Analysis of Platinum Particle-size Effect on Performance of PEFCs Using Modeling Approach

Nonthi Cherdsanguan[1], Sawanya Suwannawong[1] Vissanu Meeyoo[2] and Nuttapol Limjeerajarus[1,*]

[1] Department of Automotive Engineering, Faculty of Engineering, Thai-Nichi Institute of Technology
1771/1 Pattanakarn, Suan Luang, Bangkok 10250, Thailand
[2] Department of Chemical Engineering, Faculty of Engineering, Mahanakorn University of Technology
140 Cheum-Sampan, Nong Chok, Bangkok 10530, Thailand
*nuttapol@tni.ac.th

Abstract

The high production cost and low performance at high potentials are the major barriers preventing Polymer Electrolyte Fuel Cells (PEFCs) from wide-scale use. Many researches have been carried out in order to overcome those barriers. For example, the effect of platinum particle size on catalyst oxygen reduction reaction (ORR) activity that is a very popular issue in electrochemistry. In previous studies, there were contradictory conclusions whether the Pt particle-size affects the ORR activity or not. Nevertheless, the recent studies showed that no Pt particle-size effect on ORR activity was observed. In this study a modeling approach, which is inexpensive and less time-consuming as compared with the experimental approach was employed to verify the result of Pt particle-size effect. The model was developed based on cylindrical secondary pore structure of the catalyst layers for gas-phase PEFC Membrane Electrode Assemblies (MEAs). The simulation was carried out with the assumption that ORR activity was identical, regardless of Pt particle size. The simulation results coincided well with experimental results for the Pt particle sizes of 2–8 nm. Thus, it implied that the model was successfully developed to verify the results in previous studies that there was no Pt particle-size effect on ORR activity of gas-phase PEFC MEAs.

Keywords*:* PEFCs; ORR activity; Modeling; Pt particle-size.

1. Introduction

Since Polymer Electrolyte Fuel Cells (PEFCs) have major advantages in high energy efficiency and low pollution emissions, they are considered as one of the most promising renewable energy technologies for future power generation. However, to apply PEFCs in wide-scale use, problems on their performance and production cost still needs to be improved. There are various ways to overcome these problems like improving metal catalyst. The selection of catalyst is one of the most important issues, which leads to increase the reaction rate and to reduce the cost of PEFCs. The understanding on the effect of particle size of platinum (Pt) catalyst in oxygen reduction reaction (ORR)

activity would be useful for identifying an optimal Pt particle size, which provides high efficiency at low production cost.

However, contradictory conclusions were reported in previous studies. The first conclusion indicated that ORR activity decreased as the Pt particle size is decreased [1-2], whereas the second conclusion indicated that the optimum value of Pt particle size was in the range of 2-5 nm for the best value of ORR activity [3]. Nevertheless, the recent studies carried out under liquid-phase systems by Yano et al. [4] and gas-phase systems by Limjeerajarus et al. [5] showed the other conclusion which is no Pt particle-size effect on catalyst ORR activity.

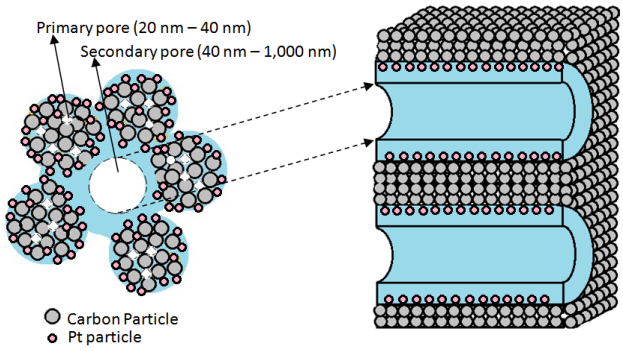
By using electrochemical nuclear magnetic resonance (EC-NMR) spectroscop, Yano et al.[4] concluded that there is an insignificant difference in the electronic properties of the surface of Pt/C catalysts due to the variation of Pt particle size ranging from 1 to 5 nm. Consequently, the ORR activities are not affected by the Pt particle size.

Moreover, according to the work by Limjeerajarus et al.[5], experimental results of Pt particle size of 2-8 nm can be demonstrated that ORR activity was constant at each cell temperature of 25 - 80^{o}C and irrespective of the Pt particle size. This can also be implied that there was no change in the ORR activity due to the Pt particle size variation.

