

Cyclic Voltammetric Measurement of Catalyst Surface Area for Pt-Black/Nafion Electrodes

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Abstract—The electrochemical surface areas of Pt-black/Nafion thin-film electrodes immersed in 0.5 M H₂SO₄ were measured using the cyclic voltammetry (CV) technique. The decrease in the catalyst surface utilization measured at high potential scan rates was due to the incomplete H-adsorption process caused by the ohmic potential drop in the solution, which resulted in the measured electrode potential being lower than the real one during the cathodic scan. The ohmic potential drop became more appreciable when the roughness factor of an electrode or the scan rate increased, due to the increase in the current. The Nafion film coating ($\leq 8 \mu\text{m}$) had a negligible effect on the surface area measurements. The real catalyst surface area of an electrode can be accurately estimated through CV, if a scan rate that does not cause appreciable ohmic potential drops is used; the appropriate scan rate becomes lower as the roughness factor of the electrode increases.

Key Words : Pt-black, Cyclic voltammetry, Catalyst surface utilization, Porous electrode, Fuel cells

INTRODUCTION

The fuel cell is a clean and efficient alternative fuel technology. Due to its potential economic, energy, and environmental benefits, this technology has been under extensive research and development (Kordesch and Simader, 1996). In particular, proton exchange membrane fuel cells (PEMFCs) have recently received much attention due to their high-power density at relatively low temperatures with zero emission of environmental pollutants (Ralph, 1997).

Platinum is the most widely used electrocatalytic material for fuel cells (Kordesch and Simader, 1996; Mehta and Cooper, 2003; Ralph, 1997). For cost reasons, lower precious metal loading is required, leading to a lot of attempts to optimize the active layer in the electrode structure (Mehta and Cooper, 2003). The catalysts used are mainly Pt-black or Pt nanoparticles dispersed on carbon (Pt/C) due to their high specific surface areas. Cost limitations have also led to the development of various impregnation techniques for incorporating the solid polymer electrolyte (*e.g.*, Nafion) into the catalyst layer (Ticianelli *et al.*, 1988; Uchida *et al.*, 1995; Wilson and Gottesfeld, 1992a, 1992b; Wilson *et al.*, 1995).

Much attention has been paid to the catalyst surface utilization for an electrode in contact with the solid polymer electrolyte (Liu *et al.*, 1999; McBreen,

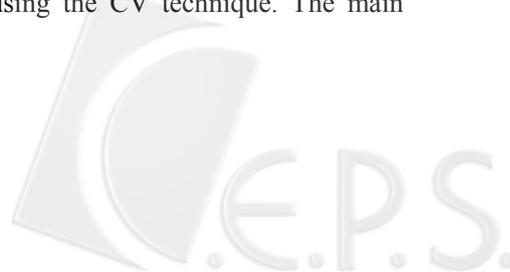
1985; Paulus *et al.*, 2003; Tu *et al.*, 1998). Cyclic voltammetric (CV) measurements have been conducted in most works to evaluate the electrochemical surface area and determine the level of catalyst surface utilization. In such measurements, the electrode potential is changed at a constant scan rate and the current is recorded. The current-potential curve shows peaks for the formation and oxidation of adsorbed hydrogen and oxygen; measurement of the areas under the peaks gives the electrochemical surface area of the electrocatalyst, assuming monolayer coverage for the adsorbed species. Results obtained using this method, however, might show great inconsistency because of the presence of other adsorbed species (Okada, 2003), the double-layer capacitance, and the solution resistance (Bard and Faulkner, 2001), or due to improper selection of the potential scan rate.

The use of rotating thin-film electrodes, which are composed of a thin catalyst layer and a thin recast Nafion film, has been reported to be a powerful method for the evaluation of the activity of electrocatalysts under the conditions prevailing in fuel cells (Schmidt *et al.*, 1998, 1999). Investigations into this type of electrode have focused mainly on the case of Pt/C; electrodes made of Pt-black have not yet been extensively studied (Lin and Shih, 2006).

In the present study, the electrochemical surface areas of the Pt-black/Nafion thin-film electrodes were measured using the CV technique. The main

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goal of this work was to examine in detail the factors affecting the catalyst surface area measurements.

EXPERIMENTAL

Materials

A Nafion solution containing 5 wt% of Nafion dissolved in a mixture of isopropanol and water (1100 equivalent weight, Ion Power) was used to recast Nafion film. Platinum black (HiSPECTM1000, Johnson Matthey) was used as the dispersed Pt catalyst. A glassy carbon (GC) disk electrode (disk area = 0.1963 cm²; shroud area = 1.131 cm², Pine Instruments) served as the substrate for the deposition of the catalyst. A smooth Pt electrode (Pine Instruments) with the same configurations was also used in this work. Prior to coating, the GC disk was polished with a 0.05 μm alumina powder (CHI Instruments), ultrasonicated to remove residual abrasive particles, thoroughly rinsed with distilled water, and wiped dry.

