

Kinetic analysis of the hydrogen oxidation reaction at Nafion film covered Pt-black rotating disk electrodes

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Abstract

The kinetics of the H₂ oxidation reaction at Nafion film covered Pt-black rotating disk electrodes (RDEs) in 0.5 M H₂SO₄ at 298 K was investigated by varying the Pt loading, Nafion film thickness, and rotating rate. The equation describing the H₂ oxidation kinetics at an RDE with a Nafion film covered porous Pt layer was derived, assuming a Tafel–Volmer mechanism and taking into account the mass transfer resistances in the aqueous electrolyte, Nafion film, and Pt layer. The H₂ oxidation reaction at the Pt layer was proved to be reversible and the measurable current density was determined entirely by the mass transfer of H₂ in the aqueous electrolyte and the Nafion film; the apparent kinetic current density measured was due to the experimental error. More accurate results of kinetic analysis were obtained in this work than our results reported previously.

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1. Introduction

Fuel cell is a clean and efficient energy technology that converts chemical energy directly into electrical energy without emissions of air pollutants. Particularly, proton exchange membrane fuel cells (PEMFCs) have recently received more attention due to their high power density at relatively low temperatures (Kordesch and Simader, 1996; Ralph, 1997). The fuel (H₂) and oxidant (O₂ or air) gases are supplied to the anode and cathode of a fuel cell, respectively, and react with the aid of catalysts to produce electricity.

Platinum and Nafion respectively serve as the most widespread electrocatalyst and polymer electrolyte in low-temperature fuel cells. Understanding the reaction kinetics at electrodes made of Pt and Nafion, including H₂ oxidation and O₂ reduction, is important to fuel cell design. Rotating disk electrode (RDE) is an effective means of studying the electrochemical reaction kinetics (Schmidt and Gasteiger, 2003). The hydrogen oxidation reaction kinetics at Nafion covered Pt-black or Pt on carbon electrodes has been studied by

several investigators using the RDE technique under fuel cell relevant conditions (Lin and Shih, 2006a, 2007; Schmidt *et al.*, 1998, 1999). For these electrodes, the catalyst powder is first immobilized on a rotating disk substrate and then the catalyst layer is coated with a Nafion film, forming a thin-layer electrode assembly similar to that used in fuel cells. Although these electrodes have a porous catalyst layer, the equation used to analyze the kinetics by the previous investigators is the Koutecky–Levich equation derived for a smooth Pt electrode (Bard and Faulkner, 2001).

The purpose of this work was to derive the equation appropriate for analyzing the hydrogen oxidation reaction kinetics at an RDE with a Nafion film covered porous Pt layer and reexamine our previous results obtained for Nafion film covered Pt-black RDEs (Lin and Shih, 2006a).

2. Experimental

2.1. Materials

A 5 wt.% Nafion solution prepared by dissolving Nafion in the mixture of isopropanol and water (1100 EW, Ion Power) was used to recast the Nafion film. Pt-black (HiSPEC™1000, Johnson Matthey) was used as the dispersed catalyst. Glassy

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Nomenclature

a	active surface area per unit volume of catalyst layer (1/cm)
b	$=\exp(nF\eta/RT)$
B	Levich constant (mC cm/mol)
C	H ₂ concentration at catalyst surface (mol/cm ³)
C_f	HC_0 (mol/cm ³)
C_N	H ₂ concentration at aqueous electrolyte/Nafion interface (mol/cm ³)
C_S	H ₂ concentration at catalyst/Nafion interface (mol/cm ³)
C_0	H ₂ concentration in the bulk of aqueous electrolyte (mol/cm ³)
D	H ₂ diffusivity in aqueous electrolyte (cm ² /s)
D_e	effective diffusivity of H ₂ in electrolyte filled catalyst layer (cm ² /s)
D_f	H ₂ diffusivity in polymer film (cm ² /s)
F	Faraday constant (96487 C/mol)
H	partition coefficient of H ₂ between Nafion film and aqueous electrolyte
i	local current density in catalyst layer (mA/cm ²)
i_k	kinetic current density (mA/cm ²)
i_l	limiting current density (mA/cm ²)
i_m	measured current density (mA/cm ²)
i_0	exchange current density (mA/cm ²)
k_m	mass transfer coefficient in aqueous electrolyte (mA cm/mol)
L	Nafion film thickness (μm)
L_c	catalyst layer thickness (μm)
n	number of electrons involved in the reaction
R	gas constant (8.314 J/(mol K))
T	absolute temperature (K)
Y_0	Levich intercept (cm ² /mA)
z	distance from the Nafion/catalyst interface (μm)

