



Short communication

Electrochemical analysis of perpendicular mesoporous Pt electrode filled with pure water for clarifying the active region in fuel cell catalyst layers

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ABSTRACT

A perpendicular mesoporous platinum film is used as a model electrode to clarify the effectiveness of catalysts inside agglomerates of fuel cell catalyst layers on the basis of experimental facts. The analysis clarifies that: (i) Pt surface even apart from Nafion ionomer phase can be electrochemically active; (ii) its response is different from that of the surface covered with ionomer; and (iii) ionic resistance in pores filled with pure water is too high (ca. 0.18 MΩ cm) for fuel cell reactions to smoothly occur. We conclude that such catalysts in pores filled with pure water are ineffective for fuel cell reactions due to the high ionic resistance, though their catalytic activity is possibly higher than that of the catalysts covered with Nafion.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) operating on hydrogen and oxygen need large catalytic surfaces; therefore, a porous catalyst layer composed of Pt supported on carbon (Pt/C) catalyst and Nafion™ ionomer is generally used. In order to let electrode reactions occur, the catalysts need to be at boundaries of three phases, i.e., electron conductive phase (carbon), ion conductive phase (Nafion) and gas or liquid phase of reactants and products (pores). Although there have been many reports dealing with the fabrication of catalyst layers, the layer conditions are considered to be still far from being ideal. For example, some portions of catalysts do not exist at the boundaries due to the formation of catalyst agglomerates covered with Nafion ionomer, as illustrated in Fig. 1a [1,2]. Thus, advances in understanding these agglomerates, especially on the effectiveness of catalysts inside the agglomerates, are of great importance to improve the performance and durability of PEFCs.

Next, we explain the current understanding of effectiveness of catalysts inside the agglomerates which has been discussed through theoretical calculation and experimental experience. Since the portion of catalysts inside agglomerates does not contact with Nafion directly, they should be ineffective for two reasons: (i) the

low ionic conductivity in agglomerates simply causes large ohmic drops, making the catalysts ineffective at large current operation and (ii) the low ionic activity probably makes electrical double layer to form along the outer surface of the agglomerates not along the walls of mesopores inside the agglomerates according to the Stern's double-layer model [3], resulting in the reduction of electrochemically active area [4]. The former has been common sense in porous electrodes as simply corroborated by physicochemical calculations [5]. The latter was experimentally proved by using a mesoporous platinum electrode in a conventional three-electrode cell containing NaF solution.

The current understanding is reasonable and probably correct, but the effectiveness of catalysts inside the agglomerates seems still open to debate. For example, some groups reported contradictory consideration about ionic resistance inside agglomerates. In detail, Jiang et al. and Mcbreen reported the experimental results which indicated such portion of catalysts even apart from Nafion could be effective due to the diffusion of ions (atoms) on the electrode surface (a phenomenon so-called "spillover") [6–9]. Moreover, it remains unclear if the electrochemical characteristics, especially electrical double-layer condition, of the electrode surface close to but tens or hundreds of nanometers apart from Nafion phase are the same as those of the catalysts directly covered with Nafion. Thus, the effectiveness of the catalysts inside agglomerates should be discussed based on more precise and practical experiments, but analysis using actual catalyst layers has hardly led to satisfactory solutions due to the inhomogeneous microstructures of conventional Pt catalyst layers (Fig. 1a).

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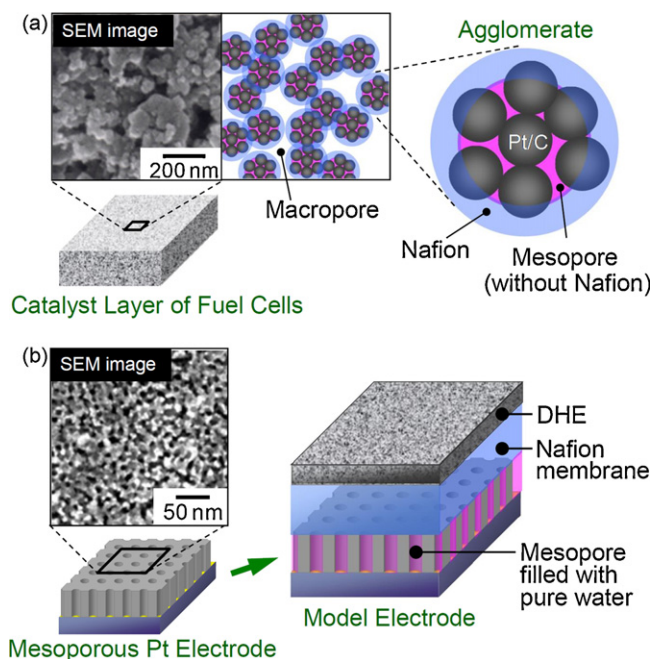


