Available online at www.sciencedirect.com
ScienceDirect
Journal of the Chinese Institute of Chemical Engineers 38 (2007) 365–370
JOURNAL OF THE CHINESE INSTITUTE OF CHEMICAL ENGINEERS
www.elsevier.com/locate/jcice

Kinetics of hydrogen oxidation reaction on Nafion-coated Pt/C electrodes under high overpotentials

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Received 12 March 2007; accepted 13 June 2007

Abstract

The influences of the Nafion film thickness and Pt loading on the kinetics of the hydrogen oxidation reaction on Nafion-coated 20 wt% Pt/C electrodes immersed in 0.5 M H_2SO_4 were investigated using a rotating disk electrode configuration. The coating of a Nafion film (≤ 8 μm) had a negligible effect on the electrochemical surface area of an electrode. The kinetic parameters were estimated at an overpotential of 0.4 V; the values obtained were shown to vary with the method of data treatment. The diffusional resistance for H_2 in the Nafion film was negligible when the film was thinner than 0.2 μm. The permeability of H_2 in the Nafion film ranged from 2.4×10^{-5} to 4.8×10^{-5} mM cm^2/s. The error analysis demonstrated that the apparent kinetic current estimated was resulted from experimental errors, instead of resulting from a chemical process as proposed by some previous investigators.

Keywords: Platinum on carbon; Nafion; Rotating disk electrode; Hydrogen oxidation; Fuel cells

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have recently been the focus of many investigations due to their high power density at relatively low temperatures (Ralph, 1997). Platinum is the most widespread electrocatalyst used in fuel cells (Kordesch and Simader, 1996; Mehta and Cooper, 2003). In PEMFCs, electrodes are prepared using a solid polymer electrolyte (*e.g.* Nafion) and a highly dispersed Pt powder (black) or Pt nanoparticles supported on various forms of carbon (Pt/C). The way of incorporating the solid polymer electrolyte into the catalyst layer has been found to markedly affect the catalyst utilization and fuel cell performance (Sasikumar *et al.*, 2004; Ticianelli *et al.*, 1988; Uchida *et al.*, 1995; Wilson and Gottesfeld, 1992a,b; Wilson *et al.*, 1995). The polymer electrolyte facilitates the transport of ions, but gives rise to an appreciable mass transfer resistance if an excess amount is used. Thus, an understanding of the mass-transfer properties of the polymer electrolyte is essential to the design of PEMFCs. Investigations of the mass-transfer resistance of the polymer electrolyte for the H_2 oxidation (Maruyama *et al.*, 1998; Watanabe *et al.*, 1995) or the O_2 reduction (Gottesfeld *et al.*, 1987; Lawson *et al.*, 1988; Zecevic *et al.*, 1997) reported in the literature are mainly for the smooth Pt electrodes coated with the polymer electrolyte and relatively fewer for electrodes consisting of Pt-black or Pt/C catalyst particles and the polymer electrolyte (Mo *et al.*, 2002; Schmidt and Gasteiger, 2003; Shan and Pickup, 2000).

The rotating disk electrode (RDE) is a useful means to study the electrocatalytic reaction kinetics (Gloaguen *et al.*, 1994; Gojkovic *et al.*, 1998; Schmidt *et al.*, 1998, 1999; Schmidt and Gasteiger, 2003) and has been widely used to study the mass transfer resistance of the polymer electrolyte to the hydrogen oxidation reaction. Most investigators estimated the resistance of each step in the hydrogen oxidation reaction at a high overpotential where the current density reaches the limiting value. However, the results reported in the literature vary considerably (Mello and Ticianelli, 1997; Schmidt *et al.*, 1998; Schmidt and Gasteiger, 2003; Watanabe *et al.*, 1995). In order to elucidate what caused the discrepancies, this work was undertaken.