Greek symbols

δ	roughness factor of electrode surface
ε	effectiveness factor
ε_l	limiting value of effectiveness factor
η	overpotential (mV)
θ_0	equilibrium coverage of catalyst surface by hydrogen at $i = 0$
ν	kinematic viscosity (cm ² /s)
Φ	Thiele modulus
Φ_l	limiting value of Thiele modulus
ω	rotation rate (rpm)

carbon (GC) disk electrode (disk area = 0.1963 cm² and shroud area = 1.131 cm², Pine Instruments) was served as the substrate for the deposition of the catalyst. The disk was polished with a 0.05 μm alumina powder (CHI Instruments) before use. The electrolyte was 0.5 M H₂SO₄ solution prepared from concentrated sulfuric acid (J.T. Baker) and ultrapure water (18 MΩ, Millipore). High purity H₂ gas (99.999%, San-Fu) was used.

2.2. Thin-film electrode preparation

Aqueous catalyst suspensions of 1–2 mg/mL were prepared by mixing 25–50 mg of Pt-black and 25 mL of deionized water under ultrasonication for about 10 min. A volume of 15–20 μL of the catalyst suspension was pipetted onto the GC disk surface. The deposit was dried at room temperature for about 1.5 h and then at 70 °C for 30 min. After the catalyst layer was dry, 20 μL of Nafion solution was put on its top. Subsequent annealing at 70 °C in a vacuum oven was made for at least 40 min to evaporate the residual solvent in the resulting thin-film electrode. This annealing treatment renders the Nafion film insoluble and with sufficient strength to bind the catalyst particles (Zook and Leddy, 1996). The concentration of Nafion solution was varied by diluting the 5 wt.% Nafion solution with isopropanol to yield recast films with thicknesses ranged from 0.1 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/cm³ (Watanabe *et al.*, 1995; Zook and Leddy, 1996). About 90% of the shroud area was found to be 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), and the difference between the measured and calculated values was about 6%.

2.3. Electrochemical experiments

The rotating disk electrode was housed in a conventional three-compartment glass cell with a saturated calomel reference electrode (SCE) and a Pt foil counter electrode. The electrochemical behavior of an electrode was measured using a potentiostat (Autolab PGSTAT30, Ecochemie) with a computer-controlled general purpose electrochemical system (GPES). Throughout this study, all potentials were referred to the reversible hydrogen electrode (RHE) scale.

Before starting the electrochemical measurement, the electrode was immersed for 8–10 h in deaerated 0.5 M H₂SO₄ solution, which exhibited a very similar pH value to that of the Nafion film. Characteristic cyclic voltammogram (CV) for an electrode in deaerated 0.5 M H₂SO₄ was obtained after cycling the potential of the electrode between 0 and 1.2 V vs. RHE for 1 h (Lin and Shih, 2006b). This long run-in period was necessary to obtain stable and reproducible data.

Experiments for the H₂ oxidation reaction at an electrode were performed by rotating the electrode immersed in H₂-saturated 0.5 M H₂SO₄ solution at room temperature (25 ± 1 °C). The rotation rates were in the range from 400 to 3600 rpm. H₂ was passed through the solution for 40 min before the experiment started and above the solution during the experiment. The potential of the electrode was changed between 0 and 0.4 V vs. RHE at a scan rate of 5 mV/s.

3. Results and discussion

3.1. Experimental results of H₂ oxidation reaction

The H₂ oxidation reaction was studied using electrodes for which the Pt-black loading varied from 76 to 204 μg/cm² and the Nafion film thickness varied from 0.1 to 8.0 μm. The voltammograms for some electrodes are represented in Fig. 1. One can see that the current density, i_m , increases with increasing overpotential, η , and reaches a limiting value when the overpotential is about 70 mV vs. RHE. At the same overpotential, the current density increases with increasing rotation rate and is larger when the Nafion film is thinner at the same rotation rate. As seen in Fig. 1(a), the increase in Pt loading did not cause the current density to change accordingly and significantly at each rotation rate; therefore, the variations of the current density were due to the experimental errors. The variations of the limiting current density were about ±0.04 to ±0.12 mA/cm² from the mean as the rotation rate was increased from 400 to 3600 rpm. The experimental errors are thought to arise mainly from the uncertainty in the measurement of the Nafion film thickness. Moreover, as shown