Thin-film porous electrode preparation

An aqueous catalyst suspension of 2 mg·mL⁻¹ was prepared by mixing 50 mg of catalyst and 25 mL of deionized water under ultrasonication for about 10 min. Diluter catalyst suspensions were prepared by lowering the catalyst weight. About 12.5–20 μL of the catalyst suspension was pipetted onto the GC disk surface. After the water evaporated under room temperature, 20 μL of Nafion solution was put on the top of the catalyst layer. Subsequent annealing in a vacuum oven (70°C) was performed for at least 40 min to evaporate the solvent in the film. This annealing rendered the stable films insoluble and gave them sufficient strength to bind the catalyst particles (Zook and Leddy, 1996). The concentration of the Nafion solution was varied by diluting the 5 wt% Nafion solution with isopropanol to yield recast films with thicknesses ranging from 0.1 μm to 8.0 μm. The film thickness was calculated from the mass and the surface area of the recast film, assuming a dry Nafion density of 1.98 g·cm⁻³ (Zook and Leddy, 1996). About 90% of the shroud area was covered by the Nafion coating, thus the geometric surface area of the film was estimated to be 1.0 cm². The film thickness was further measured using a surface texture profilometer (Dektak 3030, Sloan Technology) for some films, and the difference between the measured and calculated values was about 6%. Before the electrochemical experiment was started, the electrode was immersed for several hours in deaerated 0.5 M H₂SO₄ solution, which exhibited a very similar pH value to the recast film. This procedure permitted the complete wetting of the electrodes.

Electrochemical and physical characterization

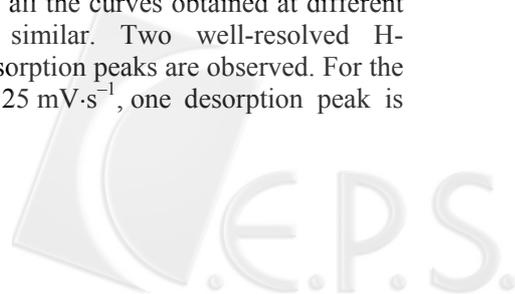
A conventional three-compartment glass cell with a saturated calomel reference electrode (SCE) and a Pt foil counter electrode was used to study the electrochemical behavior of the Pt-black/Nafion electrodes. The electrolyte was 0.5 M H₂SO₄ solution prepared from concentrated H₂SO₄ (Instruments analysed reagent, J.T. Baker) and ultrapure water (18 MΩ, Millipore). Electrochemical measurements were performed at room temperature (25±1°C) using a potentiostat (Autolab PGSTAT30, Ecochemie), and a computer-controlled general purpose electrochemical system (GPES) was used for recording voltammetric curves. Throughout this study, all potentials were referred to the reversible hydrogen electrode (RHE) scale. The cyclic voltammograms of the electrodes were obtained after scanning the potential between 0 and 1.2 V vs. RHE for several hundred cycles. This long run-in period was necessary to obtain stable and reproducible data. The CV curves were obtained using scan rates ranging from 15 to 500 mV·s⁻¹. The hydrogen adsorption/desorption charge, Q_H , was evaluated based on the CV data, and is equal to one-half of the net charge calculated by first integrating the currents for both the cathodic and anodic scans with time in the potential range between 50 and 400 mV and then subtracting the charge for the double layer (Nart and Vielstich, 2003).

The specific surface area of the Pt-black powder was determined from the nitrogen adsorption data through the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2010 analyzer. The real surface area of each electrode was determined from the Pt loading and the BET specific surface area. The roughness factor of an electrode was defined as the ratio of the real surface area to the geometric area of the electrode. The catalyst surface utilization was defined as the ratio of the electrochemical surface area to the real surface area of the electrode.

RESULTS AND DISCUSSION

Cyclic voltammograms

The typical cyclic voltammograms for the thin-film electrodes are represented in Fig. 1 for an electrode with a Pt-black loading of 102 μg·cm⁻² (the roughness factor was estimated to be about 30) and a Nafion film thickness of 8.0 μm. One can see that the general shapes of all the curves obtained at different scan rates are similar. Two well-resolved H-adsorption or -desorption peaks are observed. For the curve obtained at 25 mV·s⁻¹, one desorption peak is



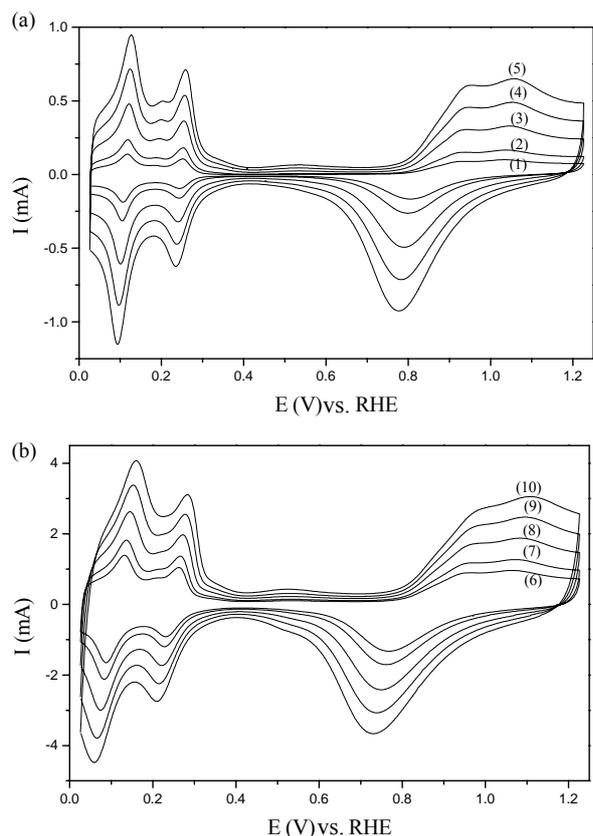


Fig. 1. Cyclic voltammograms for a thin-film electrode (Pt-black loading: $102 \mu\text{g}\cdot\text{cm}^{-2}$; Nafion film thickness: $8.0 \mu\text{m}$). Scan rates ($\text{mV}\cdot\text{s}^{-1}$): (a) (1) 15, (2) 25, (3) 50, (4) 75, (5) 100; (b) (6) 150, (7) 200, (8) 300, (9) 400, (10) 500.

