:

$$A_{11}C_1 + A_{12}C_2 + A_{13}C_3 = V_{oc} \qquad (20)$$

$$A_{21}C_1 + A_{22}C_2 + A_{23}C_3 = V_{oc} \qquad (21)$$

$$A_{31}C_1 + A_{32}C_2 + A_{33}C_3 = V_{oc} \qquad (22)$$

Solving the set of Eqs. (20)–(22) for new parameters (C_1, C_2 and C_3) we obtain the anodic and cathodic charge transfer coefficients from Eqs. (16) and (17) as shown in Appendix B:

$$\alpha_C = \frac{RT}{F}\left\{\frac{\ln(I_C/I_A)(\ln(I_C)/\ln(I_A) - 1)}{(-C_2 - C_1\ln(I_C/I_A) + C_2\ln(I_C)/\ln(I_A))}\right\} \qquad (23)$$

$$\alpha_A = \frac{RT}{(C_1 - (RT/\alpha_C F))F} \qquad (24)$$

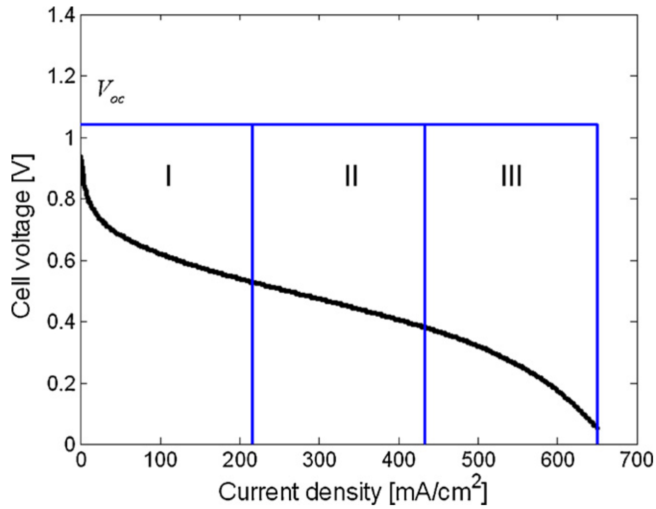

Fig. 2. Estimation of charge transfer coefficients using integral characteristics of experimental polarization curve for 50 cm^2 PEMFC [1] operating with H_2/air at 50 °C, 1 atm. $\gamma^{part\ I} = 0.6443$, $\gamma^{part\ II} = 1.2714$ and $\gamma^{part\ III} = 3.091$.

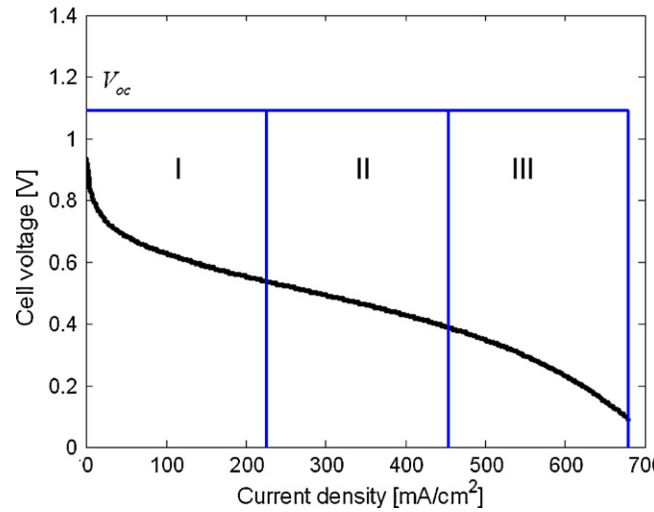

Fig. 3. Estimation of charge transfer coefficients using integral characteristics of experimental polarization curve for 50 cm^2 PEMFC [1] operating with H_2/air at 70 °C, 1 atm. $\gamma^{part\ I} = 0.7235$, $\gamma^{part\ II} = 1.3583$ and $\gamma^{part\ III} = 3.5015$.

Input data needed for solving the parameter estimation problem are

- Experimental polarization curve $V_{cell} = V_{cell}(I)$.
- Ratio of exchange current densities I_C/I_A.

The outlet parameters resulting from solving the parameter estimation problem are the anodic and cathodic charge transfer coefficients.

3. Results and discussion

We used the experimental data reported by Kim et al. [1] for 50 cm^2 PEMFC. They proposed an empirical equation for approximation of experimental PEMFC polarization curves with cathodic transfer coefficients as a fitting parameter. Figs. 2–4 illustrate application of the new technique for experimental fuel cell polarization curves.

In accordance with the new technique illustrated in Figs. 2–4, we start by dividing the current–voltage curve into three equal parts along the current density axis and progress to calculate the coefficient γ as shown in Fig. 1. With given coefficients $\gamma^{part\ I}$, $\gamma^{part\ II}$ and $\gamma^{part\ II}$, matrix elements A_{ij} are calculated from the equations given in Appendix A. Finally, solving Eqs. (20)–(22) for parameters C_1, C_2 and C_3 we find cathodic and anodic charge

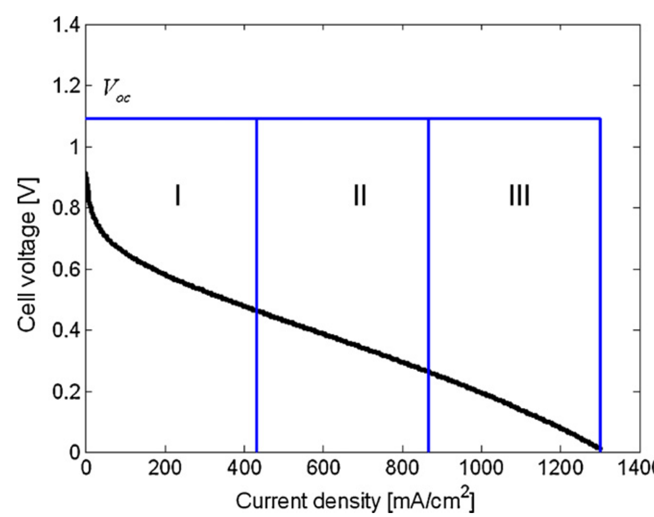

Fig. 4. Estimation of charge transfer coefficients using integral characteristics of experimental polarization curve for 50 cm^2 PEMFC [1] operating with H_2/O_2 at 70 °C, 1 atm. $\gamma^{part\ I} = 0.8304$, $\gamma^{part\ II} = 1.8927$ and $\gamma^{part\ III} = 5.4327$.