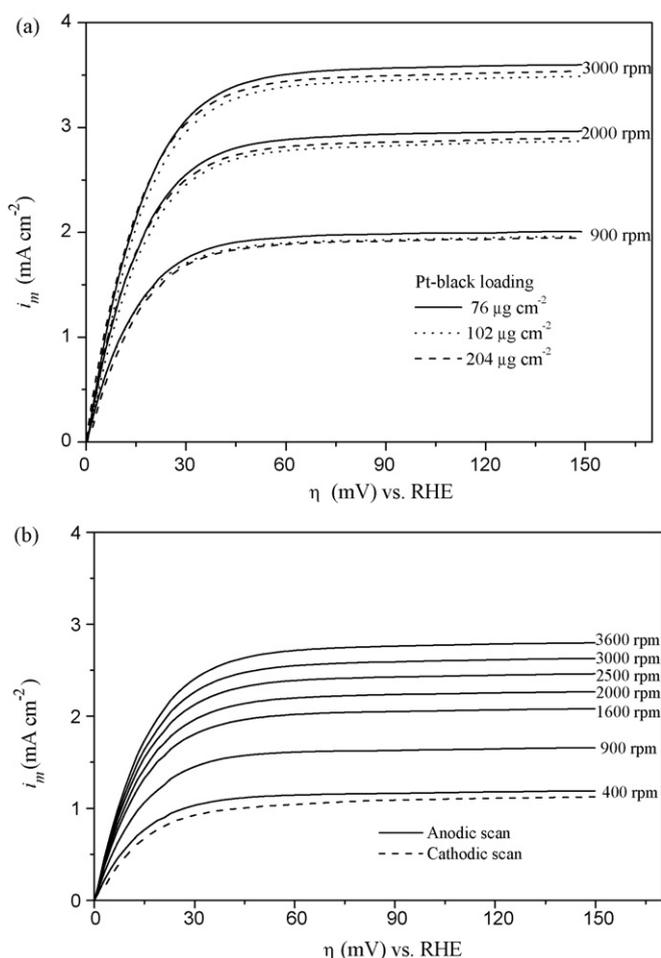
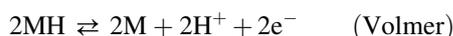


Fig. 1. Hydrodynamic voltammograms for H₂ oxidation at the Nafion film covered Pt-black electrodes with the film thicknesses of (a) 0.2 μm (Pt-black loading: 76–204 μg/cm²) and (b) 4.0 μm (Pt-black loading: 102 μg/cm²) in H₂-saturated 0.5 M H₂SO₄ electrolyte. Scan rate: 5 mV/s.

in Fig. 1(b), the hysteresis of H₂ oxidation currents between the anodic and cathodic scans caused by the double layer capacitance was minute (about 0.07 mA/cm² at 0.15 V vs. RHE). Anodic voltammograms obtained were analyzed in this study.

3.2. Equations for kinetic analysis

Vogel *et al.* (1975) have studied the H₂ oxidation reaction on Pt electrocatalysts in acid solutions. They found that the reaction follows the Tafel–Volmer sequence,



with the dissociation reaction (Tafel) rate controlling.

According to their derivation, the local current density, i , in the catalyst layer can be written as

$$i = \frac{i_0 e^{2F\eta/RT}}{C_0} \left[\frac{1}{\theta_0 + (1 - \theta_0) e^{F\eta/RT}} \right]^2 \left(C - \frac{C_0}{e^{2F\eta/RT}} \right) \quad (1)$$

where i_0 is the exchange current per unit catalyst surface area, F is the Faraday constant, η is the overpotential, R is the gas constant, T is the absolute temperature, θ_0 is the equilibrium coverage of the catalyst surface by hydrogen at $i = 0$; and C and C_0 are the hydrogen concentrations at the catalyst surface and in the bulk of the aqueous electrolyte, respectively.

For H₂ oxidation at an RDE with a Nafion film covered catalyst layer, H₂ molecules in the bulk of the aqueous electrolyte must move to the Nafion film surface, permeate through the Nafion film, and then diffuse into the pores of the catalyst layer before they react on the Pt particle surface. Therefore, the mass transfer resistances in the aqueous electrolyte, Nafion film, and catalyst layer should be taken into account.