located at around 120 mV and is hereafter designated peak I; the other peak is located at around 252 mV and is hereafter designated peak II. In the literature (Paulus *et al.*, 2003; Tu *et al.*, 1998), these two peaks are referred to the desorption of weakly and strongly adsorbed hydrogen, respectively. The weakly adsorbed hydrogen is on the Pt (110) or Pt (111) surface, and the strongly adsorbed hydrogen is on the Pt (100) surface (Gojkovic *et al.*, 1998, Schmidt *et al.*, 1998). Moreover, one can see that the peaks of the voltammograms become higher and shift to the right for the anodic scan and to the left for the cathodic scan, as the scan rate increases.

Effect of the scan rate on the peak potential and current

The hydrogen adsorption/desorption processes on an electrode surface that is in direct contact with H_2SO_4 consist of the adsorption/desorption processes of H^+ ions at the interface between the solution and the surface, and the hydrogen reduction/oxidation reaction on the surface:



where H^+ is the hydrogen ion in the solution, and H_{ad}^+ and H_{ad} represent the hydrogen ion and atom adsorbed on the electrode surface, respectively.

The theoretical cyclic voltammograms for this type of reaction were given by Bard and Faulkner (2001) for cases in which the adsorption/desorption processes of H^+ , Eq. (1), attain equilibrium.

When there is no mass transfer limitation for H^+ and the electron-transfer reaction, Eq. (2), is very fast (reversible), the peak potential (E_p) shown in the cyclic voltammogram is independent of the scan rate (ν), and the peak current (I_p) is proportional to ν and is given by

$$I_p = \frac{n^2 F^2 \nu A_r \Gamma^*}{4RT}, \quad (3)$$

where n is the stoichiometric number of electrons involved in the electrode reaction, F is the Faraday constant, A_r is the real surface area, and Γ^* is the moles of adsorbed hydrogen atoms per unit Pt surface area. R and T stand for the gas constant and temperature, respectively. If the reaction is very slow (totally irreversible), E_p shifts from the reversible value and is a linear function of $\ln(\nu)$; I_p is still proportional to ν , but is given by

$$I_p = \frac{n\alpha n_a F^2 \nu A_r \Gamma^*}{2.718RT}, \quad (4)$$

where α is the transfer coefficient and n_a is the number of electron transfer.

When the diffusion of the electroactive species in the solution side controls the reaction, the condition of semi-infinite diffusion is applicable. For the case of a reversible electrode reaction, E_p remains constant and the peak current is given by

$$I_p = 2.69 \times 10^5 n^{3/2} A C_0^* D^{1/2} \nu^{1/2}, \quad (5)$$

where A is the cross-sectional area of an electrode, C_0^* is the bulk concentration of the electroactive species in the electrolyte, and D is its diffusion coefficient. In the case of a totally irreversible electrode reaction, E_p is a linear function of $\ln(\nu)$, and I_p is given by

$$I_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} A C_0^* D^{1/2} \nu^{1/2}. \quad (6)$$

Figure 2 shows the peak potential for H-desorption as a function of $\log(\nu)$ for some thin-film electrodes. The E_p for peak I (Fig. 2(a)) is seen to shift more than the E_p for peak II (Fig. 2(b)) as ν increases; the E_p shift is more pronounced for electrodes with higher roughness factors. Moreover, it was found that the peak potential shift was independent of the Nafion film thickness, indicating that the IR drop that was due to the Nafion film resistance is negligible.

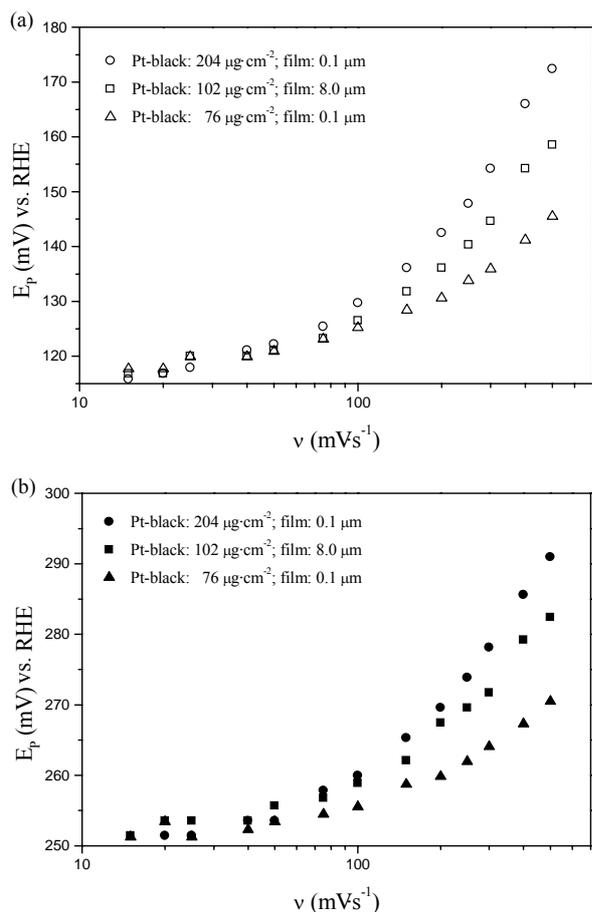


Fig. 2. E_p vs. $\log(v)$ plots for H-desorption on the Pt-black/Nafion electrodes: (a) peak I, (b) peak II.