Fig. 1. Schematic illustrations explaining the concept of use of mesoporous Pt electrode as a model electrode of a fuel cell catalyst layer. (a) Actual catalyst layer consists of catalyst agglomerates covered with Nafion ionomer. The scanning electron micrograph (SEM) shows a plan-view of a typical catalyst layer prepared using an ink consisting of Pt/C, Nafion ionomer and ethyleneglycol dimethyl ether [36]. (b) Model electrode based on a perpendicular mesoporous Pt electrode. The high-resolution SEM image shows a typical plan-view of the mesoporous Pt electrode. The electrode was analyzed in contact with a Nafion membrane. A dynamic hydrogen electrode (DHE) was used as a reference-and-counter electrode.

We here report a series of electrochemical analyses using a model electrode of a PEFC catalyst layer to carefully study the effectiveness of catalysts inside the agglomerates. As the model electrode, a platinum thin film (thickness: 210 ± 20 nm) with mesopores (diameter: *ca.* 10 nm) which were perpendicularly aligned to the film was used (Fig. 1b). Its specific surface area, 14.1 ± 1.4 m² g⁻¹, is typical for mesoporous platinum, being slightly smaller than the values of ones prepared from lyotropic liquid crystal templating due to larger pores and thicker walls [10]. This electrode is considered desirable as the model electrode in terms of (i) the mesopores can be regarded as pores inside agglomerates of actual catalyst layers (see Fig. 1b) and (ii) the well-defined structure is useful for quantitative discussion. For example, the film thickness is identical to the length of the perpendicularly aligned pores. This feature is of practical importance for the quantitative analysis of ionic resistance in the pores.

2. Experimental

The mesoporous Pt film was prepared by the following procedures published previously by us [10]. In brief, Pt was electrodeposited onto a Pt substrate covered with titania nanopillars [11], and then the nanopillars were etched with a HF solution. The surface of Pt films thus obtained was cleaned by electrochemical hydrogen evolution and by cyclic voltammetry (CV) from -0.2 to 1.0 V vs. Ag/AgCl at 200 mV s⁻¹ (20 cycles) in a conventional three-electrode cell containing a nitrogen-saturated 0.5 M sulfuric acid solution to remove residual substances of etched TiO₂ and gaseous species generated during the etching process. The CV trace was stable and typical for Pt electrode (without hydrogen oxidation current and oxygen reduction current [10]), which meant that the surface was clean Pt.

The mesoporous electrode was evaluated in a cell configuration, where the mesoporous electrode contact a Nafion membrane with keeping its pores filled with pure water (model electrode of catalyst agglomerates), and to clarify the uniqueness of the results, the results were compared with those obtained in a conventional three-electrode cell. To use the mesoporous electrode as a model electrode, the electrode after the CV treatment was immersed in pure water to replace the electrolyte solution with pure water, and then the electrode was pressed onto a Nafion membrane pretreated in boiling 3 vol.% H₂O₂, in 0.5 M H₂SO₄ and then in pure water (Fig. 1b). As a counter-and-reference electrode, a dynamic hydrogen electrode (DHE) [12] was pressed onto the opposite side of the membrane. The DHE was composed of a Pt electrode prepared by casting a mixture of Pt nanopowder (24 – 29 m² g⁻¹, Alfa Aesar, 5 mg cm⁻²) and Nafion ionomer (5 wt% solution, Aldrich) on a carbon paper (TGP-H-060, Toray), and this Pt electrode was operated as DHE by flowing hydrogen at 20 mL min⁻¹ from a hydrogen generator (OPGU-2100S, Shimadzu). The opposite side of the membrane, *i.e.*, the compartment with the mesoporous electrode, was filled with nitrogen-saturated pure water to keep the mesopores filled with pure water. In this configuration (Fig. 1b) [13], only one end of each mesopore is in contact with the Nafion electrolyte.

