New Proposal of Evaluation Method for DMFC Catalyst Layers by Means of Electrochemical Impedance Spectroscopy

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On the evaluation of catalyst layers in direct methanol fuel cell (DMFC), we applied the proposed electrochemical cell which enabled to evaluate the catalyst layers without an electrolyte solution circumstance. In addition, properties of polymer electrolytes, such as ionic conductivities inside or outside agglomerates of catalystss were evaluated separately by electrochemical impedance spectroscopy with an analysis using the proposed equivalent circuit. This method also suggested its possibility for evaluating a distribution of the electrolytes in catalyst layers.

In fuel cell operations, the three phases of reactant-and-product-transfer phase, ion-transfer phase, and electron-transfer phase are necessary to proceed the smooth electrochemical reaction on the catalysts. In the conventional catalyst layer of the direct methanol fuel cell (DMFC) consisting of Pt supported on carbon (Pt/C) particles and Nafion, as catalysts and binder respectively, some parts of catalysts do not exist in the finely formed three-phase-boundary. One reason of that is related to structure of the catalyst layer, such as pores and agglomerates. The pores can be classified into two types: primary pores are those inside the agglomerates of Pt/C particles, and secondary pores are those between the agglomerates.[1] Uchida et al. reported that Nafion clusters, the ion-transfer phase, mainly exist in the secondary pores; therefore, the three-phase-boundary is sufficiently formed at the wall of the secondary pores, while hardly formed in the primary pores.[1–3]

To improve the three-phase-boundary conditions, evaluations of them are important. When we focus on several evaluation researches on the catalyst layer,[4,5] we could classify three major types: first, the evaluation of whole membrane electrode assembly (MEA), second, the evaluation of each electrode of MEA with a pseudo reference electrode,[6,7] and third, the evaluation with a conventional three-electrode cell, which constitutes three electrodes soaked in an electrolyte solution.[8] All evaluation systems previously reported cannot or hardly have a benefit to evaluate the polymer electrolyte in the catalyst layer independently of the operation conditions.

Here, we propose the revolutionary evaluation method, which is never reported before, and apply this evaluation method to the DMFC studied.[9] This electrochemical evaluation method for catalyst layers independently offers the information on effects of polymer electrolyte in the catalyst layer of fuel cell. It is an effective method to obtain the information of useful guideline to improve the catalyst layer of DMFC; namely, the factors of precious metal catalyst efficiency and current–voltage characteristics are easily and/or independently evaluated. Specifically, the purpose of this method was to evaluate the catalyst layer in similar condition to DMFC operation. Especially, we evaluated polymer electrolyte properties in the catalyst layer, such as ionic resistivity of the primary pores as well as the secondary pores.

This method is composed of the cell shown in the Figure 1 with half membrane and electrode assembly (half-MEA) and the analysis using electrochemical impedance spectroscopy (EIS). The cell enables to evaluate the catalyst layer in a solution having no ionic conductivity; hence, only the catalyst particles having ionic path through the polymer electrolyte phase formed in the catalyst layer to Nafion membrane can contribute to the reaction and be evaluated. In addition, EIS enable to separately evaluate the electrochemical reaction parameters.[10] In this paper, we evaluated catalyst layers in aqueous methanol solutions with or without 0.5 M H_2SO_4. Additionally, catalyst layers with or without polymer electrolyte were compared to clarify the effects of polymer electrolyte in catalyst layer.

Half-MEAs were prepared as follows. A catalyst layer with polymer electrolyte (Nafion) was prepared by spreading catalyst paste, which is a mixture of Pt/C (47 wt %-Pt, Tanaka Kikinzoku) and Nafion solution (5 wt %, Sigma Aldrich) in 1,2-dimethoxyethane, onto a carbon paper (Toray). The catalyst layer with composition of 80 wt % Pt/C and 20 wt % Nafion was assembled with Nafion 112 (DuPont) by hotpress (135 °C) after drying in N_2 atmosphere (130 °C, 30 min.). A catalyst layer without polymer electrolyte was also prepared by applying PVdF-HFP (10%-HFP) instead of Nafion as a binder. The preparation procedure was almost the same as the one using Nafion, while the catalyst layer was not hot-pressed with Nafion 112 to prevent pores from squash; alternatively, the catalyst layer was mechanically attached to Nafion 112.

As shown in Figure 1, two compartments of the cell were separated by Nafion membrane. The carbon paper of the working electrode was attached to current collector (Au mesh) in the compartment 1. Reference and counter electrodes were set in the compartment 2 filled with 0.5 M H_2SO_4. While similar cells have sometimes been used for evaluation of the cathodic gas-phase reaction,[11] no application to the anodic liquid-phase reaction of the DMFC was reported so far. Moreover, our purpose is clarifying the effects of electrolytes involved in the catalyst

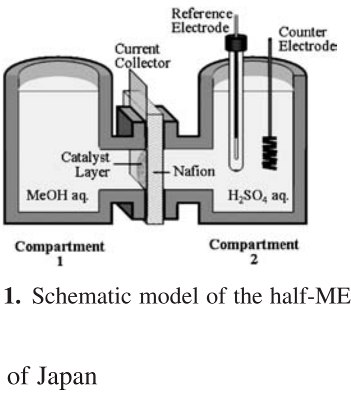

Figure 1. Schematic model of the half-MEA cell.

