Analysis of effective surface area for electrochemical reaction derived from mass transport property

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ABSTRACT

The effective surface area, S^{eff}, for electrochemical reaction at a Pt electrode was analyzed using mass transport property as a probe. This parameter is different to the so-called electrochemical surface area (ECA), which is usually obtained from the amount of protons which are underpotentially deposited, H_{UPD}, or by CO stripping. The analysis was done using both experimental and numerical methods. In experiments, a rotating disk electrode (RDE) was used under the conditions where the Pt surface can be partially covered by Pt oxides or CO. For numerical analysis, three mass transport models based on diffusion, convection and convective-diffusion were used. As a result, it was found that it is possible to estimate S^{eff} from the change in Koutecky–Levich slope at high rotation speeds. The analysis suggests that S^{eff} does decrease notably from relatively low potential (around 0.4 V), even though it is not obvious in measured currents as the effect is masked by the low rates of mass transport. The analysis also suggests that there is a large difference in S^{eff} with different methods, namely, estimation from the amount of Pt oxides and the analysis derived from mass transport property.

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1. Introduction

It is well known that a polymer electrolyte fuel cell (PEFC) is a promising primary power source for automotive use, and car manufacturers are developing fuel cell electric vehicles (FCEVs). However, there are still challenges to be addressed for the commercialization, such as power density, durability, sub-zero startup and cost reductions. From an industrial point of view, the most important aspect is cost reduction. According to recent DOE studies, Pt used as a catalyst accounts for about a quarter of the total fuel system cost [1]. Therefore, increasing the utilization of platinum in fuel cells is an important strategy in reducing total system cost.

In order to make the most of Pt, carbon supports with high surface areas (HSA carbon) and various core–shell catalysts have been developed. With HSA carbon supports, smaller Pt particles can be deposited densely, resulting in high surface area and high mass-specific activity [2,3]. On the other hand, core–shell catalysts reduce Pt usage by replacing the core of a Pt particle, which does not directly contribute to electrochemical reactions, with other less expensive materials [4,5]. In either approach, it is necessary to evaluate how much surface area contributed to electrochemical reactions under practical FCEV operation conditions.

Usually, the electrochemical surface area (ECA) of Pt is evaluated from the amount of protons which are underpotentially deposited, H_{UPD}, or by CO stripping [6]. However, the values obtained with those methods may not be applicable to practical operation conditions, for example, at high potentials (over 0.7 V). The oxygen reduction reaction (ORR) current may be modeled by considering the ORR far from the equilibrium potential having a certain platinum site dependency in which site interactions are handled by a Temkin term and expressed as [7]

$$i_k = nFkC_{O_2}(1 - \theta)^x \exp\left(-\frac{\beta F\eta}{RT}\right)\exp\left(-\frac{\gamma r\theta}{RT}\right), \qquad (1)$$

where n is the number of electrons, F is the Faraday constant, k is the rate constant, C_{O_2} is the concentration of O_2 in the solution, θ is the total surface coverage by adsorbed species, x is the number of Pt sites occupied by the adsorbate, β and γ are the symmetry factors and r is the Temkin parameter. As can be seen in Eq. (1), the ORR current strongly depends on θ. Although θ is sometimes evaluated by measuring the amount of Pt oxide [8,9], such an approach does not seem that straightforward for two reasons: the first is that we are interested in the number of free platinum sites $(1 - \theta)$ and as a range of platinum oxides are formed as a function of potential, determining this parameter is difficult; the second is that the different oxides produced may interact with the ORR intermediates in different ways, that is r is a function of E.

One of us has developed a method to evaluate the effective surface area, S^{eff}, for the hydrogen oxidation reaction (HOR) as a function of potential by using the change of mass transport properties as a probe [10]. This method is applicable to a membrane electrode assembly which has a gas diffusion layer on its catalyst layer. However, MEAs do not seem suitable for the analysis of the increase of θ at high potentials or validation of mitigation strategies for this issue. Therefore, it is desirable that this kind of technique is applied to a simpler system with which the analysis or the validation can be done more easily.

A rotating disk electrode (RDE) has been used to investigate fuel cell catalyst performance for many years [11–13]. The RDE is a useful tool for evaluating fuel cell catalyst performance because it allows extraction of the catalytic activity from the current density by control of the rotation speed. Moreover, it does not require as much catalyst material as an MEA. Furthermore MEA fabrication processes are not necessary for the RDE. However, in aqueous electrolytes such as H_2SO_4 or $HClO_4$, the concentration and diffusion coefficient of oxygen and hydrogen are quite low. Thereby, the limiting currents are considerably lower than those which would be observed with actual catalyst layers [14]. In addition, the RDE cannot enhance the mass transport that much due to the cavitation of the electrolyte at rotation rates approaching 10,000 rpm. Because of bubble formation due to cavitation, data analysis becomes significantly more complicated because the flow pattern of the solution is no longer laminar and become turbulent.