The diffusional effect of H₂ on the overall reaction rate of the catalyst layer can be represented by the effectiveness factor, ε , which is the ratio of the rate affected by the diffusion of H₂ in the catalyst layer to that unaffected. According to Stonehart and Ross (1976),

$$\varepsilon = \frac{\tanh \Phi}{\Phi} \quad (2)$$

where

$$\Phi = L_c \left(\frac{a i_0 b}{2FC_0 D_e} \right)^{1/2} \left[\frac{1}{\theta_0 + (1 - \theta_0) b^{1/2}} \right] \quad (3)$$

and L_c is the thickness of catalyst layer, a is the active surface area per unit volume of catalyst layer, D_e is the effective diffusivity of H₂ in the electrolyte filled catalyst layer, and $b = \exp(2F\eta/RT)$.

Assuming steady state, the overall reaction rate of H₂ at the catalyst layer, the mass transfer rate of H₂ through the Nafion film, and the mass transfer rate of H₂ from the bulk of the electrolyte to the Nafion film surface are equal. In this case, the current density based on the electrode geometric area, i_m , can

be written as

$$i_m = \frac{\varepsilon \delta i_0 b}{C_0} \left[\frac{1}{\theta_0 + (1 - \theta_0) b^{1/2}} \right]^2 \left(C_s - \frac{C_0}{b} \right) \\ = \frac{nFD_f H}{L} (C_N - C_s) = nFk_m (C_0 - C_N) \quad (4)$$

where δ is the roughness factor, which is the ratio of the total catalyst surface area to the electrode geometric area; C_s and C_N are the H_2 aqueous-phase concentrations at the catalyst/Nafion and the aqueous electrolyte/Nafion interfaces, respectively; n is the number of electrons (=2) involved in the electrode reaction; D_f is the diffusivity of H_2 in the Nafion film; H is the partition coefficient of H_2 between the Nafion film and the aqueous electrolyte; L is the thickness of the Nafion film; and k_m is the liquid-phase mass transfer coefficient of H_2 . For an RDE, nFk_m is given by (Bard and Faulkner, 2001)

$$nFk_m = 0.62nFD^2/3 \nu^{-1/6} \omega^{1/2} = B\omega^{1/2} \quad (5)$$

where D is the reactant diffusivity in the electrolyte, ν is the electrolyte kinematic viscosity, and ω is the rotation rate. It should be noted that ε or Φ is not a function of C_s (see Appendix A) and is not affected by the presence of the mass transfer resistances in the Nafion film and aqueous electrolyte.

The relations expressed by Eq. (4) can be rearranged to give an equation similar to the Koutecky–Levich equation (Bard and Faulkner, 2001),

$$\frac{1}{i_m} = \left(\frac{b}{b-1} \right) \\ \times \left\{ \frac{1}{\varepsilon \delta i_0 b / [\theta_0 + (1 - \theta_0) b^{1/2}]^2} + \frac{1}{nFD_f C_f / L} + \frac{1}{BC_0 \omega^{1/2}} \right\} \quad (6)$$

where $C_f = HC_0$. Eq. (6) is also applicable to smooth Pt RDEs by letting $\varepsilon = 1$; in this case, the term $\delta i_0 b / [\theta_0 + (1 - \theta_0) b^{1/2}]^2$ is called the kinetic current density.

As seen from the above equation, when η is large enough, i_m reaches the limiting value, i_l , given by

$$\frac{1}{i_l} = \frac{1}{\varepsilon_1 \delta i_0 / (1 - \theta_0)^2} + \frac{1}{nFD_f C_f / L} + \frac{1}{BC_0 \omega^{1/2}} \quad (7)$$

where ε_1 is the limiting value of ε when Φ reaches Φ_1 at large enough η ; Φ_1 is given by

$$\Phi_1 = L_c \left[\frac{a i_0}{2FC_0 D_e (1 - \theta_0)^2} \right]^{1/2} \quad (8)$$

If $\Phi_1 \gg 1$, Eq. (2) reduces to

$$\varepsilon_1 = \Phi_1^{-1} \quad (9)$$

and the denominator of the first term of Eq. (7) becomes

$$\varepsilon_1 \delta i_0 (1 - \theta_0)^{-2} = (2FC_0 D_e a i_0)^{1/2} (1 - \theta_0)^{-1} \quad (10)$$

Therefore, when $\Phi_1 \gg 1$, i_l is independent of L_c or the Pt loading provided a is kept constant.

