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Effects of catalytic activity improvement on polymer electrolyte fuel cell performance using the dimensionless cathode catalyst layer model

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Highlights

- Usefulness of the dimensionless analysis of PEFC is demonstrated.
- Improvement in catalytic activity can improve the cell performance more than the proportion.
- The dimensionless solutions make the case studies possible with no numerical simulation.

1. Introduction

Although residential polymer electrolyte fuel cells (PEFCs) and fuel cell vehicles have been commercialized, the cost reduction of the cell is strongly required for expanding its application and usage.

Protons generated in the anode are transported by the electrostatic drag through the anode catalyst layer and the proton exchange membrane (PEM) to the cathode. Electrons are generated in the anode and transported through the external circuit to the cathode. In the cathode of the PEFC, the following oxygen reduction reaction (ORR) takes place:

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O. \quad (1)$$

Since the porous electrode is employed, oxygen is transported by diffusion and convection in the gas phase from the gas diffusion layer (GDL), while protons and electrons are transported by the drag respectively in the ionomer (ion-conductive polymer) phase from the PEM and through carbon black particles used as a catalyst support from the GDL. To reduce the expensive electrocatalyst usage, improvement in the catalytic activity is being intensively studied.[1] The current authors proposed dimensionless analysis of competition between the ORR and the transports of oxygen and protons.[2, 3] In this study, how the actual current density is calculated from dimensionless general solutions and how the theoretical case studies on the activity and cell performance can be done using the dimensionless moduli we proposed.

2. Methods

The ORR rate per volume of cathode catalyst layer (CCL), r_{vc}, at a cathode electromotive force (emf) of E_c, is generally expressed, if the backward reaction is neglected, as follows:

$$r_{vc} = k_{vc}^{\oplus} \exp(-E_c / b_c)\, p_O \ [\mathrm{mol/(m^3 \cdot s)}], \quad (2)$$

where b_c is the Tafel slope, p_O is the partial pressure of O_2, and $k_{vc}^{\oplus}$ is the reaction rate constant at $E_c = 0$. The O_2 transport resistance reduces the O_2 partial pressure while the H^+ transport resistance increases the cathode emf. The H^+ transport resistance affects the reaction rate by reducing the H^+ potential and increasing the cathode emf. The Thiele modulus and our modulus are defined at the PEM–CCL boundary as follows:

$$M_{\mathrm{O}\,m}^{(\mathrm{C})} = \delta^{(\mathrm{C})} \sqrt{\frac{k_{vcm} P}{C_g D_{eO}}}, \quad M_{\mathrm{p}\,m}^{(\mathrm{C})} = \delta^{(\mathrm{C})} \sqrt{\frac{4F k_{vcm} p_{Oc}}{\sigma_{ep} b_c}}, \quad (3)$$

where $\delta^{(C)}$ is the thickness of CCL, k_{vcm} is the first-order ORR rate constant at the PEM–CCL boundary, p_{Oc} is the O_2 partial pressure at the CCL–GDL boundary, P is the total pressure, C_g is the total gas molar concentration, D_{eO} is the effective oxygen diffusivity, and σ_{ep} is the effective proton conductivity.

Profiles of dimensionless oxygen partial pressure, dimensionless cathode emf (= electron potential – proton potential), and hence dimensionless reaction rate or local current density and the effectiveness factor are governed by two dimensionless moduli defined by Eq. (3).

3. Results and discussion

The general solution of the effectiveness factor with respect to the dimensionless moduli was presented.[2, 3] It was demonstrated that the ionomer-to-carbon ratio in the CCL could be optimized in terms of the effectiveness factor on the M_{Om}–M_{pm} diagram with the effectiveness factor contours.[4] The current density at a given cell voltage can be calculated as a product of the effectiveness factor and the ORR rate expected without any transport resistances. This means the polarization curve can be estimated using the general solution without carrying out complex numerical simulations as far as the intrinsic ORR rate is known.

The current density expected with the improved catalytic activity was examined with the proposed method. If the CCL thickness was fixed, the current density did not increase proportionally to the catalytic activity as shown in Fig. 1(a), since the transport resistances relative to the activity, M_{Om} and M_{pm}, increased and hence the effectiveness factor decreased. On contrary, if the CCL thickness was changed in inverse proportion to the specific activity, the transport resistances decreased and hence the effectiveness factor increased. As a result, the current density was predicted to increase more than the proportion as shown in Fig. 1(b).

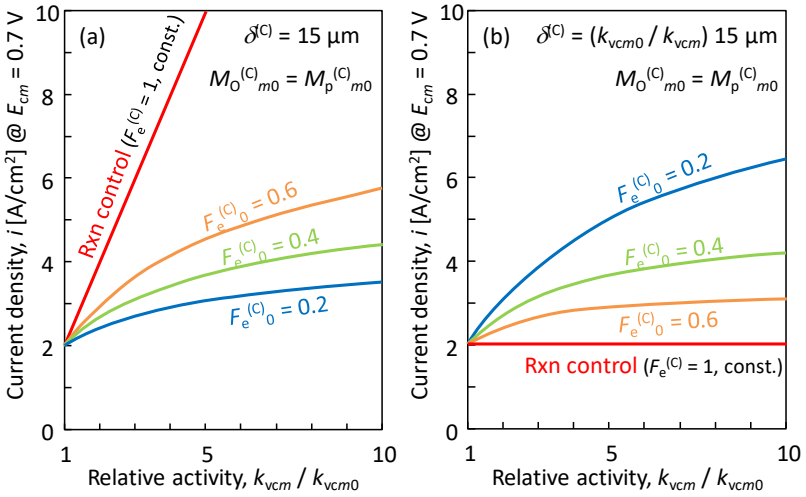

Figure 1. Effects of catalytic activity on current density, (a) Case 1: Fixed thickness, (b) Case 2: Fixed total catalytic activity.

4. Conclusions

Referring to the general solutions of the effectiveness factor with respect to two dimensionless moduli that represent the CCL properties and other two dimensionless numbers that represent the operation conditions, the actual current density can be estimated as a function of the cell voltage. It was demonstrated this method can be used effectively for carrying out case studies, for example, improvement in catalytic activity being capable to improve the cell performance more than the proportion if the CCL thickness is reduced as well.

References

[1] M. Inaba, H. Ito, H. Tsuji, T. Wada, M. Banno, H. Yamada, M. Saito, A. Tasaka, ECS Trans. 33(1), (2010) 231–238.
[2] M. Kawase, *24th Int. Symp. Chem. React. Eng.* (*Minneapolis, June, 2016*) #392.
[3] M. Kawase, K. Sato, R. Mitsui, H. Asonuma, M. Kageyama, K. Yamaguchi, G. Inoue, AIChE J. 63, (2017) 249–256.
[4] M. Kawase, K. Yamaguchi, M. Kageyama, K. Sato, G. Inoue, ECS Trans. 75(14), (2016) 147–156.

Keywords
Polymer electrolyte fuel cell, Dimensionless modeling, Oxygen reduction reaction, Catalytic activity