To clarify this contradiction, the use of experimental approaches is time-consuming and costly. Thus, in this study, a modeling approach, which is less-time consuming and inexpensive, has been employed so as to investigate the effect of Pt particle size on catalyst ORR activity under gas-phase conditions.

2. Model Description

As stated in previous section, this work has studied the effect of Pt particle size on ORR activity by modeling approach, thus the present model was focused on catalyst layers at which the electrochemical reactions occurred. The catalyst layers have three main components; noble metal (normally refers to Pt), carbon particles, and the polymer electrolyte. Fig. 1a represents the major structures of catalyst layers like primary pores and secondary pores. A primary pore, which has a dimension of about 20 - 40 nm, is the gap surrounded by each carbon particle. A Secondary pore is the gap surrounded by agglomeration of carbon particles, which has a wide range of pore sizes between 40 – 1000 nm.



(a) (b)

Fig. 1 Schematic illustration of the structural model considered in (a) the typical model and (b) the cylindrical secondary pore model.

This study has improved the previous model developed by Limjeerajarus et al. [6] which was developed based on cylindrical secondary pore structure, as shown in Fig. 1b. The model was considered as one-dimensional (sandwich) model in which reaction and

transports can be clearly investigated, especially in catalyst layers.

2.1 Model assumptions

As presented in Fig. 2, the major assumptions of model are described below.

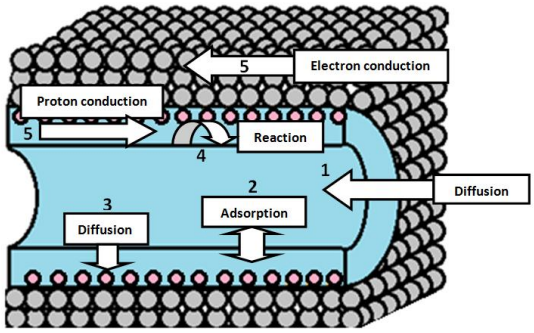


Fig. 2 Schematic illustration of the structural model of the physic-electrochemical phenomena considered in the cylindrical secondary pore model.

- Diffusion and reaction phenomena in primary pores inside catalyst agglomerate are not taken into account since these phenomena in primary pores are more limited than those in secondary pores [6].
- The developed model is based on cylindrical secondary pore structure. According to previous assumption, utilizable Pt particles are assumed to exist only at the surface of secondary pores, thus, cylindrical structure can be applied in this model.
- The model is considered in gas phase, which is the practical condition of PEFCs.
- The temperature distribution across the layers in sandwich one-dimensional model is basically uniform (around 1°C). Thus, isothermal assumption is valid and applied in this study.

2.2 Model equations

The overall transport and reaction phenomena taken place in secondary pores inside catalyst layers can be derived as the model equations referred to previous study[6] described as 5 processes.

2.2.1 Gas diffusion into secondary pores inside catalyst layers, which can be described by Fick's law. The reactant gas concentration C_i in a secondary pore is governed by mass balance equation as follow:

$$\pi r_{\text{pore}}^2 \frac{\partial J_i}{\partial x} + \pi r_{\text{pore}}^2 \frac{\partial J C_i}{\partial t} = \frac{U_{\text{Pt}} \cdot S \cdot A_s}{N_{\text{pore}}} \cdot \frac{v(x)}{zF} \qquad (1)$$

where J_i is the reactant gas flux of species i diffusing in a secondary pore (mol/m^2.s), C_i is the reactant gas concentration of species i in a secondary pore (mol/m^3). x is the thickness of catalyst layer. r_{pore} represents radius of a secondary pore. A_s is the specific surface area of Pt (m^2/g). U_{Pt} stands for Pt utilization measured by cyclic voltammetry. N_{pore} and S stand for number of secondary pores within one layer of secondary particles and Pt loading, respectively. v is the reaction rate (A/m^2). z refers to number of electrons transferred per reaction. F is Faraday's constant.

2.2.2 Adsorption of the diffused gasses (i.e. H_2, O_2, H_2O) onto electrolyte at the gas electrolyte film interface, which can be expressed by Henry's law.