Table 1
Charge transfer coefficients estimated from PEMFC polarization curves.

Experimental PEMFC polarization curve [1]	Tafel parameter [1]	Ratio, I_C/I_A	New technique	
			Cathode, α_C	Anode, α_A
Fig. 2, H_2/air, 50 °C, 1 atm	$\alpha_C = 0.45$	1/5,000,000[a]	1.01	4.27
		1/7500[b]	0.58	2.04
		1/2000[c]	0.49	1.27
Fig. 3, H_2/air, 70 °C, 1 atm	$\alpha_C = 0.48$	1/5,000,000[a]	0.89	2.92
		1/7500[b]	0.51	2.09
		1/2000[c]	0.43	1.22
Fig. 4, H_2/O_2, 70 °C, 1 atm	$\alpha_C = 0.49$	1/5,000,000[a]	1.37	1.03
		1/7500[b]	0.79	0.67
		1/2000[c]	0.47	0.42

[a] Taken from Um et al. [6].
[b] Taken from Siegel et al. [7].
[c] Taken from Larminie and Dicks [8].

transfer coefficients from Eqs. (23) and (24). Table 1 lists the charge transfer coefficients estimated from polarization curves in Figs. 2–4.

The exchange current density includes the kinetics of electrochemical reactions and characterizes the current at equilibrium. It is a function of temperature, catalyst loading and catalyst specific area. The magnitude of exchange current density is increased with electrocatalyst surface area. The anode exchange current density is usually very high compared to the cathode one. In parameter estimation, anode contribution with exchange current and transfer coefficient to the polarization is often neglected. New technique with integral characteristics revealed the linkage between transfer coefficients and the ratio of cathodic and anodic exchange current densities. Physical meaning of the charge transfer coefficient is associated with symmetry of polarization curves. In Table 1, transfer coefficients are calculated with different the ratio of exchange current densities taken from the literature [5–8]. Larminie and Dicks [8] noted the following typical values for ratio of cathodic and anodic exchange current densities: $I_C/I_A \approx 10^{-5}$. Cathodic charge transfer coefficients estimated with the typical ratio in Table 1 agree with experimental cathodic transfer coefficient reported by Kim et al. [1] for 50 cm^2 PEMFC.

Modeling of transfer processes is used in fuel cell design for understanding of complex phenomena and identification of critical parameters with great impact on performance. Theoretical fuel cell models require the knowledge of parameters including anodic and cathodic charge transfer coefficients. To improve fuel cell design, there is a great need to identify, understand and predict fuel cell kinetics and transfer processes. The new technique proposes an alternative way of estimating anodic and cathodic charge transfer coefficients from fuel cell current voltage curves [9]. The estimated parameters will provide a better understanding of main phenomena governing electrochemical reactions in fuel cells.

4. Conclusions

This paper presents a new method for estimating anodic and cathodic charge transfer coefficients for a PEMFC. The method is based on analysis of integral characteristics of experimental fuel cell polarization curves. In contrast to conventional approaches, the developed method allows estimation of anodic and cathodic charge transfer coefficients simultaneously. The method is valuable in parameter estimation using PEMFC current–voltage curves. This approach can be extended in the future for exploring SOFC and DMFC.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.09.022.

References

[1] J. Kim, S.-M Lee, S. Srinivasan, Modeling of proton exchange membrane fuel cell performance with an empirical equation, J. Electrochem. Soc. 142 (1995) 2670–2674.
[2] P. Spinelli, C. Francia, E.P. Ambrosio, M. Lucariello, Semi-empirical evaluation of PEMFC electro-catalytic activity, J. Power Sources 178 (2008) 517–524.
[3] M.G. Santarelli, M.F. Torchio, P. Cochis, Parameters estimation of a PEM fuel cell polarization curve and analysis of their behavior with temperature, J. Power Sources 159 (2006) 824–835.
[4] B. Carnes, N. Djilali, Systematic parameter estimation for PEM fuel cell models, J. Power Sources 144 (2005) 83–93.
[5] C. Spiegel, PEM Fuel Cell Modeling and Simulation Using MATLAB, Elsevier Inc, New York, 2008.
[6] S. Um, C.-Y. Wang, K.S. Chen, Computational fluid dynamics modeling of proton exchange membrane fuel cells, J. Electrochem. Soc. 147 (2000) 4485–4493.
[7] N.P. Siegel, M.W. Ellis, D.J. Nelson, M.R. von Spakovsky, A two-dimensional computational model of a PEMFC with liquid water transport, J. Power Sources 128 (2004) 173–184.
[8] J. Larminie, A. Dicks, Fuel Cell Systems Explained, John Wiley & Sons Ltd, Chichester, GB, 2000.
[9] V.A. Danilov, M.O. Tade, A new technique of estimating anodic and cathodic charge transfer coefficients from SOFC polarization curves, Int. J. Hydrogen Energy 34 (2009) 6876–6881.