5th International Conference on Sustainable Energy and Environment (SEE 2014):
Science, Technology and Innovation for ASEAN Green Growth
19-21 November 2014, Bangkok, Thailand

Electrochemical oxygen reduction reaction rate in polymer electrolyte fuel cell

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Abstract:
Since optimization of the catalyst layer structure is necessary for reducing the cost of polymer electrolyte fuel cell (PEFC), formulation of the oxygen reduction reaction (ORR) rate in the cathode of PEFC is highly required for carrying out the numerical simulation for the design purpose. The ORR rate was measured with reducing the catalyst layer thickness for lowering the mass transfer resistance to oxygen, proton, and electron. Dependencies of the ORR rate on the oxygen partial pressure, relative humidity, and cell voltage were analyzed. The rate was of the first order with respect to the oxygen partial pressure up to 220 kPa. The first-order reaction rate constant was an exponential function of the cathode electromotive force. The exponent and preexponential factors were different in high and low cathode electromotive force regions. These kinetic parameters were formulated as functions of relative humidity. It was found that the exponent and preexponential factors were in strong correlation regardless of the relative humidity but depending on the cathode electromotive force region.

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1. Introduction

Polymer electrolyte fuel cell (PEFC) is being commercialized since the low-temperature operation and the daily start and stop are possible. However, further improvement in efficiency is required for cost reduction. As long as platinum is employed as cathode catalyst for reaction,

$$2\,H^+ + (1/2)O_2 + 2\,e^- \rightarrow H_2O, \tag{1}$$

optimization of the catalyst layer design is most desired for the improvement. That is why a design-purpose mathematical model of PEFC is required (Kawase, et al., 2008, Kawase, et al. 2011) and the oxygen reduction reaction (ORR) rate should be theoretically formulated (Chin, et al. 2011; Kawase, et al. 2012). Whereas ordinary chemical reaction rate is a function of concentrations and temperature, the electrochemical reaction rate is a function of concentrations, temperature, and potentials. Dependencies of the ORR rate on the oxygen partial pressure, relative humidity (RH), and operation cell voltage as well as the effects of the catalyst layer (CL) thickness were investigated in this study.

2. Material and methods

Fig. 1 shows a schematic of the apparatus employed in the study. Membrane electrode assemblies (MEAs) were composed of Nafion® NRE-211 (25.4 μm thick) membrane and catalyst layers made of Pt/ graphitized Ketjenblack® (GKB) catalyst (Pt/C weight ratio = 50 %) particles with Nafion ionomer (ionomer/carbon weight ratio = 0.9). The platinum loading was $0.12 - 0.71$ mg/cm² depending on the thickness of $3.3 - 20.0$ μm. The active area was $2\,cm \times 2\,cm$. Carbon papers (Toray TGP-H-060, 190 μm thick) were used as gas diffusion layer. These components were set in a Japan Automobile Research Institute standard cell. The cell was operated at 80°C. As shown in Fig. 1, hydrogen and oxygen (undiluted or diluted in nitrogen) were humidified and supplied to the cell at flow rates of 600 and 300 cm³/min (STP), which were high enough to attain low conversion of 0.1 at a current density of 2 A/cm². Polarization curve and high frequency resistance were measured.
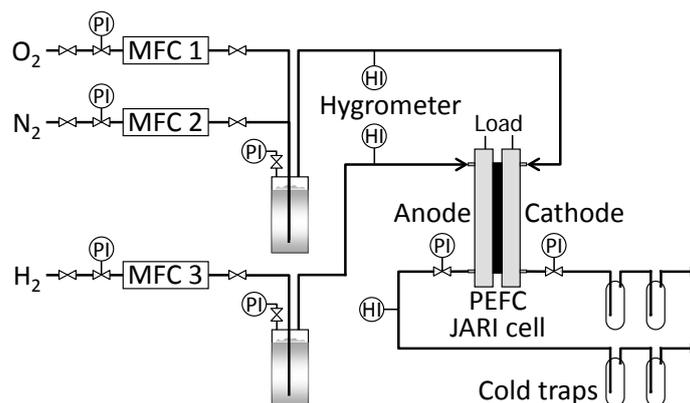
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Fig. 1 Schematic of PEFC apparatus.
(MFC: mass flow controller; PI: pressure indicator; HI: humidity indicator)

3. Results and discussion
3.1. Catalyst layer thickness

The gas-diffusion electrode is employed in PEFC. Due to the mass transfer resistance to oxygen in the gas phase, proton in the ionomer phase, and electron in the carbon phase, the gradients in the oxygen partial pressure and the proton and electron potentials are created through the catalyst layer as illustrated in Fig. 2. That is why the observed reaction rate, i.e. current density, is different from that expected from those supplied to the CL. In order to reduce the mass transfer resistance, the CL thickness was reduced and the CL thickness dependency of the current density was measured.