2.2.3 The adsorbed gases diffuse into proton-conducting polymer described by Fick's law.

2.2.4 Electrochemical reaction phenomena on the surface of Pt particle at three-phase boundary described by Tafel equation. Diffusion fluxes in process 2.2.3 are assumed to be completely consumed by reaction. Thus, diffusion fluxes of dissolved gases in the earlier

process are equal to the fluxes of gases used in electrochemical reaction, the mass balance equation in the polymer phase can be expressed as follow:

$$2\pi r_{\text{pore}} \frac{D_{\text{i}}^{\text{poly}}}{l^{\text{poly}}} \left[C_{\text{i}}^{\text{poly0}}(x) - C_{\text{i}}^{\text{polyL}}(x)\right] = \frac{U_{\text{Pt}} \cdot S \cdot A_{\text{s}}}{N_{\text{pore}}} \cdot \frac{v(x)}{zF} \quad (2)$$

$$v(x) = i_{0,\text{Pt}} \frac{C_{\text{O}_2}^{\text{polyL}}}{C_{\text{ref}}} \exp\left(\frac{\alpha F}{RT} \eta_{\text{act}}(\text{x})\right) \quad (3)$$

where l_{poly} is the thickness of polymer. $i_{0,\text{Pt}}$ and α represent the ORR activity per unit active Pt surface area (A/cm^2-Pt) and charge transfer coefficient, respectively. $C_{\text{O}_2}^{\text{polyL}}$ is oxygen concentration at interface between electrolyte and Pt particle surface at three-phase boundary and C_{ref} is the reference of oxygen concentration.

2.2.5 The migrations of protons in the polymer and electrons in the carbon are described by Ohm's law.

Note that other details of the model and parameters can be found in the previous study [6, 7].

3. Simulation

The model was developed by using an implicit method on Microsoft Visual C++ has three sub-models, i.e. cathode, anode, and electrolyte membrane. To clarify the effect of Pt particle size, the structural parameters, which depend on Pt particle size, were varied according to experimental results obtained in previous study [5] at a cell temperature of 60°C, as presented in Table 1. Afterward, the cell performance curves were predicted from model and the simulation results were compared with the experimental results.

Table. 1 Structural and reaction parameters obtained from experiment in previous study [5]

Parameters \ Pt size (nm)	2.1	4.5	7.9
Structural Parameters			
Pt catalyst loading (*S*), mg/cm^2-electrode	0.41	0.41	0.49
Specific surface area (A_{s}), m^2-Pt/g-Pt	132.2	75.9	55.4
Pt/C mass ratio of the catalyst (*m*), wt%	46.5	50.6	70.1
Electrochemical surface area (*ESA*), cm^2-Pt/cm^2-electrode	227	132	129
Reaction Parameter			
$i_{0,\text{Pt}}$, μA/cm^2-Pt	2.6	2.6	2.6

4. Results and discussion

4.1 Model validation

The validation of the model was carried out by comparing the results of I-V performance curves obtained from simulations with those obtained from experiments in our previous study [5]. As presented in Fig. 3a-3c, the simulation results coincided with experimental results for all Pt particle sizes, i.e. 2.1 nm, 4.5 nm, and 7.9 nm. These correspondences can verify that there was no Pt particle-size effect on catalyst ORR activity, since the ORR activity ($i_{0,\text{Pt}}$) of each Pt particle size used in the simulations is identical (equals to 2.6x10^{-6} A/cm^2-Pt, see Table 1.)

Considering the comparison of I-V cell performance curve in Fig. 3a-3c, the developed model can satisfactorily predict the PEFC performance curve. However, in the case of 7.9

nm, there were slight discrepancy between the simulation and experimental results (Fig. 3C) in high potential region (above 0.7 V) and low potential region (below 0.7 V) which may be caused by two assumptions.

Firstly, the discrepancy at high potentials may be caused by the error of experimental results of 7.9 nm, whereas the cell performances obtained from experiment of 2.1 nm and 4.5 nm are clearly coincide with those obtained from simulation (Fig. 3a-3b).

Secondly, the discrepancy in low potential region could be explained by the effect of secondary pore size, r_{pore}. Since r_{pore} can be derived by Eq. (4)

$$N_{\text{pore}} = \varepsilon_{\text{CL}} \left(\frac{10^{-4}}{\pi r_{\text{pore}}^2} \right) \tag{4}$$

where ε_{CL} is the porosity of the catalyst layer.