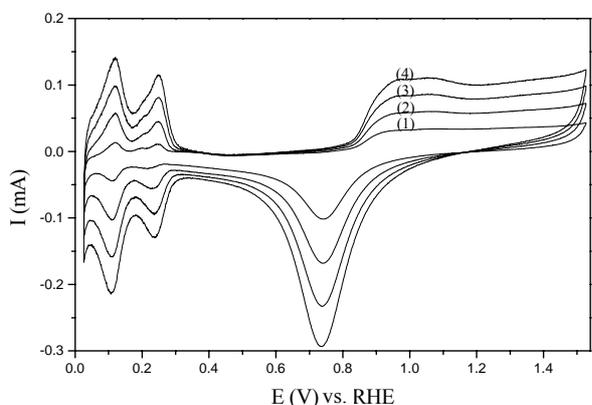


Fig. 3. Cyclic voltammograms for a Nafion-coated smooth Pt electrode (Nafion film thickness: $4.0 \mu\text{m}$). Scan rates ($\text{mV}\cdot\text{s}^{-1}$): (1) 100, (2) 200, (3) 300, (4) 400.

From Fig. 2, one can see that the peak potential increases non-linearly with $\log(v)$ when $v > 40 \text{ mV}\cdot\text{s}^{-1}$. This result indicates that the E_p shift was not due to the irreversibility of the electrode reaction.

For a comparison, cyclic voltammograms for a Nafion-coated smooth Pt electrode (the roughness factor was estimated to be 2.16) are shown in Fig. 3. As seen in Fig. 3, the peak potentials for all the peaks are independent of the scan rate. The peak cur-

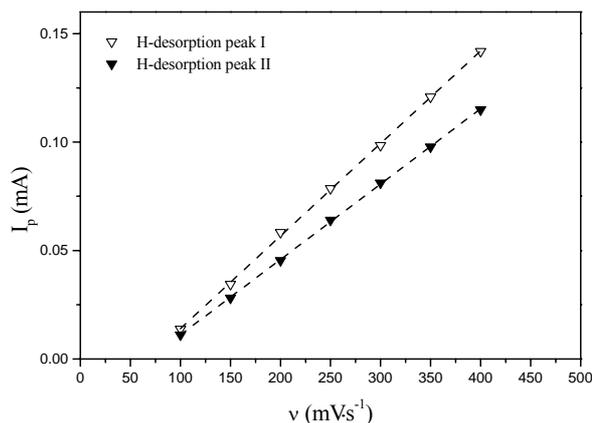


Fig. 4. I_p vs. v plots for H-desorption on a Nafion-coated smooth Pt electrode (Nafion film thickness: $4.0 \mu\text{m}$).

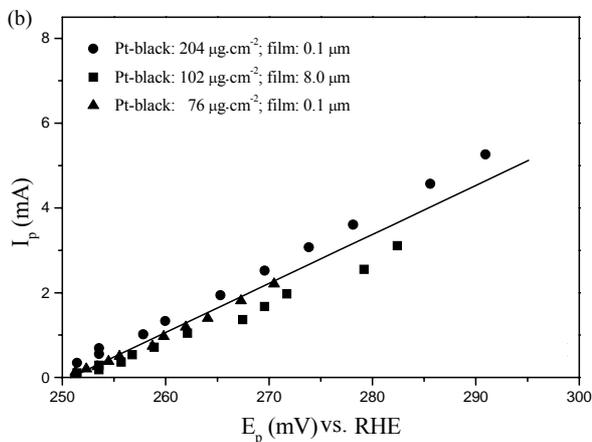
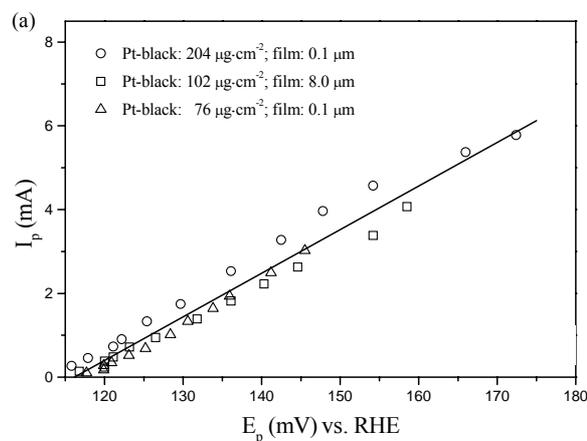


Fig. 5. I_p vs. E_p for H-desorption on the Pt-black/Nafion electrodes: (a) peak I, (b) peak II.

rents for the respective H-desorption peaks, as shown in Fig. 4, are linearly proportional to the scan rate. These results show that on the smooth Pt electrode, the H-adsorption/desorption processes are reversible.

By comparing Fig. 1 with Fig. 3, one can see that the I_p values for the thin-film electrodes are much greater than those for the smooth Pt electrode when at the same scan rate. Thus, the E_p shift (ΔE_p) for the former electrodes may be caused by the ohmic

Table 1. The experimental and theoretical I_{PH} values (mA) at various scan rates for the Pt-black/Nafion electrodes.