The Pt electrode was evaluated by CV and by electrochemical impedance spectroscopy (EIS) using PARSTAT 2273 (Princeton Applied Research) at room temperature. CV was performed in a potential range of 0 – 1.2 V (vs. DHE) at 50 mV s⁻¹. EIS was performed in a frequency range of 100 kHz– 100 mHz with a DC bias of 0.5 V (vs. DHE) and an AC amplitude of 10 mV. This technique enables quantitative analyses of each individual parameter affecting electrochemical phenomena [14]. For comparison, the mesoporous electrode was evaluated also in a conventional three-electrode cell containing 0.5 M H₂SO₄ using a silver/silver chloride (Ag/AgCl) reference electrode (KCl saturated). The potential referring to the DHE (E_{DHE}) was translated into that referring to silver/silver chloride (Ag/AgCl) ($E_{\text{Ag/AgCl}}$) by assuming $E_{\text{Ag/AgCl}} = E_{\text{DHE}} - 0.199$ (V). In addition, to demonstrate catalytic reactions on the mesoporous Pt electrode, oxygen reduction reaction currents were measured by hydrodynamic voltammetry using a rotating-disc-electrode in an oxygen-saturated 0.5 M H₂SO₄ at room temperature.

3. Results and discussion

First of all, important preconditions for the following analysis, *i.e.*, that the mesopores were filled with solution and that the electrode surface in the mesopores was electrochemically active, were confirmed by the evaluation of the mesoporous Pt electrode in a conventional three-electrode cell. As we describe in detail in the next paragraph, the CV response from the mesoporous Pt surface was confirmed to be typical for polycrystalline Pt electrode. The roughness factor was over 40, which was determined from a charge associated with hydrogen desorption obtained by cyclic voltammetry in a 0.5 M H₂SO₄ solution. Considering the dimensions (pore size, wall thickness and film thickness), the roughness value is reasonable and moreover a few times larger than the value of an ideal mesoporous film (see the supplementary information file) probably because of the microscopic roughness of the real electrode. This indicates that the mesoporous were actually filled with solution. Moreover, Fig. 2 shows the oxygen reduction performance of the mesoporous electrode (roughness factor, $R_f = 68.0$) compared with that of a flat non-porous Pt electrode ($R_f = 3.8$). The apparently larger current of the mesoporous Pt electrode above 0.55 V reflects positive effect of the larger surface area. To discuss this point in detail, kinetically controlled currents obtained from the Koutecký–Levich plots are shown in the inset of Fig. 2. Although depending on the potential, the current of the mesoporous Pt was

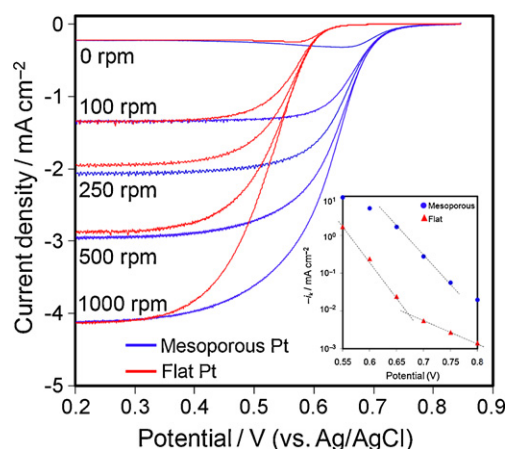


Fig. 2. Hydrodynamic voltammograms of oxygen reduction reaction on a perpendicular mesoporous Pt electrode (blue lines) and a flat non-porous Pt electrode (red lines) in an oxygen-saturated 0.5 M H_2SO_4 at room temperature ($\sim 25^\circ\text{C}$). Scan range: from open-circuit potential to 0.2 V. Scan rate: 1 mV s^{-1} . Rotating rate: 0, 100, 250, 500 and 1000 rpm. The inset shows Tafel plots of kinetically controlled current density (i_k) obtained from analysis based on Koutecký–Levich plots of the voltammograms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

~ 14 times larger than that of the flat Pt at 0.8 V. It is confirmed that the difference of the reduction currents reflected the increase in the roughness factor, *i.e.*, surface area. Thus, we conclude that the mesopores were sufficiently filled with electrolyte solution and moreover the surface in mesopores was electrochemically active.