Eq. (7) shows that a plot of $1/i_m$ vs. $\omega^{-1/2}$ at a sufficiently high overpotential is a straight line with a slope of $1/BC_0$ and an intercept, Y_0 , corresponding to

$$Y_0 = \frac{1}{\varepsilon_1 \delta i_0 / (1 - \theta_0)^2} + \frac{L}{nFD_f C_f} \quad (11)$$

According to Eq. (11), the values of $D_f C_f$ and $\varepsilon_1 \delta i_0 (1 - \theta_0)^{-2}$ can be determined by plotting Y_0 vs. L .

If the H_2 oxidation reaction is very rapid, i.e., $\varepsilon \delta i_0 \rightarrow \infty$, Eqs. (6) and (7) become

$$\frac{1}{i_m} = \left(\frac{b}{b-1} \right) \frac{1}{i_l} \quad (12)$$

$$\frac{1}{i_l} = \frac{1}{nFC_f D_f / L} + \frac{1}{BC_0 \omega^{1/2}} \quad (13)$$

Eq. (12) can be rearranged to give

$$e^{-2F\eta/RT} = 1 - \frac{i_m}{i_l} \quad (14)$$

or

$$\eta = \frac{-2.303RT}{2F} \log \left(1 - \frac{i_m}{i_l} \right) \quad (15)$$

Therefore, a plot of η vs. $\log[(i_l - i_m)/i_l]$ will yield a straight line with a zero intercept and a slope of $-2.303RT/2F$, no matter what Pt loading, rotation rate, and Nafion film thickness are used.

3.3. Estimation of kinetic parameters

Fig. 2 shows the plots of $\log[(i_l - i_m)/i_l]$ vs. η . One can see that the plots are linear and nearly coincide for different rotation rates and Nafion film thicknesses. The inverse of the slope of the plot was found to be -34.8 ± 1.5 mV/dec in average, which is in good agreement with the theoretical value (-30 mV/dec at 25°C) given by Eq. (15). This result indicates that the H_2 oxidation reaction at the catalyst layer was very facile, or a so-called reversible reaction (Bard and Faulkner, 2001), and the oxidation rate was entirely controlled by the mass transfer of H_2 in the aqueous electrolyte and the Nafion film. This result also explains why the current density was unaffected by the Pt loading. Mello and Ticianelli (1997) have reported that the H_2 oxidation reaction at bare and Nafion covered smooth Pt RDEs in 0.5–0.01 M H_2SO_4 solutions is reversible. Because the roughness factors of our electrodes (which is about 23 for $76 \mu\text{g}/\text{cm}^2$ Pt loading) are much greater than that of a smooth Pt electrode, the H_2 oxidation reaction at our electrodes must be reversible also.

The i_m^{-1} vs. $\omega^{-1/2}$ plots for different Nafion film thicknesses at $\eta = 100$ mV are shown in Fig. 3. These plots are linear and parallel to each other. The slopes of the lines are $1/BC_0$ according to Eq. (7). The average value of BC_0 obtained from the line slopes is $(6.68 \pm 0.09) \times 10^{-2}$ mA/(cm² rpm^{1/2}). This BC_0 value is in excellent agreement with that, 6.54×10^{-2} mA/(cm² rpm^{1/2}), calculated by Gasteiger *et al.*