Scan Rate ($\text{mV}\cdot\text{s}^{-1}$)	Pt-Black Loading ($\mu\text{g}\cdot\text{cm}^{-2}$)								
	204			102			76		
	I_{PH}^I	I_{PH}^{II}	I_{PH}^{Ta}	I_{PH}^I	I_{PH}^{II}	I_{PH}^{Ta}	I_{PH}^I	I_{PH}^{II}	I_{PH}^{Ta}
500	5.22	4.70	12.12	3.77	2.81	6.06	2.75	1.94	4.55
400	4.94	4.14	9.70	3.18	2.35	4.85	2.29	1.61	3.64
300	4.26	3.29	7.27	2.45	1.79	3.64	1.78	1.24	2.73
250	3.71	2.82	6.06	2.09	1.53	3.03	1.52	1.07	2.27
200	3.07	2.32	4.85	1.71	1.25	2.42	1.23	0.87	1.82
150	2.38	1.79	3.64	1.31	0.97	1.82	0.94	0.66	1.36
100	1.66	1.24	2.42	0.90	0.66	1.21	0.64	0.46	0.91
75	1.27	0.96	1.82	0.69	0.51	0.91	0.49	0.35	0.68
50	0.86	0.69	1.21	0.47	0.35	0.61	0.33	0.24	0.45
40	0.71	0.53	0.97	0.37	0.28	0.48	0.27	0.19	0.36
25	0.45	0.34	0.61	0.23	0.18	0.30	0.17	0.12	0.23

^a Calculated using Eq. (3) and $\Gamma^*=210 \mu\text{C}\cdot\text{cm}^{-2}\cdot\text{F}^{-1}=2.18\times 10^{-9} \text{ mol}\cdot\text{cm}^{-2}$.

potential drop due to the resistance (R_s) of the electrolyte, *i.e.*,

$$\Delta E_p = I_p R_s. \quad (7)$$

The ohmic potential drop increases when the current passing through the electrolyte increases. Since the current increases as the scan rate or the roughness factor of an electrode increases, the ΔE_p value will be significant for an electrode which has a high roughness factor and is subjected to a high scan rate. This interpretation is verified by the linear relationship between the E_p and I_p values for the thin-film electrodes shown in Fig. 5. As seen in the figure, the data for different H-desorption peaks and different electrodes exhibit almost the same linear relationship, indicating that the resistance is entirely in the electrolyte. The average value of R_s was determined to be $9.6\pm 1.0 \Omega$. With this value for R_s , the ΔE_p for peak I for the smooth Pt electrode at $500 \text{ mV}\cdot\text{s}^{-1}$ was estimated to be $< 2 \text{ mV}$, which is negligibly small.

Whether the mass transfer of H^+ ions affects the electrode processes can be ascertained according to the dependence of the I_p value on the scan rate. Since the measured current includes the double-layer charging current (I_c), the I_p value due to H-desorption (I_{PH}) should be obtained by subtracting the I_c value from the measured I_p value.

The I_c values estimated from the CV measurements are shown in Fig. 6. The data at $v \geq 15 \text{ mV}\cdot\text{s}^{-1}$ are seen to follow the relationship (Bard and Faulkner, 2001):

$$I_c = a + A_p C_d v, \quad (8)$$

where a is a constant and C_d is the capacitance of the double layer. The average C_d value was determined to be $(1.10\pm 0.14)\times 10^{-4} \text{ F}\cdot\text{cm}^{-2}$. Generally speaking, the contribution of I_c to the I_p values was small, the highest value being about 10%.

The values of I_{PH} for the two peaks, I_{PH}^I and

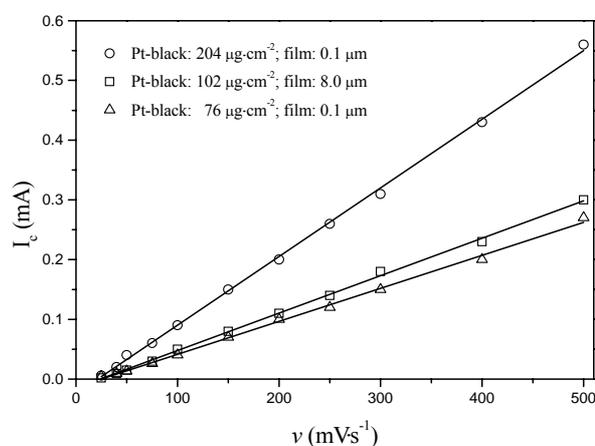


Fig. 6. I_c vs. v plots for the Pt-black/Nafion electrodes.

I_{PH}^{II} , are listed in Table 1. As depicted in Fig. 7, I_{PH} follows a linear relationship with v (the dashed lines shown in the plot) before v reaches $250 \text{ mV}\cdot\text{s}^{-1}$; I_{PH} deviates slightly from the linear relationship as v increases further for 76 and $102 \mu\text{g}\cdot\text{cm}^{-2}$ Pt-black loadings, but markedly for a $204 \mu\text{g}\cdot\text{cm}^{-2}$ Pt-black loading. Furthermore, the negative deviations are more pronounced for peak I than for peak II. However, as seen in Fig. 8, the I_{PH} vs. $v^{1/2}$ plots do not show the linear relationship given by Eq. (5). Also, the I_p values for H-adsorption calculated using Eq. (5) were found to be one order of magnitude greater than the experimental I_p values. Therefore, it is evident that the electrode processes did not take place under the diffusion control condition.