Next, the mesoporous electrode was used as a model electrode, and the result was compared with that obtained in the three-electrode cell containing sulfuric acid solution. The CV of the mesoporous Pt electrode filled with pure water (referred to as “mPt-PW”) is compared with that filled with 0.5 M H_2SO_4 (referred to as “mPt-SA”) in Fig. 3a. The CV trace for mPt-SA is typical for a Pt electrode (without mesopores) scanned in a sulfuric acid solution, judging from the sharp peaks in the hydrogen region (-0.2 to 0.2 V), the oxide formation current (>0.6 V) and oxide reduction current (0.3 – 1.0 V) [15]. The CV of mPt-PW shows the response mainly from the Pt surface in the mesopores filled with pure water, judging from the roughness factor of the electrode ($R_f = 42$, this electrode was a different sample from one in Fig. 2) obtained by the calculation of hydrogen adsorption charge. Interestingly, the CV trace for mPt-PW is quite different from that for mPt-SA (Fig. 3a), for example, the onset potentials of the oxide formation current and the oxide reduction current were shifted toward lower potentials (the reduction peak-potential was shifted from 0.61 to 0.54 V). In addition, the hydrogen region currents apparently decreased, and their peaks were broadened and slightly shifted toward lower potentials by 5–10 mV.

These unique behaviors of mPt-PW can be attributed to (i) increase in local pH in the mesopores, (ii) lack of anion adsorption on the Pt surface, and (iii) influence of physical contact with a Nafion membrane. First, the increase in local pH in the mesopores is considered to shift the peaks, but the potential shifts are regarded too small for the presence of pure water according to Nernst equation (-0.059 V per ΔpH , under standard conditions). Since the influence of ionic impurities are negligible as we discuss below, the pure water in the mesopores should be acidified probably by the influence of the Nafion. Indeed, our calculation according to the Gouy–Chapman theory suggested that protons can exist in the mesopores apart from the membrane by $>900\text{ nm}$ (supplementary information). Second, the lack of anion adsorption, *i.e.*, sulfate ions, is considered to dominate the unique CV trace of mPt-PW, because it was reported that the anion adsorption mainly shifted the oxide