Regardless of the drawbacks, it was still thought to be useful to develop a similar method for evaluating S^{eff} in a simpler system due to its feature of controllable mass transport. In this study, we investigated a new experimental method for evaluating S^{eff} under the conditions where Pt surface can be partially covered. The validity of the method was examined by numerical approaches.

2. Experimental

2.1. Experimental setup

All the electrochemical measurements were performed using a three-electrode electrochemical cell consisting of three compartments for a reference electrode (RE), a counter electrode (CE) and a working electrode (WE). A reversible hydrogen electrode (RHE) was employed as reference electrode, and all the potentials are referred to this electrode. A Pt wire served as a counter electrode. Before the electrochemical measurements, all glassware and electrodes were soaked in acidified potassium permanganate over 8 h, rinsed with acidified hydrogen peroxide and then rinsed at least six times with ultra pure water (Millipore Milli-Q, 18.2 MΩ cm). Gas purities of ⩾5.8 N (Air Products) were utilized with 6 N rated regulators (GCE DruVa). An aqueous 0.1 M $HClO_4$ solution was used as the electrolyte. The solution was prepared from 70% $HClO_4$ (Suprapur®, Merck) and ultrapure water. Pt rotating disk electrodes with a diameter of 2 or 5 mm (AFE2M020PT or AFE2M050PT, PINE instruments) which are applicable up to 7000 rpm were used as the WE. The RDE was attached to a modulated speed rotator (AFMSRCE, PINE instruments) and its rotation was controlled with the system while the potential was controlled by a Gamry Reference 600 potentiostat. All electrochemical experiments were conducted at room temperature.

2.2. Conditioning of Pt RDE and roughness factor measurement

Prior to the HOR measurements, the potential of the WE was electrochemically cleaned by cycling 100 times between 0 and 1.4 V at 0.5 V s^{-1} in 0.1 M $HClO_4$ saturated with N_2 gas. After that, cyclic voltammetry was carried out to determine the roughness factor of the Pt disk. The potential of the WE was scanned between 0.02 and 1.2 V vs. RHE at a scan rate of 50 mV s^{-1} for several cycles. The amount of H_{UPD}, Q_H was calculated by extracting the quantity of electricity due to hydrogen evolution reaction (HER) from total reduction current below the potential where the double layer region was observed. The detail was explained in Ref. [15]. Then, the roughness factor was evaluated from Q_H, the geometrical area of the disk electrode and a charge to Pt surface area conversion factor of 210 µC cm$^{-2}_{Pt}$ for a smooth polycrystalline Pt.

2.3. HOR measurement

After the roughness factor measurement, the solution was saturated with H_2. Hydrodynamic voltammograms for the HOR were obtained by cycling the potential from 0 to 1.1 V at 10 mV s^{-1} under the rotating rates of 400–6800 rpm. The conditions for HOR measurement is summarized in Table 1.

2.4. Partial blocking with carbon monoxide

For comparison between the free Pt surface determined from integration of Pt oxide charge, the Pt disk was also partially blocked by carbon monoxide (CO). First, CO was bubbled into the solution for about 15 min whilst the electrode potential was held at 0.05 V. Next, CO was purged with N_2 for over 30 min while the potential of the WE was held at 0.05 V so as to keep the adsorbed CO still on the Pt surface. The potential of the Pt disk was then cycled once between 0.05 and 0.7 V at a scan rate of 10 mV s^{-1}. In this way, the partially blocked Pt disk electrode was prepared. After that, the solution was saturated with H_2 and the HOR measurement with the electrode was carried out. With this electrode, the upper vertex potential for the HOR measurement was set at 0.4 V so as not to oxidize the remaining CO. After the HOR measurement, the remaining CO was quantified by CO stripping voltammetry. CO stripping voltammetry was performed in N_2 saturated solution and the potential was cycled between 0.02 and 1.2 V at a scan rate of 10 mV s^{-1} for 3 times.

2.5. Observation of Pt disk surface

The crystallographic orientation of a Pt disk surface was investigated by electron backscatter diffraction (EBSD). The EBSD measurements were conducted using a field-emission scanning electron microscope (FE-SEM, ULTRA55; Carl Zeiss) operated at an accelerating voltage of 15 kV, and the collected EBSD patterns were analyzed using Channel 5 system and a Nordlys II detector (Oxford/HKL). The measurements were carried out at a step size of 0.1 µm. To fit the sample stage of the FE-SEM, a detachable Pt disk insert (AFED050P040PT, PINE instruments) was used for the analysis.

3. Results and discussion

3.1. Change in Koutecky–Levich slope

Cyclic voltammograms of the Pt disks are shown in Fig. 1. The shapes were very similar to those of the literature [16,17], thereby the whole system was thought to have been cleaned well. The roughness factors of the Pt disks were determined from these voltammograms to be ca. 1.5 (diameter: 5 mm) and ca. 1.6 (diameter: 2 mm). The hydrodynamic voltammograms obtained with the Pt disk (diameter: 5 mm) for the HOR are shown in Fig. 2. The current density increased with potential and reached a limiting current density below 0.2 V and looked independent of potential up to