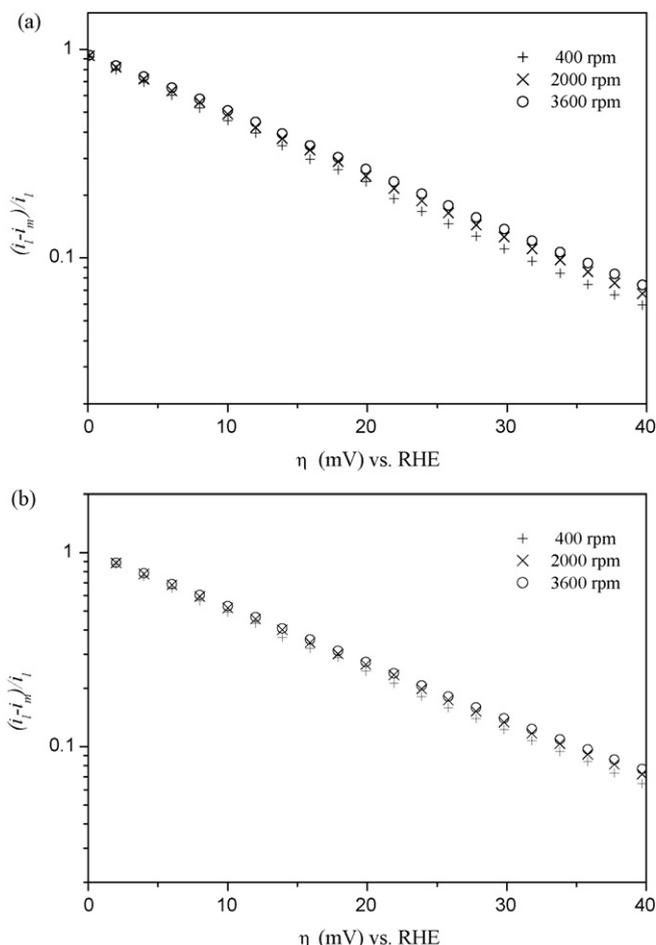


Fig. 2. Mass transfer corrected Tafel plots for H_2 oxidation at the Nafion film covered Pt-black electrodes (Pt-black loading: $102 \mu\text{g}/\text{cm}^2$) with the film thickness of (a) $0.2 \mu\text{m}$ and (b) $8.0 \mu\text{m}$ in H_2 -saturated $0.5 \text{ M } H_2SO_4$ electrolyte.

(1995) at 25°C , using $n = 2$, $D = 3.7 \times 10^{-5} \text{ cm}^2/\text{s}$, $\nu = 1.07 \times 10^{-2} \text{ cm}^2/\text{s}$, and $C_0 = 7.14 \times 10^{-4} \text{ M}$ (their original C_0 value should be corrected by dividing by 10).

The intercepts (Y_0) obtained from the i_m^{-1} vs. $\omega^{-1/2}$ plots at $\eta = 400 \text{ mV}$ are plotted in Fig. 4 as a function of L . One can see

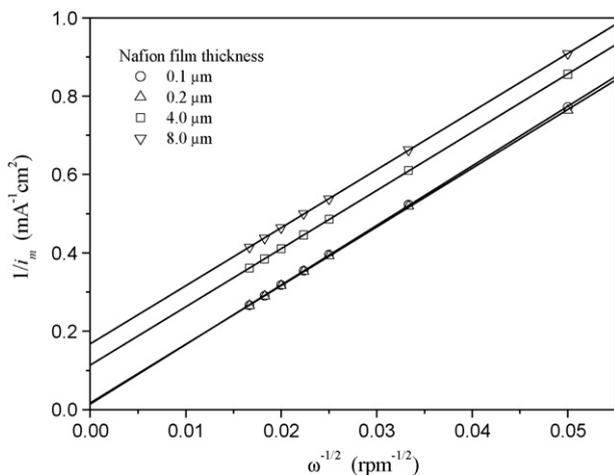


Fig. 3. Koutecky–Levich plots for H_2 oxidation at $\eta = 100 \text{ mV}$ at the Nafion film covered Pt-black electrodes (Pt-black loading: $102 \mu\text{g}/\text{cm}^2$) with various film thicknesses.

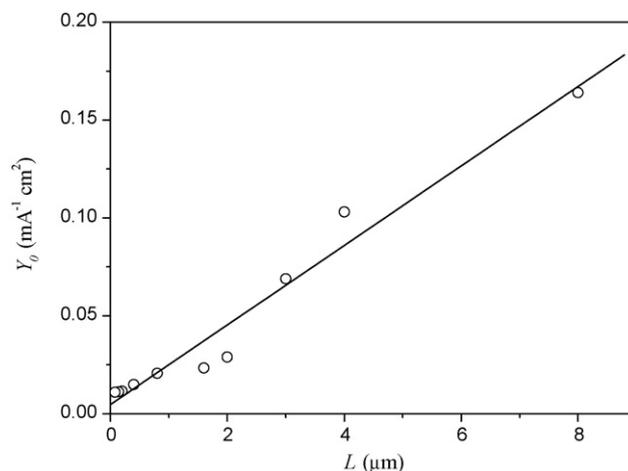


Fig. 4. Y_0 vs. L plots for H_2 oxidation at $\eta = 400 \text{ mV}$ at the Nafion film covered Pt-black electrodes (Pt-black loading: $102 \mu\text{g}/\text{cm}^2$) with various film thicknesses.