The theoretical values of I_{PH} , I_{PH}^T , for the electrodes at different scan rates were calculated using Eq. (3) with a Γ^* value of $210 \mu\text{C}\cdot\text{cm}^{-2}\cdot\text{F}^{-1}$ for the polycrystalline Pt surface (Nart and Vielstich, 2003; Paulus *et al.*, 2003). As shown in Table 1, the experimental I_{PH} values for peaks I and II are smaller than I_{PH}^T at each scan rate. The larger I_{PH}^T values are reasonable, because Eq. (3) is based on the assumption that the entire surface of the electrode has the

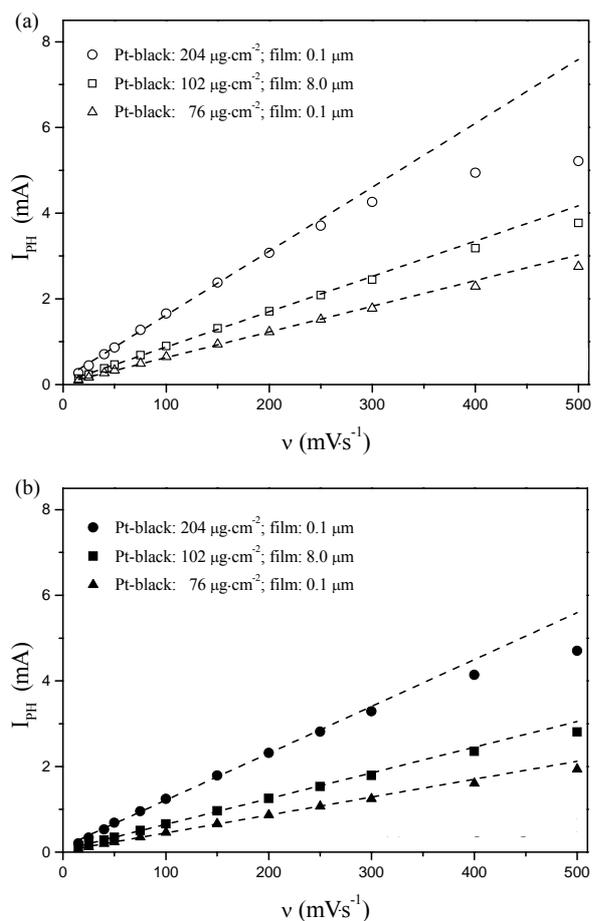


Fig. 7. I_{PH} vs. v plots for H-desorption on the Pt-black/Nafion electrodes: (a) peak I; (b) peak II.

same activity for adsorption, but this is not the case for H-adsorption on a Pt surface as indicated by the two H-adsorption/desorption peaks in the cyclic voltammogram.

The negative deviations of the I_{PH} values measured at high scan rates, as shown in Fig. 7, are thought to be the result of the insufficient adsorption of hydrogen during the cathodic scan. The lowest potential in the CV measurements was 25 mV vs. RHE. From Fig. 1, one can see that the H-adsorption wave corresponding to peak I near the lowest potential of the cathodic scan was well developed when the scan rate was sufficiently low (Fig. 1(a)), but became less well developed when the scan rate was high (Fig. 1(b)). This phenomenon was caused by the ohmic potential drop as discussed above, which resulted in the measured electrode potential being lower than the real one during the cathodic scan. Thus, when the scan rate was high, the amount of hydrogen adsorbed on an electrode was less than the true equilibrium value at 25 mV vs. RHE before the anodic scan was started, and the amount adsorbed decreased as the scan rate increased. The incomplete H-adsorption process mainly reduced the amount of weakly adsorbed hydrogen and, therefore, mainly affected the I_{PH} for peak I of the H-desorption. Furthermore, the

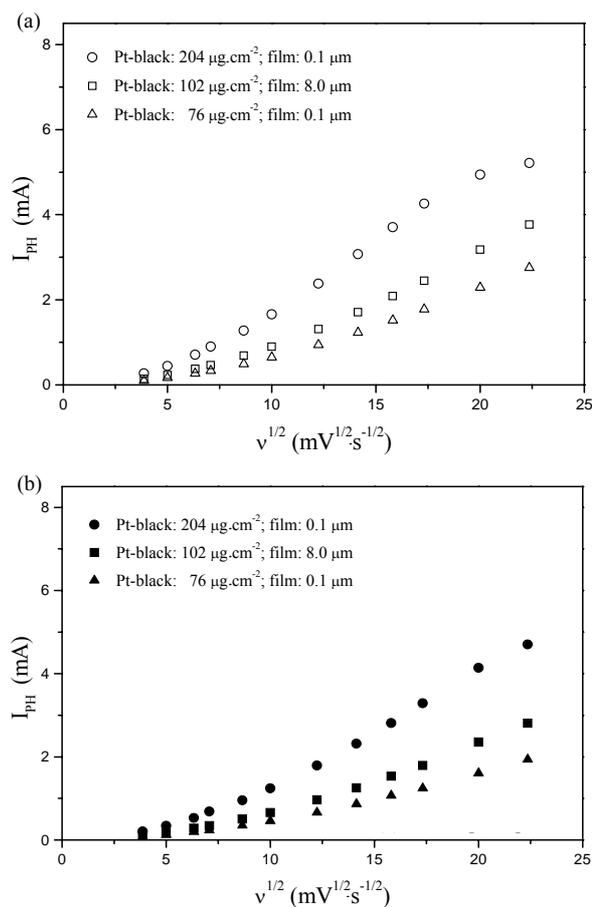


Fig. 8. I_{PH} vs. $v^{1/2}$ plots for H-desorption on the Pt-black/Nafion electrodes: (a) peak I; (b) peak II.

electrode with a higher roughness factor had a larger H-adsorption capacity, which resulted in higher H-adsorption/desorption currents and larger ohmic potential drops in the CV measurements; hence, the departure from the complete adsorption process was more appreciable for the electrode.