As shown in Fig. 3, the current density per unit Pt mass reached close to the upper limit when the CL thickness was lower than 6 μm, although the mass transfer resistance was still observed in the considerably high current region. In the following subsections, dependency of the ORR rate on the gas composition and operation cell voltage was examined basically using sufficiently thin CL with which the mass transfer resistance could be neglected.
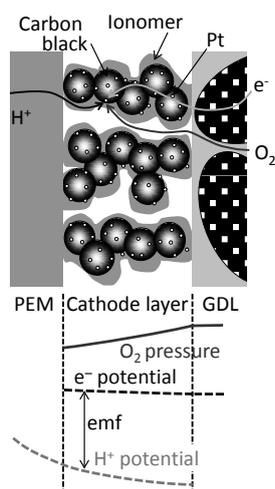

Fig. 2 Schematic of oxygen distribution and potential profiles in cathode layer. (PEM: polymer electrolyte membrane; GDL: gas diffusion layer, emf: electromotive force)
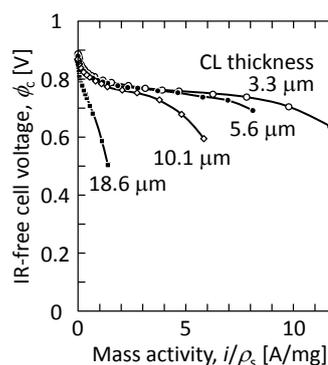
Fig. 3 Effects of catalyst layer thickness on current density per unit Pt mass (Anode gas: H_2, RH 100%; Cathode gas: O_2, RH 75%).

3.2. Oxygen partial pressure

Dependency of the ORR rate on the oxygen partial pressure was measured using 3.3 μm thick CL.

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As shown in Fig. 4, good linearity was observed between the ORR rate and the oxygen partial pressure if compared at a fixed IR-free cell voltage condition. This was also confirmed at elevated pressure. The ORR rate, $-r_{mO_2}$, was proportional to the oxygen partial pressure up to 220 kPa, i.e.

$$-r_{mO_2} = k_m \, p_{O_2}. \qquad (2)$$

3.3. Relative humidity

Fig. 5 shows the RH dependency of the ORR rate constant k_m. The ORR rate constant was the higher, the higher RH was. RH can affect the oxygen partial pressure and the moisture content of ionomer. The gas composition changes the forward and backward reaction rates and the electromotive force. The moisture content changes the proton conductivity and the oxygen permeability through ionomer. Contribution of each factor has not been elucidated yet.

Fig. 4 Dependency of ORR rate on oxygen partial pressure (CL thickness: 3.3 μm; Anode gas: H_2, RH 100%; Cathode gas: O_2/N_2, RH 75%).

3.4. Potentials

Varying the proton and electron potentials in the cathode, the energy of the reactants is altered, and hence the actual activation energy changes; the ORR rate changes. As shown in Figs. 4 and 5, lowering the IR-free cell voltage, i.e. cathode electromotive force, increases the first-order ORR rate constant k_m. k_m is an exponential function of the cathode electromotive force ϕ_c as follows:

$$k_m = A \exp(-B\phi_c). \qquad (3)$$

The slope B in Fig. 5 shows two different values in high and low cathode electromotive force regions. This is known as the double-Tafel slopes (Sepa et al. 1986, Limkeerajarus et al. 2009). At high potential, the platinum surface is oxidized and hence the catalytic activity is different from that of platinum.

The results in Fig. 5 show the preexponential factor A and exponent factor B in Eq. (3) depend on RH. In the low cathode electromotive force region, i.e. over platinum, the potential dependency of the ORR rate constant was stronger in case of higher RH. On the other hand, the potential dependency of the ORR rate constant was weaker in case of high RH in the high potential region, i.e. over platinum oxide.
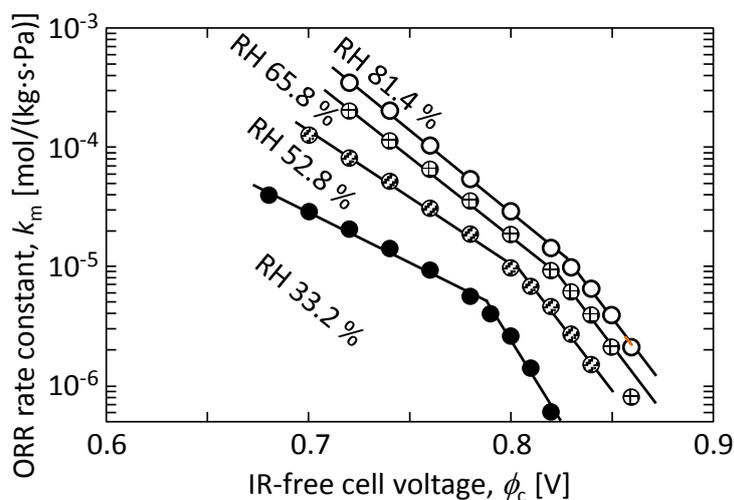

