

# ELECTROCHEMICAL REACTION ENGINEERING OF POLYMER ELECTROLYTE FUEL CELL

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## *Abstract*

Although the fuel cell is a sort of reactor, the methods of kinetic analysis and reactor modeling from viewpoint of chemical reaction engineering have not been established yet. The rate of electrochemical reactions is a function of concentrations, temperature, and interfacial potential difference. The dependency of the reaction rate on these factors has to be formulated. The cathode reaction in which oxygen and proton react over platinum in the catalyst layer of polymer electrolyte fuel cell was investigated. Dependencies of the oxygen reduction reaction rate on the oxygen partial pressure and the cathode electromotive force were formulated. Resistance to proton transport decreases proton potential, lowering the electromotive force, and hence reducing reaction rate. The effectiveness factor of the cathode catalyst layer is determined by competition between reaction and mass transfer of oxygen and proton. Two dimensionless moduli which govern the cathode behavior are proposed for depicting the situation.

## *Keywords*

Polymer electrolyte fuel cell, Modeling, Electromotive force.

## **Introduction**

Polymer electrolyte fuel cell (PEFC) has been commercialized owing to the low-temperature operation and daily start and stop capability. However, further improvement in efficiency is required for cost reduction. The largest part of cost is ascribed to catalyst platinum.

Rate of ordinary chemical reactions is a function only of concentrations and temperature; the rate of electrochemical reaction is a function of them and interfacial potential difference (electromotive force, emf). Although it makes the modeling complicated, the emf is, from the viewpoint of chemical reaction engineers, an unprecedented intrinsic parameter which can control the rate.

A design-purpose model of PEFC is required for optimization of the catalyst layer (CL) design (Kawase *et al.*, 2008). Since the gas-diffusion electrode is employed in PEFC, the O<sub>2</sub> pressure and the H<sup>+</sup> potential distributions

are determined by resistance to O<sub>2</sub> transport in pores and resistance to H<sup>+</sup> transport in ionomer. In order to characterize variety of CL structure and difference in operation conditions quantitatively, the author proposes two dimensionless moduli governing the cathode behavior.

## **Experimental**

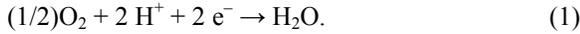
The kinetic data were measured using a single fuel cell. A Nafion® NRE-211 membrane and catalyst layers made of Pt/graphitized Ketjenblack® catalyst (Pt/C weight ratio = 0.5) with Nafion ionomer (ionomer/carbon weight ratio = 0.9) were installed. The active area was 2 cm × 2 cm. Carbon papers (Toray TGP-H-060) were used as gas diffusion layer (GDL). The cell was operated at 80 °C. H<sub>2</sub> and O<sub>2</sub> (undiluted or diluted in nitrogen) were humidified and supplied to the cell at flow rates high enough to attain low conversion of 0.1 at a current density of 2 A/cm<sup>2</sup>.

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## Experimental Results

The rate of the following oxygen reduction reaction (ORR) was measured in the polarization curve:



The mass transfer resistance could be eliminated if the CL thinner than 6  $\mu\text{m}$  (Chin *et al.*, 2011). The ORR rate was proportional to the oxygen partial pressure up to 220 kPa if compared at a fixed cathode emf (Nagayoshi *et al.*, 2013). The first-order ORR rate constant  $k_{\text{m,ORR}}$  was an exponential function of the cathode emf  $E_c$  (Kawase *et al.*, 2014). The two parameters depended on relative humidity.

## Theoretical Model

To predict the distribution of ORR rate in the CL, distribution of  $\text{O}_2$  and cathode emf are required. Mass balance equations lead to the following dimensionless fundamental equations:

$$\frac{d}{d\zeta} \left( \frac{1}{1+y_0} \frac{dy_0}{d\zeta} - S_0^{(C)} \frac{y_0}{1+y_0} \right) - M_0^2 y_0 = 0 \quad (2)$$

$$d\varepsilon_c / d\zeta = \{A_p / (1+y_0)\} (S_0^{(C)} y_0 - dy_0 / d\zeta) + \Omega^{(C)} \quad (3)$$

$$M_0^{(C)} = \delta^{(C)} \sqrt{\frac{\rho_b k_{\text{m,ORR}}(E_c, \text{RH}, T) P_1}{C_g D_{\text{eO}}}}, \quad A_p = \frac{4FC_g D_{\text{eO}}}{\sigma_{\text{ep}} E_{\text{cm}}} \quad (4)$$