Catalyst surface utilization

As shown in Fig. 9, for all the electrodes with a Nafion thickness of 0.2 μm and Pt-black loadings ranging from 64 to 204 $\mu\text{g}\cdot\text{cm}^{-2}$, the hydrogen adsorption/desorption charge, Q_H , evaluated at a scan rate of 25 $\text{mV}\cdot\text{s}^{-1}$ was a linear function (a correlation coefficient of 0.9997) of the Pt-black loading. The slope (62.10 $\text{mC}\cdot\text{mg}^{-1}$) of the line was almost identical with the value (62.37 $\text{mC}\cdot\text{mg}^{-1}$) calculated from the surface charge of 210 $\mu\text{C}\cdot\text{cm}^{-2}$ for the polycrystalline Pt surface (Nart and Vielstich, 2003; Paulus *et al.*, 2003) and the BET surface area (29.7 $\text{m}^2\cdot\text{g}^{-1}$) of Pt-black. This result indicates that the electrochemical surface area of each electrode was the same as its real surface area. In other words, the utilization of the catalyst surface was 100% for these electrodes.

Additionally, it was found that at the same Pt-black loading, the Q_H values measured were essen-

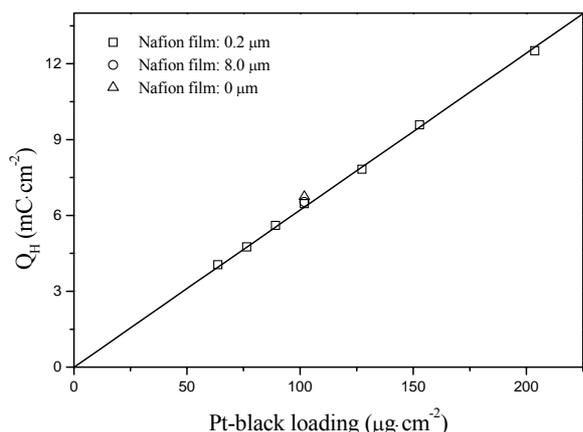


Fig. 9. The charge in the hydrogen adsorption/desorption region vs. the Pt-black loading for the Pt-black/Nafion electrodes. Scan rate: $25 \text{ mV}\cdot\text{s}^{-1}$.

tially the same for different Nafion film thicknesses from 0.1 to 8.0 μm , but they were a little bit smaller than that for the electrode without a Nafion film, as shown in Fig. 9 for the Pt-black loading of $102 \mu\text{g}\cdot\text{cm}^{-2}$. This result seems to suggest that little penetration of the Nafion binder into the catalyst layer occurred, and that the direct contact between the film and the catalyst layer was limited to the skin surface of the catalyst layer; thus, the possible site-blocking effect of Nafion on the active sites for the hydrogen electrochemical process was about the same for different film thicknesses.

The results shown in Fig. 9 indicate that the utilization of a Pt-black catalyst surface is nearly 100% at a low scan rate of $25 \text{ mV}\cdot\text{s}^{-1}$, and these thin-film electrodes behave like planar electrodes with an electrochemically extended surface area under this condition. Thus, the real surface area of an electrode with a roughness factor as high as 60 can be accurately evaluated at scan rates of $\leq 25 \text{ mV}\cdot\text{s}^{-1}$. However, as discussed below, when the scan rate was sufficiently rapid, the electrochemical surface area evaluated decreased with the increasing scan rate.

The electrochemical surface areas obtained from the Q_H measurements at various scan rates were normalized by dividing by the value at a scan rate of $25 \text{ mV}\cdot\text{s}^{-1}$, and are plotted in Fig. 10. As can be seen from the figure, when $v \geq 40 \text{ mV}\cdot\text{s}^{-1}$, the surface utilization for each electrode decreased as the scan rate increased. The reduction in the surface utilization was more marked when the Pt-black loading was higher. For example, at $500 \text{ mV}\cdot\text{s}^{-1}$, the surface utilizations were 87.7% and 76.6% for Pt-black loadings of 76 and $204 \mu\text{g}\cdot\text{cm}^{-2}$, respectively. However, due to the uncertainty in the estimated Q_H value, the differences in the surface utilizations were not significant between the electrodes with Pt-black loadings of 76 and $102 \mu\text{g}\cdot\text{cm}^{-2}$.