In the present work, the hydrogen oxidation reaction on the Nafion-coated Pt/C electrodes was investigated using the RDE technique. This work showed that the values of the kinetic

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doi:10.1016/j.jcice.2007.06.002

Nomenclature

B	Levich constant (mC cm/mol)
C_f	H_2 solubility in Nafion film (mol/cm^3)
C_0	H_2 solubility in aqueous electrolyte (mol/cm^3)
D	H_2 diffusivity in aqueous electrolyte (cm^2/s)
D_f	H_2 diffusivity in Nafion film (cm^2/s)
E	potential of an electrode versus a reference (V)
F	Faraday constant (96,485 C/mol)
i_d	current density limited by diffusion in aqueous electrolyte (mA/cm^2)
i_f	current density limited by diffusion in Nafion film (mA/cm^2)
i_k	kinetic current density (mA/cm^2)
i_m	measured current density (mA/cm^2)
L	Nafion film thickness (μm)
n	number of electrons involved in the reaction
Y_0	Levich intercept (cm^2/mA)
Greek symbols	
ν	kinematic viscosity (cm^2/s)
ω	rotation rate (rpm)

parameters estimated may differ due to different methods of data treatment and that a small apparent chemical reaction resistance may be measured due to the experimental errors in the kinetic measurements.

2. Experimental

The Pt catalyst used was 20 wt% platinum on Vulcan XC-72R carbon black (HiSPEC^{TM}3000, Johnson Matthey). The Pt active surface area was 110 m^2/g_{Pt} determined by gas-phase CO chemisorption. The Pt crystal size was 2.6 nm determined by X-ray diffraction. A glassy carbon (GC) disk electrode (disk area = 0.1963 cm^2 and shroud area = 1.131 cm^2, Pine Instruments) was served as the substrate for the deposition of the catalyst. A 5 wt% Nafion solution prepared by dissolving Nafion in a mixture of isopropanol and water (1100 equivalent weight, Ion Power) was used to recast the Nafion film. The electrolyte was 0.5 M H_2SO_4 solution prepared form concentrated sulfuric acid (J.T. Baker) and ultrapure water (18 MΩ, Millipore). High purity H_2 gas (99.999%, San-Fu) was used.

Aqueous catalyst suspensions (1–2 mg/mL) were prepared by mixing Pt/C catalyst particles and deionized water under ultrasonication for about 10 min. About 10–20 μL of the catalyst suspension was pipetted onto the GC disk surface. The deposit dried at room temperature. After the catalyst layer was dry, 20 μL of Nafion solution was put onto its top. Subsequent annealing in a vacuum oven (70 °C) for at least 40 min rendered the recast 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 ranging 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/cm^3 (Schmidt and Gasteiger, 2003; Watanabe *et al.*, 1995; Zook and Leddy, 1996). The geometric area of the Nafion coating was ≈1.0 cm^2. The film thickness (in the range from 0.5 to 3.0 μm) was further measured using a surface texture profilometer (Dektak 3030, Sloan Technology), and the average difference between the measured and calculated values was about 6%.

The electrochemical behaviors of the Nafion-coated Pt/C electrodes were studied using a conventional three-compartment glass cell with a saturated calomel reference electrode (SCE) and a Pt foil counter electrode. Electrochemical measurements were conducted at room temperature (25 ± 1 °C) using a potentiostat (Autolab PGSTAT30, Eco-chemie) with a computer-controlled general purpose electrochemical system (GPES). All potentials were referred to the reversible hydrogen electrode (RHE) scale. Before the electrochemical measurement started, the electrode was immersed in deaerated 0.5 M H_2SO_4 solution for 8–10 h. Characteristic cyclic voltammograms were obtained after scanning the potential of the electrode between 0 and 1 V versus RHE for hundreds of cycles. Experiments for the oxidation of H_2 on the Nafion-coated Pt/C electrodes were performed in H_2-saturated 0.5 M H_2SO_4 electrolyte at several rotation rates in the range from 400 to 3600 rpm. H_2 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 0.5 V versus RHE at a scan rate of 5 mV/s.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows the typical cyclic voltammogram (CV) for the thin-film porous electrodes for an electrode having a Pt loading of 40.8 $\mu g/cm^2$ and a Nafion film thickness of 0.2 μm. The CV shows two well-resolved H-adsorption or desorption peaks. The hydrogen adsorption/desorption charge, Q_H, was evaluated from the CV data in the potential range between 0.05 and