that Y_0 data approach to a small positive value, about $0.011 \text{ cm}^2/\text{mA}$, when $L \leq 0.2 \mu\text{m}$. The inverse of this Y_0 value, about $90 \text{ mA}/\text{cm}^2$, was taken as the value of the kinetic current density, i_k , in our previous work (Lin and Shih, 2006a). However, because the H_2 oxidation reaction is reversible, Y_0 should be zero when L is zero according to Eq. (11). Therefore, the small Y_0 value at $L \leq 0.2 \mu\text{m}$ are considered to be due to the error in Y_0 estimated. This explanation was confirmed by the error analysis of the estimated value of Y_0 at $L = 0$. The linear regression of the data in Fig. 4 using Eq. (11) gave a value of Y_0 at $L = 0$ of $0.0047 \text{ cm}^2/\text{mA}$ and its standard error of $0.0042 \text{ cm}^2/\text{mA}$. The 95% confidence interval of Y_0 at $L = 0$ was calculated to be $0.0047 \pm 0.0098 \text{ cm}^2/\text{mA}$. This confidence interval reveals that the true value of Y_0 at $L = 0$ is essentially zero because Y_0 cannot be negative.

Some previous investigators (Schmidt *et al.*, 1998; Schmidt and Gasteiger, 2003; Watanabe *et al.*, 1995) also obtained small Y_0 values for the H_2 oxidation reaction at Pt electrodes with or without a very thin Nafion film at high overpotentials. Their corresponding i_k values range from 40 to $60 \text{ mA}/\text{cm}^2$. Watanabe *et al.* (1995) attributed their i_k values to some rate-limiting chemical process. However, Schmidt and Gasteiger (2003) attributed the i_k values to the error in Y_0 estimated and the residual resistance due to the thin Nafion film.

The slope of the linear regression line in Fig. 4 gave a $D_f C_f$ value of $(2.6 \pm 0.2) \times 10^{-11} \text{ mol}/(\text{cm s})$ according to Eq. (11); this $D_f C_f$ value is very close to that, $2.4 \times 10^{-11} \text{ mol}/(\text{cm s})$, obtained when zero intercept was assumed. This $D_f C_f$ value is considered to be more accurate than that, $5.2 \times 10^{-11} \text{ mol}/(\text{cm s})$, obtained previously by the nonlinear regression of the Y_0^{-1} vs. L^{-1} data (Lin and Shih, 2006a), because the linear regression method gave a Y_0 value at $L = 0$ very close to that should be for the reversible H_2 oxidation reaction.

The $D_f C_f$ value determined is close to the product of the hydrogen solubility, C_0 , and diffusivity, D , in $0.5 \text{ M } H_2SO_4$ mentioned previously or reported by Mello and Ticianelli (1997) ($0.59 \times 10^{-6} \text{ mol}/\text{cm}^3$ and $3.8 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively), but is higher than the values for recast Nafion films

reported in literatures (Maruyama *et al.*, 1998; Mello and Ticianelli, 1997; Watanabe *et al.*, 1995). For instance, a $D_f C_f$ value of 9.0×10^{-12} mol/(cm s) for those immersed in 0.5 M H_2SO_4 was reported by Mello and Ticianelli (1997). The discrepancy in the $D_f C_f$ values reported can be explained partly by the errors in the experimental measurements, especially in the estimation of the film thickness, and the different methods of data treatment. Furthermore, the structural properties of the Nafion film, such as the pore size and the distribution of the hydrophilic and hydrophobic phases, are known to affect the $D_f C_f$ value significantly (Gottesfeld *et al.*, 1987; Zook and Leddy, 1996). It should be noted that the Nafion films prepared in this study are much thinner than those used by the previous authors.