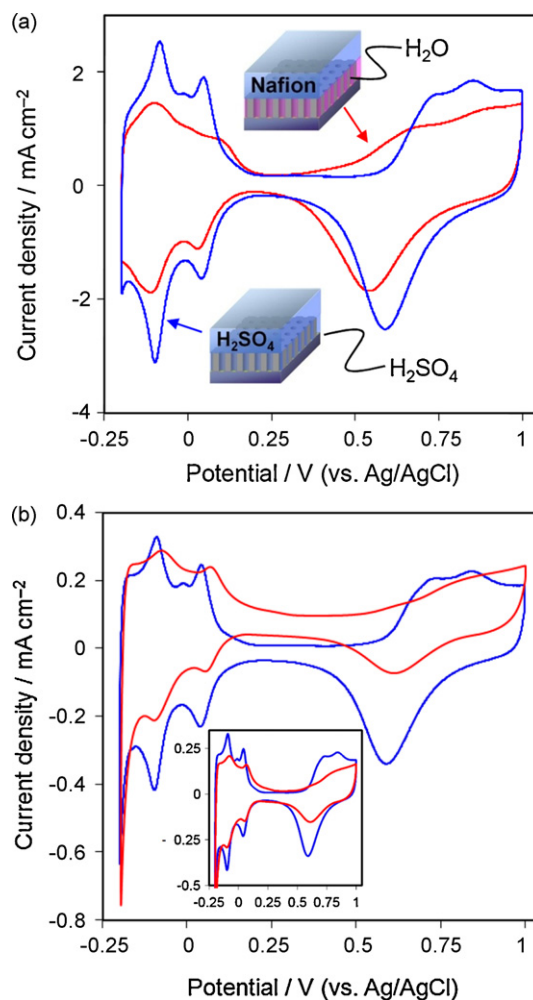


Fig. 3. Cyclic voltammograms of (a) a perpendicular mesoporous Pt electrode and (b) a non-porous Pt electrode evaluated in two different cell configurations: the model electrode configuration (red lines) and the conventional three-electrode configuration (blue lines). In the former, the electrodes physically contacted a Nafion membrane and were evaluated using a dynamic hydrogen electrode (DHE) as a reference-and-counter electrode to keep the mesoporous Pt electrode filled with pure water. In the latter, the cell contained a nitrogen-saturated 0.5 M H_2SO_4 . The red line shown in the inset of ‘b’ shows a voltammogram obtained by subtracting the oxidation current associated with hydrogen permeation to clarify the decrease in peak currents (by shifting the whole voltammogram downward by the oxidation current shown in the double-layer region). Scan rate: 50 mV s^{-1} . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

formation potential toward the higher potential [16]. Actually, the oxide formation of mPt-PW occurred at a lower potential than that of mPt-SA. Third, the physical contact with a Nafion membrane probably influenced the voltammogram. The result of a flat non-porous Pt electrode in the same cell configuration (Fig. 3b) indicates that the physical contact with a Nafion membrane decreased the peak currents compared with the result in a three-electrode cell, but did not obviously shift their positions. This result is consistent with the discussion in literatures [17,18]. The decrease in the currents is attributed to the adsorption of Nafion molecules and some contaminant from the cell. The slight peak-potential shifts toward higher potentials are attributed to the strong acidity of Nafion membrane or to polarization of the DHE. Based on these considerations, we naturally conclude that the electrochemical response from the Pt catalysts inside catalyst agglomerates should be different from those covered with Nafion. In detail, the catalyst in pores filled with pure water is more active in fuel cell reactions (*e.g.*, oxy-

gen reduction reaction because of decrease in adsorbed anions (e.g., SO_4^{2-}) [19], and CO oxidation and methanol oxidation because of the negative shift of surface hydroxylation potential [16]) than that covered with Nafion ionomer.

As we discussed above, the Pt surface in the mesopores filled with pure water is electrochemically responsive. This is contrary to our prediction that the double-layer capacitance of the electrode filled with pure water probably decreases according to Stern's model [4]. Indeed, the capacitance of mPt-PW appears to be similar to that of mPt-SA as shown around the electrical double-layer region ($\sim 0.3\text{V}$ in Fig. 3a). This was also confirmed by the following EIS analysis (85Fcm^{-3} for mPt-PW and 116Fcm^{-3} for mPt-SA). As described in the introduction, Boo et al. reported that the capacitance of a mesoporous Pt electrode clearly decreased under highly dilute electrolyte conditions [4], and we confirmed that this phenomenon occurred in a porous carbon electrode composed of carbon black in the same electrochemical cell as used in this study [13]. Thus, one may concern about the ionic impurity in the pores which might be from Nafion and/or the mesoporous electrode [10,18]. In view of the ionic resistance in the mesopores determined by the following EIS analysis, the influence of such ionic impurities was negligible. Thus, we speculate that the relatively large pores in our mesoporous Pt film compared with those of Boo et al. enabled the electrochemical response from Pt surface even in the pores filled with pure water [4]. Or in view of the small peak-shifts in CVs, which meant that the mesopores were acidified, there is a possibility that protons of Nafion somehow influenced the double layers in the mesopores. Though detailed investigations are required to clarify the mechanism, the experimental facts indicate that the catalysts inside the agglomerates are electrochemically responsive.