Fig. 5 RH and potential dependency of ORR rate constant (CL thickness 8.7 μm; Anode gas RH = cathode gas RH).
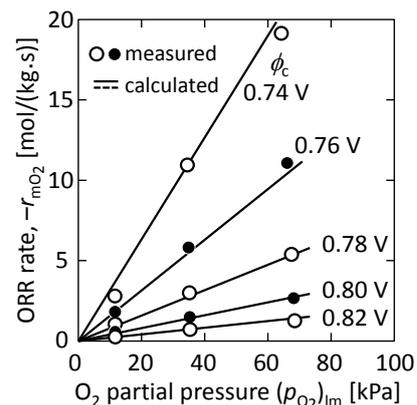
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The values of *A* and *B* are plotted against RH in Fig. 6. Although it is difficult to predict the effects of RH theoretically, the values of *A* and *B* can be known in Fig. 6 when RH is specified. Furthermore, it was found in the present study that the preexponential factor *A* and exponent factor *B* were in strong correlation. It was formulated as follows:

$$A = \begin{cases} 3.01 \times 10^4 \, \text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \, \exp(0.541 \, \text{V} \, B) & (\text{high} \, \phi_c) \\ 1.96 \times 10^{-4} \, \text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \, \exp(0.952 \, \text{V} \, B) & (\text{low} \, \phi_c) \end{cases}. \quad (4)$$

The two correlation equations were determined in the electromotive force regions above and below the crossing point of two trendlines in Fig. 5.
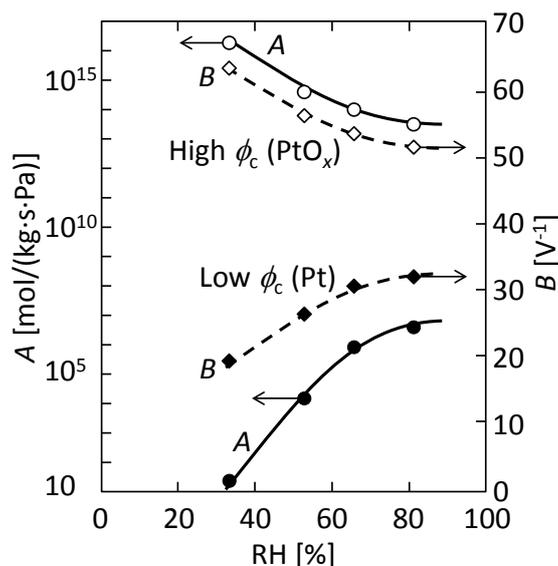

Fig. 6 Effects of RH on exponent and preexponential factors of potential dependency of ORR rate.

4. Conclusion

The ORR rate was analyzed with varying the CL thickness, oxygen partial pressure, RH, and operation cell voltage. The mass transfer resistance could be virtually neglected if the CL thickness was less than 6 μm. The intrinsic ORR rate was of the first order with respect to the oxygen partial pressure. The first-order reaction rate constant was the exponential function of the cathode electromotive force. The exponent and preexponential factors were different in the high and low cathode electromotive force regions. The crossing point was located around the IR-free cell voltage of 0.8 V. This can be explained by the surface oxidation of platinum. The RH dependencies of the exponent and preexponential factors were also measured. Strong correlation between these two parameters was observed. The preexponential factor was found to be an exponential function of the exponent factor.

5. Acknowledgement

6. References

Chin, S.T., Kawashima, S., Kageyama, M., Kawase, M., and Miura, K. 2011. Analysis of the oxygen reduction reaction of a PEFC. In Abstracts for 6th APCRE Symposium, paper ID A-5. Beijing: Asian-Pacific Chemical Reaction Engineering Working Party.

Kawase, M., Chin, S.T., Kageyama, M., and Miura, K. 2011 Meeting Abstracts, 220th ECS Meeting, 11th Polymer Electrolyte Fuel Cells, Abs#1209. Boston, Electrochemical Society.

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Kawase, M., Inagaki, T., and Miura, K. 2008. Nonisothermal through-plane transport model of PEMFC with local VLE assumption. ECS Transactions 16(2): 563–573.

Kawase, M., Inoue, G., Chin, S.T., and Kageyama, M. 2012. Dependency of oxygen reduction reaction rate on cathode potential in a polymer electrolyte fuel cell. Abstracts of 22nd Int. Symp. Chem. React. Eng., Abs#482. Maastricht: European Federation of Chemical Engineering.

Limkeerajarus, N., Yanagimoto, T., Yamamoto, T., Ohashi, H., Ito, T., and Yamaguchi, T. 2009. J. Chem. Eng. Japan 42: 39–46.

Sepa, D.B., Vojnovic, M.V., Vracar, L.M., and Damjanovic, A. 1986. Apparent enthalpies of activation of electrodic oxygen reduction at platinum in different current density regions—I. Acid solution. Electrochim. Acta 31: 91–96.