By considering Eq. (2) and (4), the reaction rate, v, will decrease as the reaction site (number of pore) decreases, which occurs when pore size is larger. The decrease in reaction rate results in the rapid drop of potential in the low potential region.

To verify this assumption, the secondary pore size was reasonably assumed to be increased with increasing Pt particle size by considering the model's structure. The I-V cell performance curves for Pt particle size of 7.9 nm were plotted by varying secondary pore sizes from 100 nm to 200 nm.

As expected, the results of I-V performance curve show more correspondence with increasing r_{pore} as shown in Fig. 4.

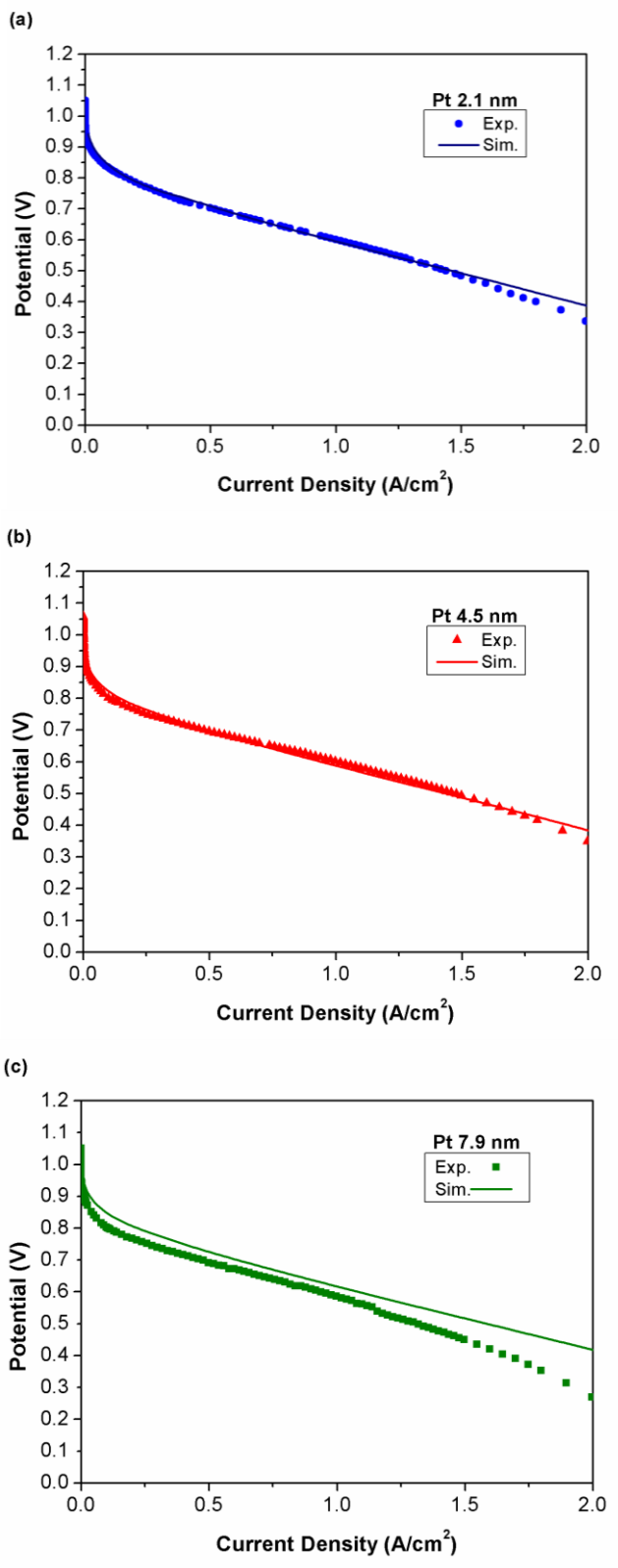


Fig. 3 Comparison of I-V cell performance curve obtained from simulations and experiment for Pt particle sizes of (a) 2.1 nm, (b) 4.5 nm, and (c) 7.9 nm.