To confirm the absence of ionic contaminant in the mesopores, the ionic resistivity in the mesopores was evaluated through the analysis of EIS data (Fig. 4a). The complex-plane impedance diagrams showed a vertically linear relationship of typical capacitive behavior. These spectra are clearly different in the high-frequency region (see the inset). The spectrum of mPt-PW is linear with a slope of $\sim 45^\circ$, indicating a high resistance in a porous electrode [20–22]. This behavior was confirmed not to be observed in the case of a flat non-porous Pt electrode (Fig. 4b). Moreover, about ten times smaller Z_{im} values of the mesoporous Pt electrode (roughly $600\text{--}800\ \Omega\ \text{cm}^2$ at $0.1\ \text{Hz}$ in Fig. 4a) than those of the flat Pt electrode ($6000\text{--}10000\ \Omega\ \text{cm}^2$ at $0.1\ \text{Hz}$ in Fig. 4b) reflected the larger surface area. The ionic resistance of the entire electrode ($R_i, \Omega\ \text{cm}^{-1}$) was determined by confronting theoretical plots obtained from the following equation based on a conventional transmission line model [20–23] with the experimental plots as shown in Fig. 4a:

$$Z = R_b + \sqrt{\frac{R_i}{C_p(j\omega)^\beta}} \coth \left(L \sqrt{R_i C_p(j\omega)^\beta} \right) \quad (1)$$

where $Z(\Omega)$ is total impedance, $R_b(\Omega)$ ionic resistance for the bulk, $C_p(\text{Fcm}^{-1})$ capacitance per unit length, $L(\text{cm})$ length of the pores, and $\beta(-)$ is an exponent of constant phase element. The obtained values for mPt-PW were $R_b = 16(\Omega)$, $R_i = 3.8(\text{M}\Omega\ \text{cm}^{-1})$, $C_p = 6.0(\text{Fcm}^{-1})$ and $\beta = 0.83(-)$ by assuming that the length of the pores equals to the thickness of the film (*ca.* $210\ \text{nm}$). The ionic resistivity in the pores ($R_{\text{ip}}, \Omega\ \text{cm}$) was determined to be *ca.* $0.18\ \text{M}\Omega\ \text{cm}$ by multiplying the R_i value by the porosity (*i.e.*, 0.66) and the geometrical area (*i.e.*, $0.071\ \text{cm}^2$) (see also the supplementary information file). Such a high resistivity value confirmed that the pores were filled with pure water ($18\ \text{M}\Omega\ \text{cm}$).

Since the resistivity was significantly larger than that of general fuel cell electrodes ($0.1\text{--}1.0\ \text{k}\Omega\ \text{cm}$ [20,24,25]), it is concluded that such pores without Nafion are ineffective for reactions for the lack of smooth ion-transport. For example, the resistivity