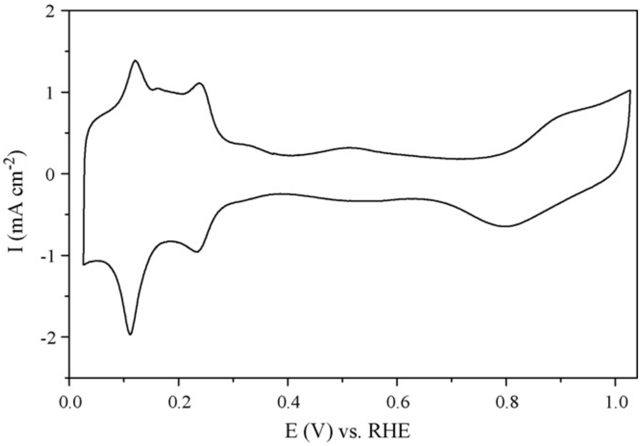

Fig. 1. Cyclic voltammogram for a thin-film porous electrode (Pt loading: 40.8 $\mu g/cm^2$; Nafion film thickness: 0.2 μm). Scan rate: 20 mV/s.

0.40 V. The electroactive surface area of an electrode calculated from Q_H (Lin and Shih, 2006; Nart and Vielstich, 2003; Schmidt *et al.*, 1998) was found to be the same as the real Pt surface area of the electrode and independent of the Nafion film thickness. This result indicates that the penetration depth of Nafion into the catalyst layer was shallow and the area of the catalyst surface blocked by the Nafion coating was very small as compared with the total catalyst surface area.

3.2. Method of kinetic analysis

For a smooth Pt RDE coated with a Nafion film, the measured current density, i_m, for a first-order reaction on the electrode under an overpotential at which the backward reaction can be neglected (Schmidt *et al.*, 1998; Watanabe *et al.*, 1995) is given by

$$\frac{1}{i_m}=\frac{1}{i_k}+\frac{1}{i_f}+\frac{1}{i_d} \tag{1}$$

where i_k represents the kinetic current density in the absence of mass transfer resistances in the aqueous electrolyte and Nafion film and i_d or i_f represents the limiting current density when the reaction rate is controlled solely by the diffusion of the reactant in the aqueous electrolyte or in the Nafion film. The latter two limiting current densities can be expressed by

$$i_d = 0.62nFD^{2/3}\nu^{-1/6}C_0\omega^{1/2} = BC_0\omega^{1/2} \tag{2}$$

$$i_f = nFC_fD_fL^{-1} \tag{3}$$

Combining Eqs. (1)–(3) gives

$$\frac{1}{i_m}=\frac{1}{i_k}+\frac{L}{nFC_fD_f}+\frac{1}{BC_0\omega^{1/2}} \tag{4}$$

For an RDE made by depositing a layer of catalyst powder and coated with a Nafion film, Eq. (4) is still valid, but i_k may be affected by the diffusion of the reactant in the catalyst layer (Stonhart and Ross, 1976).

According to Eq. (4), a plot of $1/i_m$ versus $\omega^{-1/2}$ (Koutecky–Levich plot) is linear with a slope equal to $1/BC_0$ and an intercept (Levich intercept), Y_0, corresponding to

$$Y_0=\frac{1}{i_k}+\frac{L}{nFC_fD_f} \tag{5}$$

Thus Y_0 is a linear function of L with a slope equal to $1/nFC_fD_f$ and an intercept equal to $1/i_k$. The inverse of Y_0 (Schmidt *et al.*, 1998) is

$$\frac{1}{Y_0}=\frac{1}{(1/i_k)+(1/(nFC_fD_f)L^{-1})} \tag{6}$$

According to Eq. (6), $1/Y_0$ approaches i_k when L^{-1} is sufficiently large and approaches i_f when L^{-1} is sufficiently small.