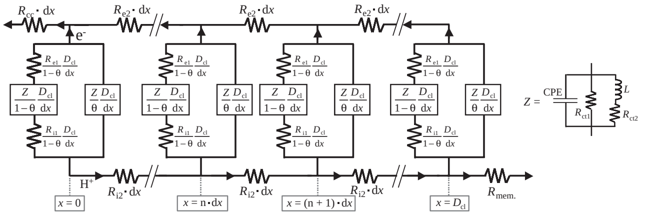

Figure 2. Equivalent circuit based on transmission line for the DMFC catalyst layer.

layer, thus, different from those literatures.

The catalyst layers of half-MEAs were evaluated by EIS (10 k to 10 mHz, 0.4 V vs Ag/AgCl) with 1 M methanol solution containing 0 or 0.5 M H_2SO_4 in compartment 1, with PARSTAT 2263 (Prinston Applied Research). The permeation of H_2SO_4 through Nafion membrane[12] was confirmed to hardly influence the results in the time range of these experiments.

The EIS results were analyzed with the equivalent circuit shown in Figure 2. This circuit was postulated to express the multistep reaction of methanol oxidation proposed by Müller.[13] In addition, this circuit was based on the transmission line to represent the thickness of catalyst layer D_{cl}. The significance of the circuit is to assume individual ionic resistivity of each primary and secondary pores and parallel reactions in those pores. The equivalent circuit includes methanol oxidation reaction impedance Z, ionic resistances R_i, electron conducting resistances R_e, and a factor of current distribution ratio θ. Z consists of a methanol dehydrogenation reaction resistance R_{ct1}, an electric double layer capacitance C_{dl}, an intermediate-oxygenation resistance R_{ct2} (for CO_{ad}), a pseudo inductance L representing the oxidation of the adsorbing intermediates.[10,13,14] R_i's are categorized as a resistance to primary pores R_{i1}, a resistivity to secondary pores R_{i2} and a solution resistance R_{sol} (the sum of Nafion 112 and 0.5 M H_2SO_4 in component 2). R_e's are categorized as resistances to primary pores R_{e1}, secondary pores R_{e2}, and current collector R_{cc}. These R_e's are assumed to be negligible in this study.[15] A time constant τ of Z is probable to be distributed because of the high surface roughness of the catalyst layers, inhomogeneities of reaction rates, electric double layer capacitance, and so on; hence, the distribution of τ is able to be represented with general method using a constant phase element (CPE), that is defined as $C_{dl}(j\omega)^{\beta}$, while ω is an angular frequency, j is imaginary unit, and β $(0 < \beta < 1)$. If the distribution of τ is sharp, CPE is consistent with C_{dl} $(\beta = 1)$.

The remarkable difference among the results of EIS for the catalyst layers with different electrolyte was obtained as shown in Figure 3. In the low frequency region of Figure 3a, all the diagrams had another arc below Z_{Re} axis, which is originated from the oxidation of the intermediate.[5]

To analyze the results, the diagrams were applied for curve fitting, and the fitting results obtained for methanol oxidation without H_2SO_4 were shown in Figure 3. Almost all the plots showed good fits, and the parameters estimated by fitting are summarized in Table 1. From the results, ionic resistances in both primary and secondary pores were able to be evaluated separately. The results shown in Table 1 indicate that the addition of H_2SO_4 or using Nafion as binder could effectively reduce R_{i1} and R_{i2}. As for β, the additions of H_2SO_4 increased β for the catalyst layer both with Nafion and PVdF-HFP. This result indicated that the ionic circumstances surrounding catalysts, such as ionic concentration and pH, might be different especially without H_2SO_4. Such a difference suggested that the polymer electrolyte does not distribute uniformly in the catalyst layer.

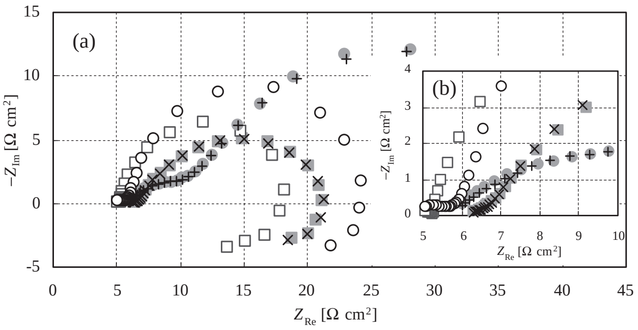

Figure 3. Complex-plane impedance diagram of methanol oxidation on catalyst layers including different electrolytes, Nafion as binder ■: without (×: fitting plots) and □: with 0.5 M H_2SO_4 in compartment 1, PVdF-HFP as binder ●: without (+: fitting plots) and ○: with 0.5 M H_2SO_4. (a) Overall diagram, (b) high frequency region.

Table 1. Fitting parameters of impedance diagram in Figure 3

	Nafion		PVdF-HFP	
	without H_2SO_4	with H_2SO_4	without H_2SO_4	with H_2SO_4
R_{sol} [Ω cm²]	6.17	5.19	5.66	5.51
R_{i1} [Ω cm²]	0.20	0.01	1.5	0.01
R_{i2} [Ω cm]	700	100	8500	600
R_{ct1} [Ω cm²]	16	15	31	19.8
R_{ct2} [Ω cm²]	20	7.0	29	23
L [H cm²]	450	200	1000	730
C_{dl} [F cm⁻²]	0.031	0.054	0.033	0.046
β [—]	0.72	0.90	0.83	0.93
θ [—]	0.50	0.50	0.23	0.23

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