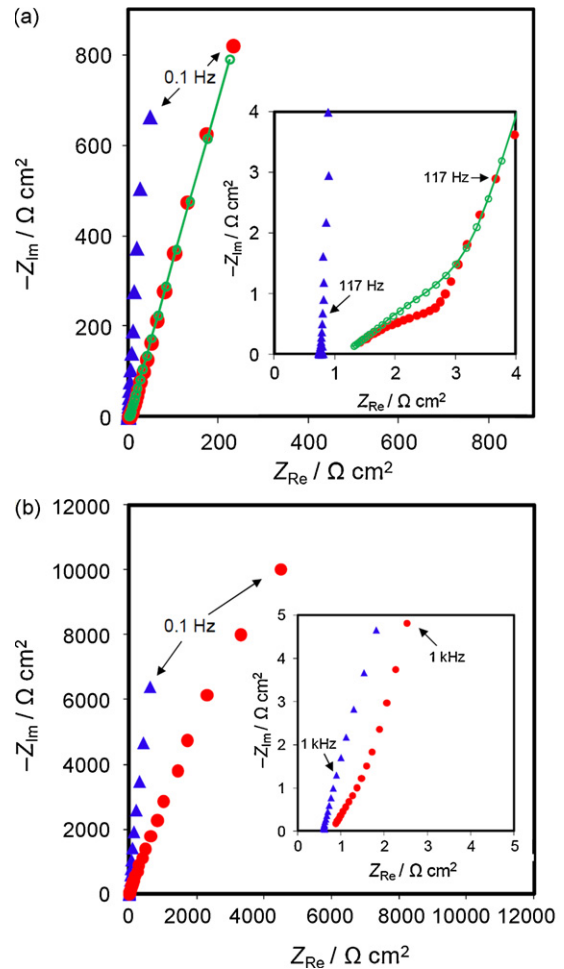


Fig. 4. Complex-plane impedance diagrams of (a) a perpendicular mesoporous Pt electrode filled with pure water (●) and with $0.5\text{M H}_2\text{SO}_4$ (▲) and (b) a flat non-porous Pt electrode contacting with a Nafion membrane (●) and soaked in $0.5\text{M H}_2\text{SO}_4$ (▲). Frequency range: $100\ \text{kHz}\text{--}100\ \text{mHz}$ (46 plots). DC bias: $0.5\ \text{V}$ vs. DHE. AC amplitude: $10\ \text{mV}$. The inset shows magnified diagrams in the high-frequency region. The open dots show the calculated value based on a conventional transmission line model (fitting plots).

means that Pt surface in the pores with only a 10-nm distance to Nafion phase has an ionic resistance of $0.18\ \Omega\ \text{cm}^2$. Compared with charge-transfer resistance of fuel cell reactions, which depends on electrode potentials (or operation currents), the resistance is not negligible, especially for PEFCs operating on hydrogen and oxygen. Makharia et al. reported that the charge-transfer resistance became less than $0.2\ \Omega\ \text{cm}^2$ even at a low current, around $0.2\ \text{A cm}^{-2}$ [20]. Thus, most of the Pt surface apart from Nafion is concluded to be ineffective for fuel cell reactions.

Next, we discuss catalyst utilization degrees also through the CV analysis, which was used in the literatures proposing the possibility that the surface even apart from Nafion can be effective for fuel cell reactions [6–9]. As commonly performed to evaluate effective surface area of fuel cells, the utilization degree of the Pt catalyst was determined by a widely adopted CV measurement. The degree is often calculated from the quantity of electrical charge involved in electrochemical reactions of adsorption/desorption, e.g., hydrogen adsorption and carbon monoxide stripping, occurring in the CV measurements [15,26–28]. The degree for mPt-PW was determined to be 79% by comparing the charges involved in hydrogen adsorption of mPt-PW and mPt-SA (Fig. 2). If this percentage really indicates the actual surface area effective for fuel cell reactions, the value of 79% means that some portion of the Pt surface is effective

even though it is not in contact with Nafion. This contradicts the conclusion derived from the EIS results. This contradiction can be solved on the basis of the fact that the influence of a series ionic resistance on the capacitance is different from that on the reaction resistance. Firstly, ionic resistance is considered only to delay the response from the capacitance, resulting in incomplete charging process of the capacitor. That is, the degree of charging is found to depend on the scan rate of CV measurements. This is supported by the experimental results reported by Paulus et al. [29] and Umeda et al. [30]. Secondly, in contrast to the influence on capacitors, ionic resistance directly reduces current flow through the reaction resistance according to the Kirchhoff's law [5,31,32]. As a consequence, we can conclude that the degree of the catalyst utilization calculated from CV does not necessarily indicate the actual performance of fuel cell electrodes, although this technique is useful for the evaluation of the electrochemically active surface area of a catalyst as a material screening procedure [33–35].

4. Conclusion

The experimental results using a perpendicular mesoporous electrode clarified that the Pt surface in pores without Nafion was electrochemically active, that its response was different from that from the Pt surface covered with Nafion, and that the ionic resistance in pores without Nafion was too high for fuel cell reactions to occur. Based on these experimental facts, we conclude that most of catalysts in pores without Nafion are not effective for fuel cell reactions even though their catalytic activity, e.g., for oxygen reduction reaction, CO oxidation reaction and methanol oxidation reaction, is possibly higher than that of catalysts covered with Nafion. Moreover, as has often been discussed theoretically [5], actual effective area should be discussed based on ionic resistance and kinetics of electrode reactions, which depends on the systems and electrode potentials [13].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jpowsour.2009.11.002](https://doi.org/10.1016/j.jpowsour.2009.11.002).

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