3.3. Kinetic analysis of H_2 oxidation reaction

Experiments for the H_2 oxidation reaction were conducted on the electrodes for which the Nafion film thickness ranged from 0.1 to 8.0 μm and the Pt loading ranged from 10.2 to 30.6 μg/cm². The hydrodynamic voltammograms for the electrodes with film thicknesses of 0.2 and 4.0 μm are represented in Fig. 2. One can see that the current density increases as the potential increases, and reaches a limiting value at about 0.07 V. The limiting current density increases with increasing rotation rate, and it is smaller when the Nafion film is thicker at the same rotation rate. As seen from Fig. 2(a), the increase in Pt loading does not cause the limiting current density at each rotation rate to change accordingly and significantly. Therefore, the small variations in the limiting current density at each rotation rate, about ±0.03 to ±0.04 mA/cm² from the mean when the rotation rate increased from 400 to 3600 rpm, were due to experimental errors. Data for the cathodic scan, represented by a dashed line, are plotted for the case of 3600 rpm in Fig. 2(b). The hysteresis caused by the double layer capacitance, less than 25 μA/cm² at 0.4 V versus RHE, is negligible.

Fig. 3 shows a Koutecky–Levich plot of the data obtained at 0.4 V versus RHE. As demonstrated in the figure, the data agree very well with Eq. (4) and the slopes of the linear fitting lines are almost equal. The average value of BC_0 determined, 6.50 × 10^{-2} mA/cm²/rpm$^{1/2}$ (±4.5%), is in excellent agreement with the value at 298 K, 6.54 × 10^{-2} mA/cm²/rpm$^{1/2}$, calculated by Gasteiger *et al.* (1995) from Eq. (2) using $n = 2$,

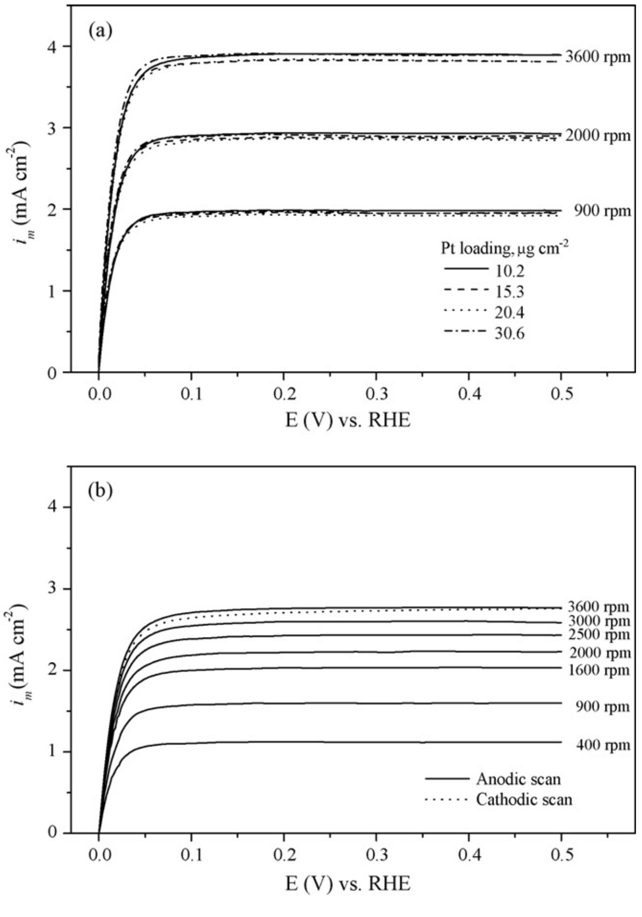

Fig. 2. Hydrodynamic voltammograms for H_2 oxidation on the electrodes with Nafion film thicknesses of (a) 0.2 μm (Pt loading: 10.2–30.6 μg/cm²) and (b) 4.0 μm (Pt loading: 10.2 μg/cm²) in H_2-saturated 0.5 M H_2SO_4 electrolyte. Scan rate: 5 mV/s.