It was found that the Nafion film affected the

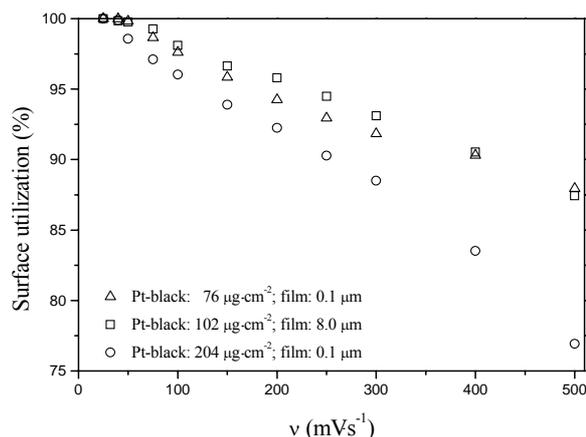


Fig. 10. Catalyst surface utilization as a function of the scan rate for the Pt-black/Nafion electrodes.

surface utilization only slightly, even at high scan rates. For example, for a Pt-black loading of $102 \mu\text{g}\cdot\text{cm}^{-2}$, a surface utilization of 90.1% was obtained at $v = 500 \text{ mV}\cdot\text{s}^{-1}$ for a $0.2 \mu\text{m}$ Nafion film and one of 87.4% was obtained for an $8.0 \mu\text{m}$ film.

The decrease in the catalyst surface utilization at high scan rates was a direct result of the decrease in the amount of hydrogen adsorbed at high scan rates as set forth in the preceding section. Therefore, when the electrochemical surface area of a Pt electrode is evaluated using the CV technique, an appropriate scan rate that does not cause excessive ohmic potential drops must be used. Otherwise, the voltammetric wave for the H-adsorption process will move in the negative direction, thus resulting in an incomplete H-adsorption process and lower catalyst surface utilization. Because the measured currents increase as the roughness factor of an electrode increases, the ohmic potential drop will be larger for the porous thin-film electrodes than for the smooth Pt electrodes under the same scan rate. This effect limits the scan rate used in the CV measurements to a low value for the accurate evaluation of the true surface area of an electrode with a high roughness factor.

CONCLUSION

The electrochemical surface areas of Pt-black/Nafion thin-film electrodes immersed in 0.5 M H_2SO_4 were measured using the cyclic voltammetry technique. The factors affecting the measurements have been examined in detail.

The H-adsorption/desorption processes on the electrodes were reversible. At potential scan rates of $\leq 40 \text{ mV}\cdot\text{s}^{-1}$, the real surface areas of the electrodes, which had roughness factors of as high as 60, were accurately evaluated. The decrease in the catalyst surface utilization measured at high potential scan

rates was due to the incomplete H-adsorption process caused by the ohmic potential drop in the solution, which resulted in the measured electrode potential being lower than the real one during the cathodic scan. The ohmic potential drop became more appreciable when the roughness factor of an electrode or the scan rate increased, due to the increase in the current. The Nafion film coating ($\leq 8 \mu\text{m}$) had a negligible effect on the electrochemical surface area measurements. The real catalyst surface area of an electrode can be accurately estimated through CV, if a scan rate that does not cause appreciable ohmic potential drops is used; the appropriate scan rate becomes lower as the roughness factor of the electrode increases.

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NOMENCLATURE

A	cross-sectional area of an electrode, cm^2
A_r	real surface area of an electrode, cm^2
a	constant defined in Eq. (8), mA
C_0^*	bulk concentration of H^+ ions, $\text{mol}\cdot\text{cm}^{-3}$
C_d	capacitance of the double layer, $\text{F}\cdot\text{cm}^{-2}$
D	diffusion coefficient of H^+ ions in the electrolyte, $\text{cm}^2\cdot\text{s}^{-1}$
E	potential of an electrode versus a reference, V
E_p	peak potential, mV vs. RHE
F	faraday constant, $96485 \text{ C}\cdot\text{mol}^{-1}$
I	current of an electrode, mA
I_c	double-layer charging current, mA
I_{PH}^I	peak current for H-desorption, mA
I_{PH}^I	peak current for H-desorption peak I, mA
I_{PH}^{II}	peak current for H-desorption peak II, mA
I_{PH}^T	theoretical peak current for H-desorption peaks, mA
I_p	peak current, mA
n	number of electrons involved in the reaction, dimensionless
n_a	number of electrons involved in the r.d.s., dimensionless
Q_H	hydrogen adsorption/desorption charge, $\text{mC}\cdot\text{cm}^{-2}$
R	gas constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
R_s	solution resistance, Ω
T	temperature, K

Greek symbols

α	transfer coefficient, dimensionless
Γ^*	moles of adsorbed hydrogen atom per unit Pt surface area, $\text{mol}\cdot\text{cm}^{-2}$
ΔE_p	peak potential shift, mV
ν	scan rate, $\text{m}\cdot\text{V}\cdot\text{s}^{-1}$

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以循環伏安法量測鉑黑/Nafion 電極之觸媒表面積

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摘 要

本研究以循環伏安法量測浸沒在 0.5 M 硫酸溶液中的鉑黑/Nafion 薄膜電極之電化學表面積。在高電位掃描速率下觸媒表面利用率減少，是由於不完全的氫吸附程序所致，溶液電阻所造成的歐姆電位降使得在負電位方向掃描時所測得的電極電位低於其真實值。當電極粗糙度或掃描速率增加時，歐姆電位降將隨著相應的電流增加而更為顯著。Nafion 膜的厚度 ($\leq 8 \mu\text{m}$) 對表面積量測幾無影響。在掃描速率未造成大幅歐姆電位降的情況下，電極觸媒的表面積可以被精確地測定；適當的掃描速率將隨電極粗糙度增加而減小。