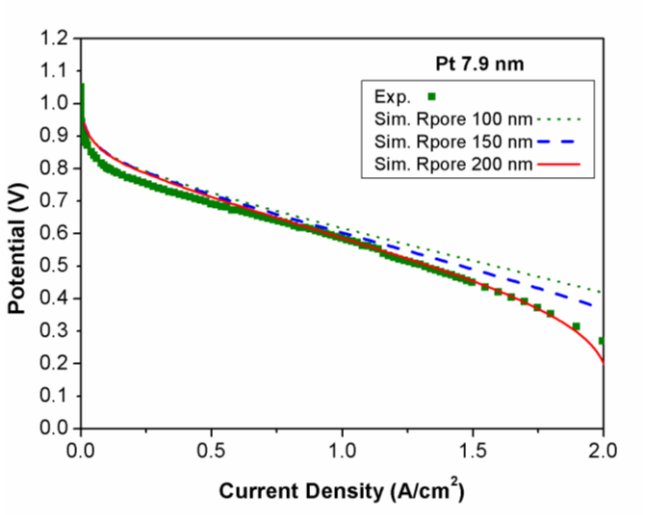


Fig. 4 Comparison of I-V cell performance curve obtained from experiment and simulations for Pt particle size of 7.9 nm, with secondary pore size of 100 nm, 150 nm and 200 nm.

However, due to limitation of experiment results used in developing the model, the secondary pore size of 2.1-nm-Pt catalyst (100 nm) was used and assumed to be constant for all other Pt sizes in the simulations. This was the reason why the discrepancy existed in the low potential region. This explanation shows that in fact, the secondary pore size used in the simulations should be different for each Pt particle size. Thus, to archive more accurate result, the structural parameters like secondary pore size used in the simulation need to be collected correctly in the future work.

5. Conclusion

In this study, the simulation model that can predict cell performance of PEFC MEAs, which consists of different Pt particle sizes in the range of 2-8 nm, has been successfully developed. More importantly, the effect of Pt particle size on catalyst ORR activity was verified using the developed model by which no Pt particle-size effect was observed. The result obtained by modeling approach in this study concurs with that obtained by experimental approaches reported in previous study[5].

6. Acknowledgement

The authors are grateful for the financial support provided by the Thailand Research Fund (TRF) and Thai-Nichi Institute of Technology (TRG 5380009).

7. References

[1] Bregoli, L. J. (1987). The influence of Platinum Crystallite Size on the Electrochemical Reduction of Oxygen in Phosphoric Acid. in *Electrochem. Acta.,* 23 (6), pp.489-492.

[2] Antoine, O.; Bultel, Y.; Durand, R. (2001). Oxygen Reduction Reaction Kinetics and Mechanism on Platinum Nanoparticles inside Nafion®. in *J. Electrochem.*, 499 (1), pp. 85-94.

[3] Antolini, E.; Salgado, J. R. C.; Giz, M. J.; Gonzalez, E. R. (2005). Effect of Geometric and Eletronic Factors on ORR Activity of Carbon Supported Pt-Co Electrocatalysis in PEM Fuel Cells. *Int. J. Hydrogen Energy*, 30(11), pp.1213-1220.

[4] Yano, H., et al. (2006) Particle-size Effect of Nanoscale Platinum Catalysts in Oxygen Reduction Reaction: an Electrochemical and ^{195}Pt EC-NMR Study. in *Phys. Chem. Chem. Phys.*, 8(42), pp. 4932-4939.

[5] Limjeerajarus, N., Yamaguchi, T. (2010). Effect of Platinum Size on Catalyst Activity in Practical Gas-Phase PEFCs MEAs. in *Proceedings of the ASME 8th International Fuel Cell Science, Engineering, and Technology,* 1–4 (Fuel Cell2010–33076).

[6] Limjeerajarus, N.;Nishiyama, Y.;Ohashi, H.;Ito, T.;Yamaguchi, T. (2009). Modeling for PEFCs MEAs Based on Reaction Rate on Pt Surface and Microstructures of Catalyst Layers. In *J. Chem. Eng. Jpn*., 42(8), pp.616-631.

[7] Limjeerajarus N.; Yanagimoto T., Ohashi H., Ito T., Yamaguchi T. (2009). Polymer Electrolyte Fuel Cell Modeling Considering Catalyst Activity and a Microscopic Reaction Phenomenon: Coverage of Oxygen-Containing Species, *J. Chem. Eng. Japan*, 42(10), 771-781