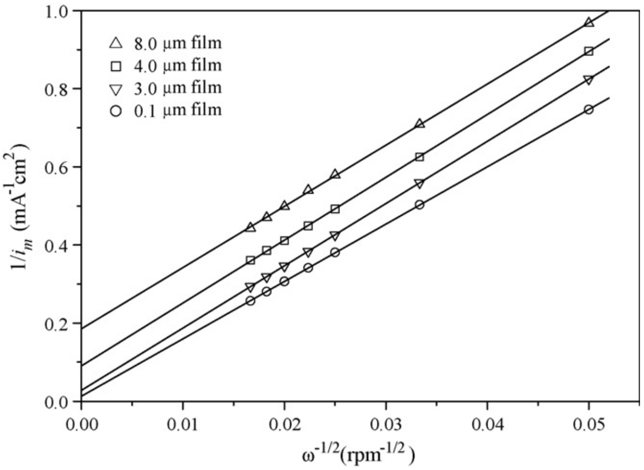

Fig. 3. Koutecky-Levich plots at 0.4 V vs. RHE for H_2 oxidation on the electrodes with several Nafion film thicknesses (0.1–8.0 μm) (Pt loading: 10.2 μg/cm^2).

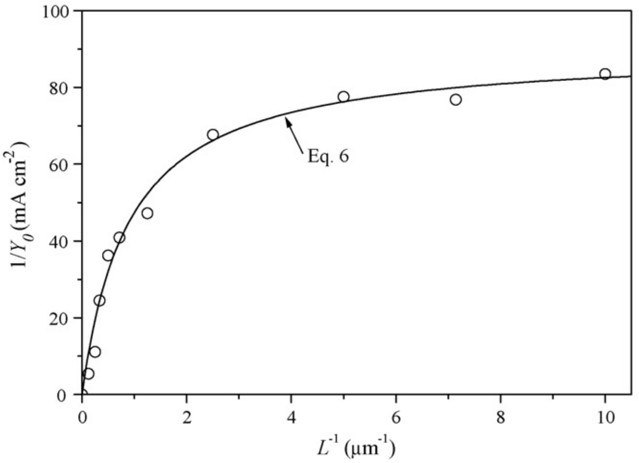

Fig. 4. The inverse of the Levich intercept of Fig. 3 as a function of the inverse of the Nafion film thickness.

$D = 3.7 \times 10^{-5}$ cm^2/s, $\nu = 1.07 \times 10^{-2}$ cm^2/s, and $C_0 = 7.14 \times 10^{-4}$ M.

The data of the inverse of Y_0 versus L^{-1} are plotted in Fig. 4. One can see that $1/Y_0$ increases linearly in the L^{-1} range from 0 to 0.5 1/μm and levels off after 5 1/μm. Thus, $1/Y_0$ approaches i_k when L^{-1} is larger than 5 1/μm (or $L \leqq 0.2$ μm) according to Eq. (6). The critical film thickness, 0.2 μm, at which the diffusional resistance of the film becomes negligible, is the same as that determined in our previous work (Lin and Shih, 2006) for Pt-black/Nafion electrodes and that reported by Watanabe *et al.* (1995) for Nafion coated smooth Pt electrodes, but is thinner than the thickness of 0.3 μm reported by Schmidt and Gasteiger (2003) or 0.5 μm reported by Schmidt *et al.* (1998).

The nonlinear regression of the data shown in Fig. 4 using Eq. (6) gave 4.8×10^{-5} mM cm^2/s and 90 mA/cm^2 for C_fD_f (the permeability of H_2 in Nafion film) and i_k. The C_fD_f and i_k values determined from the linear plot of Y_0 versus L according to Eq. (5) (Fig. 5) were 2.4×10^{-5} mM cm^2/s (±9%) and 885 mA/cm^2. The difference between the two C_fD_f or i_k values are caused by the errors in Y_0 and L and different ways of data treatment. In the former method, the weighting of the deviation of Y_0 increases as Y_0 or L decreases, whereas equal weighting is taken in the latter method. The latter method would give nearly the same results as those obtained by the former method, if only the data for small L values ($\leqq 3$ μm) were considered. The C_fD_f value determined by the latter method is considered more accurate for thicker Nafion films. The extremely large i_k value determined by the latter method also agrees better with the order of magnitude of the true i_k at 0.4 V (see the next section).