Because the H_2 oxidation reaction is reversible, the value of i_0 cannot be determined in this work. The values of i_0 reported in the literature, however, vary markedly. Vogel *et al.* (1975) reported that i_0 values for smooth Pt, Pt black, and Pt on carbon are of no difference, about 22 mA/cm² in 96 wt.% $HClO_4$ at 22 °C. A value of 1.62 mA/cm² was reported by Markovic *et al.* (1997) for a Nafion coated smooth Pt electrode in 0.1 M $HClO_4$. A value of 0.25 mA/cm² was obtained by Jiang and Kucernak (2004) for their porous Pt microelectrodes in 0.5 M H_2SO_4 at 293 K. Markovic *et al.* (1997) found that the i_0 for the H_2 oxidation on Pt is unique with respect to the crystal surfaces. From their results obtained in 0.05 M H_2SO_4 , the i_0 values on Pt (1 1 0), Pt (1 0 0), and Pt (1 1 1) surfaces at 298 K were estimated to be 0.92, 0.55, and 0.40 mA/cm², respectively. One of the possible reasons for this great variation of i_0 value is that the electrochemical reaction itself is so rapid that the mass transfer resistance is relatively much greater than the electrochemical reaction resistance and, therefore, i_0 cannot be determined or accurately determined. In order to obtain accurate i_0 value for the H_2 oxidation reaction on Pt by using the RDE technique, the catalyst surface area per unit volume of catalyst layer, a , should be made very small.

For electrodes used in this study, the kinetics of H_2 oxidation reaction can be described by Eqs. (12) and (13). The i_m values calculated using Eqs. (12) and (13) and the parameters estimated were in good agreement with measured values; the differences between the calculated and measured i_1 values were less than 10%.

4. Conclusion

The kinetics of the hydrogen oxidation reaction at Nafion film covered Pt-black RDEs in 0.5 M H_2SO_4 at 298 K was investigated. The equation describing the H_2 oxidation kinetics at an RDE with a Nafion film covered porous Pt layer was derived, assuming a Tafel–Volmer mechanism and taking into account the mass transfer resistances in the aqueous electrolyte, Nafion film, and Pt layer. The hydrogen oxidation reaction at the Pt layer was proved to be reversible and the measurable current density was determined entirely by the mass transfer of hydrogen in the aqueous electrolyte and the Nafion film. The apparent kinetic current densities measured were due to experimental errors. The $D_f C_f$ value obtained for Nafion films was affected by the method of data treatment; the value

obtained in this work is considered to be more accurate than that reported in the previous work (Lin and Shih, 2006a). In order to obtain accurate exchange current density by using the RDE technique, the Pt surface area per unit volume of Pt layer should be made very small.

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Appendix A

For H_2 oxidation at a Nafion covered catalyst layer RDE immersed in acid solution, the diffusion of H_2 in the catalyst layer can be described by the following equations:

$$D_e \frac{d^2 C}{dz^2} - \frac{ai}{2F} = 0 \quad (A-1)$$

$$C = C_s \quad \text{at} \quad z = 0 \quad (A-2)$$

$$\frac{dC}{dz} = 0 \quad \text{at} \quad z = L_c \quad (A-3)$$

where z is the distance from the Nafion/catalyst interface and the other symbols have the same meanings as in the text. The expression of i is given by Eq. (1). Eqs. (A-1)–(A-3) can be solved to give the concentration profile:

$$\frac{(C/C_0) - 1/b}{(C_s/C_0) - 1/b} = \frac{\cosh[\Phi(1 - (z/L_c))]}{\cosh \Phi} \quad (A-4)$$

where Φ is given by Eq. (3).

From the definition of ε ,

$$\varepsilon = \frac{\int_0^{L_c} (C - (C_0/b)) dz}{(C_s - (C_0/b))L_c} = \frac{\tanh \Phi}{\Phi} \quad (A-5)$$

Therefore, ε is not a function of C_s , and is the same as that obtained with $C_s = C_0$.

The measurable electrode current density is given by

$$i_m = 2FD_e \left. \frac{dC}{dz} \right|_{z=0} = 2FD_e C_0 \left(\frac{C_s}{C_0} - \frac{1}{b} \right) \left(\frac{\Phi}{L_c} \right) \tanh \Phi \quad (A-6)$$

Combining with Eqs. (A-5) and (3), Eq. (A-6) can be expressed in terms of ε :

$$i_m = \frac{\varepsilon \delta i_0 b}{C_0} \left[\frac{1}{\theta_0 + (1 - \theta_0)b^{1/2}} \right]^2 \left(C_s - \frac{C_0}{b} \right) \quad (A-7)$$

When the mass transfer resistances in the Nafion film and the aqueous electrolyte are absent, C_s is equal to C_0 , and Eq. (A-6) or (A-7) reduces to that given by Stonehart and Ross (1976).

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