where  $\zeta$  is the location,  $y_0$  is the  $\text{O}_2$  fraction,  $\varepsilon_c$  is the dimensionless cathode emf,  $\rho_b$  is the Pt packing density,  $D_{\text{eO}}$  is the effective  $\text{O}_2$  diffusivity, and  $\sigma_{\text{ep}}$  is the effective  $\text{H}^+$  conductivity. Two moduli  $M_0^{(C)}$  and  $A_p$  are important, while the effects of  $S_0^{(C)}$  and  $\Omega^{(C)}$  are not significant.

## Dimensionless Model Analysis

$M_0^{(C)}$  is a Thiele modulus representing ratio of reaction to  $\text{O}_2$  transfer.  $A_p$  is the ratio of  $\text{O}_2$  transfer to  $\text{H}^+$  transfer. When  $\text{H}^+$  transfer is fast (low  $A_p$ ) reaction takes place near the GDL, and vice versa, as shown in Fig. 1.

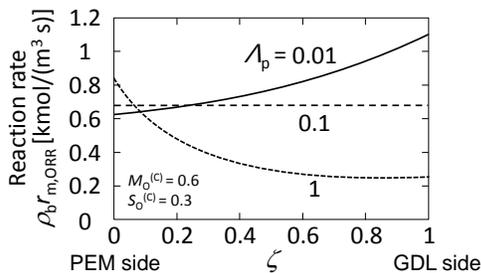


Figure 1.  $A_p$  determines where reaction occurs

At a fixed  $A_p$ , the effectiveness factor, defined as the ratio of the observed rate to the intrinsic rate without mass transfer resistance, is determined by  $M_0$  as shown in Fig. 2. When  $M_0$  is high, i.e. fast reaction, the effectiveness factor is low. Typical effectiveness factor is estimated 0.6 at the

present. Reduction in  $M_0$  is advised for improving the efficiency.

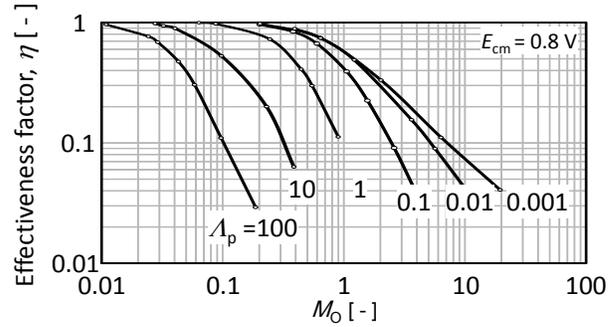


Figure 2. Effectiveness factor determined by  $M_0$  and  $A_p$

The behavior of the PEFC cathode is mostly governed by competition of  $\text{O}_2$  transfer,  $\text{H}^+$  transfer, and catalytic reaction as shown in Fig. 3.

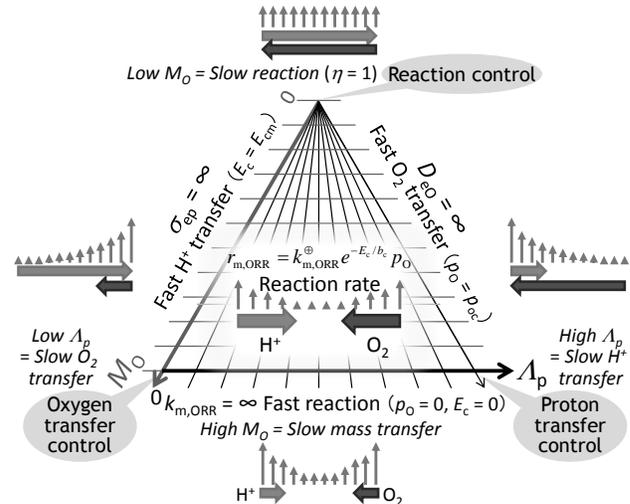


Figure 3. Three processes which govern cathode behavior

## Conclusions

The ORR rate was analyzed and chemical reaction engineering model was built. The reaction competes with mass transfer incoming from opposite two directions. Model analysis demonstrated that their interplay can be quantitatively described by the dimensionless moduli,  $M_0$  and  $A_p$ . CRE is useful even for electrochemical reactions.

## References

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