The above two C_fD_f values are in good agreement with the values of 5.2×10^{-5} (Lin and Shih, 2006) and 2.6×10^{-5} (Lin and Shih, 2005) mM cm^2/s determined using the two methods for our Pt-black/Nafion electrodes. It is worthy to note that our C_fD_f values are close to the C_0D value, 2.6×10^{-5} mM cm^2/s, in the 0.5 M H_2SO_4 solution. In the literature, Schmidt *et al.* (1998) reported a C_fD_f value of 7.8×10^{-5} mM cm^2/s for their recast Nafion film coated on a layer of 20 wt% Pt/C catalyst in a similar RDE configuration, and Watanabe *et al.* (1995) and Mello and Ticianelli (1997) reported values of 4.7×10^{-6} and 9.0×10^{-6} mM cm^2/s for their films coated on smooth Pt RDEs, respectively. The differences between the C_fD_f values reported can be explained partly by the errors in the experimental measurements and the different ways of data treatment, and partly by the difference in the film preparation process that is known to significantly affect the microstructure and hence the mass-transfer property of a recast Nafion film (Maruyama *et al.*, 1998).

3.4. Discussion on the apparent i_k value

As seen in Fig. 4, the value of i_k determined by the non-linear regression is higher than but close to the $1/Y_0$ data at $L \leqq 0.2$ μm. The previous investigators (Schmidt *et al.*, 1998; Schmidt and Gasteiger, 2003; Watanabe *et al.*, 1995) took the i_k values as the values of $1/Y_0$ obtained at $L \leqq$ the critical film thickness. Our i_k values obtained in this way, ranging from 66 to 104 mA/cm^2, are of the same order of magnitude as that (40–60 mA/cm^2) obtained for smooth Pt RDEs (Gasteiger *et al.*, 1995; Schmidt and Gasteiger, 2003; Watanabe *et al.*,

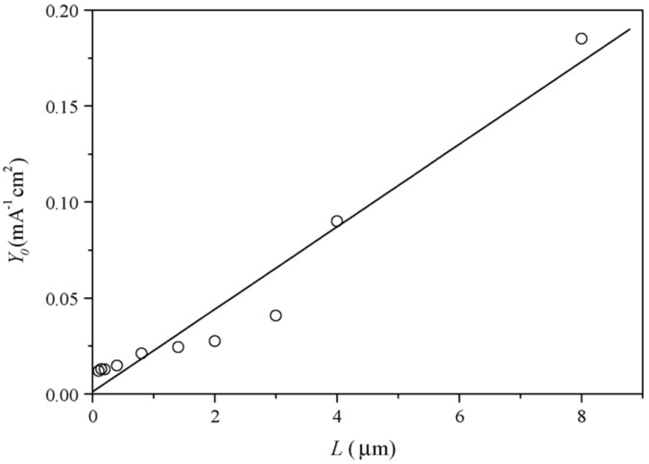

Fig. 5. The Levich intercept of Fig. 3 as a function of the Nafion film thickness.

1995), that (40 mA/cm^2) for Nafion-coated 20 wt% Pt/C electrodes (7 $\mu g_{Pt}/cm^2$, E-TEK) used by Schmidt *et al.* (1998), and that (89 mA/cm^2) for our Pt-black/Nafion electrodes (102 $\mu g_{Pt}/cm^2$) (Lin and Shih, 2006). These values of i_k indicate that the apparent values of i_k estimated under high overpotentials are not very sensitive to the type of Pt, the loading of Pt, and the structure of catalyst layer.

Schmidt and Gasteiger (2003) pointed out that the values of i_k estimated at a high overpotential for their smooth Pt and Pt/C electrodes were many-fold smaller than the true i_k value estimated at that overpotential. Hence, they attributed their i_k values determined at 0.2 V versus RHE to the error in estimating Y_0 by extrapolation and the residual resistance due to the thin Nafion film. However, Watanabe *et al.* (1995) attributed the values of i_k determined at 0.4 V versus RHE for their smooth Pt electrodes to some rate-limiting chemical process preceding or following the electron transfer process in the H_2 oxidation reaction.

Because the apparent value of i_k was taken as the value of $1/Y_0$ at $L \leqq 0.2$ μm, the error of Y_0 was estimated in order to clarify whether the value of i_k was resulted from the experimental errors. Using the i_m data at 0.4 V for all the electrodes with different Pt loadings and $L \leqq 0.2$ μm, the linear regression according to Eq. (4) gave a Y_0 value of 0.0116 cm^2/mA and a standard error of Y_0 of ± 0.0092 cm^2/mA. The 95% confidence interval of Y_0 (Skoog and West, 1969) was 0.0116 ± 0.0236 cm^2/mA. The confidence interval of Y_0 includes negative values. But the true Y_0 can never be negative. Thus, we may conclude that the true Y_0 is essentially zero and the Y_0 value determined is the value of the determinate error in the Y_0 measurement (Skoog and West, 1969). Accordingly, the true i_k, the inverse of the true Y_0, is extremely large, and the apparent i_k, the inverse of the determinate error, is much smaller (86 mA/cm^2). This interpretation on the apparent i_k value can explain why we obtained about the same i_k values for Pt/C (86 mA/cm^2) and Pt-black (89 mA/cm^2) (Lin and Shih, 2006) electrodes; because the same instrument and method were employed in both investigations, the determinate error should be about the same in both cases. However, we are unable to identify what caused the determinate error. The i_k values at high overpotentials reported by other investigators (Gasteiger *et al.*, 1995; Schmidt *et al.*, 1998; Schmidt and Gasteiger, 2003; Watanabe *et al.*, 1995) most probably are also resulted from the determinate errors in their measurements.

It should be noted that the deviation of Y_0 from zero value at $L \leqq 0.2$ μm in this study is small, thus it affects very little the values of BC_0 (Fig. 3) and C_fD_f (Fig. 5) determined. Furthermore, since the i_k and C_fD_f values estimated with Eq. (5) are more accurate than those estimated with Eq. (6), it is more appropriate to use Eq. (5) in estimating the kinetic parameters.

4. Conclusion

The kinetics of hydrogen oxidation reaction on Nafion-coated 20 wt% Pt/C electrodes immersed in 0.5 M H_2SO_4 was investigated using a rotating disk electrode configuration. The Nafion film coating ($\leqq 8$ μm) had a negligible effect on the electrochemical surface area of an electrode. The kinetic parameters were estimated at an overpotential of 0.4 V. The values obtained varied with the method of data treatment; the use of Eq. (5) gave more accurate results than Eq. (6), which was commonly used by previous investigators. The permeability of H_2 in the Nafion film was in the range of 2.4×10^{-5} to 4.8×10^{-5} mM cm^2/s, depending on the method of data treatment. The diffusional resistance for H_2 in a Nafion film can be neglected when the film thickness was thinner than 0.2 μm. The intrinsic reaction rate was very high and the apparent kinetic current density estimated was resulted from the small determinate error in the kinetic measurements, instead of resulting from some chemical processes as proposed by Watanabe *et al.* (1995).

Acknowledgements

The authors would like to express sincere appreciation to the National Science Council (Taiwan) for the financial support. We are greatly indebted to Professor Yi-Der Tai for the invaluable help. We also thank Mr. Lun-Chai Yang for the technical assistance.

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Nafion 覆蓋 Pt/C 電極在高過電位下氫氣氧化反應的動力學

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摘　要

本研究以旋轉電極探討浸沒在 0.5 M 硫酸溶液中的 Nafion 覆蓋 20wt% Pt/C 電極之 Nafion 膜厚與鉑黑負載量對氫氣氧化反應動力學的影響。Nafion 膜的厚度(≦8 μm)對表面積量測幾無影響。在高過電位(0.4 V)下所估算的動力學參數因著數據處理方法而有所不同。Nafion 膜厚度小於 0.2 μm 時，膜內的氫氣質傳阻力可以忽略。氫氣在 Nafion 膜中的滲透係數介於 2.4×10^{-5}~ 4.8×10^{-5} mM cm^2/s 之間。誤差分析顯示所估算的視動力電流是由於實驗誤差所致，而非如先前研究者所提出是由於化學程式所致。