Rational determination of exchange current density for hydrogen electrode reactions at carbon-supported Pt catalysts

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ABSTRACT

The rotating disk electrode (RDE) is a useful technique for precise determination of exchange current density (j_0) in electrochemistry. For the study of powder catalysts, a common practice is to apply the powder onto an inert disk substrate (such as glassy carbon). However, this approach in its usual version will lead to wrong results for the exchange current density of hydrogen electrode reactions at carbon-supported Pt nanoparticles (Pt/C) because of the poor utilization of the loaded Pt nanoparticles. Our new approach is to dilute the Pt/C powder with a large amount of pristine carbon support to make the catalyst layer. In this way, all the catalyst particles in the catalyst layer have nearly the same and much enhanced mass transport so that rational exchange current density can be obtained. Using the new approach, the current density for hydrogen electrode reactions at Pt/C in 0.1 M perchloric acid at 25 °C is found to be 27.2 ± 3.5 mA/cm^2 with an apparent activation energy 43 kJ/mol. These results are in agreement with the j_0 estimation based on real fuel cell experiments.

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1. Introduction

The hydrogen electrode reactions, including hydrogen oxidation and evolution, are classical topics of electrochemistry and the exchange current densities for hydrogen electrode reactions are naturally fundamental electrochemical parameters, especially for Pt [1]. In the literature, there have been numerous papers concerning the determination of the exchange current density, j_0, of hydrogen electrode reactions at Pt. However, the results obtained in acidic media were severely scattered (Table 1). The reported values obtained at room temperature spanned over two orders of magnitude. The j_0 values obtained from rotating disk electrode (RDE) measurements [3–5,13–15,17,18] are usually much lower than those estimated from fuel cell practices [6,8,9].

Driven by the research and development of fuel cells, especially the proton exchange membrane fuel cells (PEMFC), the j_0 of hydrogen electrode reactions for carbon-supported Pt, Pt/C, has been attracting much attention in recent years. A highly concerned relevant question is what would be the low limit of Pt loading for the hydrogen anode in PEMFC. In order to answer this question it is necessary to know the accurate j_0 for Pt nanoparticles, especially the practical form of catalyst Pt/C. However, the reported j_0 values for Pt/C also differed from each other remarkably. In particular, the j_0 estimated from the data of real fuel cells [6,8] or gas-diffusion

electrodes [9] were often larger by orders of magnitude than the values obtained from Pt/C-coated RDE measurements.

The reasons for the data scattering shown in Table 1 are not single, but the dominant factor should be the various extents of interference from the limited mass transport. It is noted that the highest j_0 values were obtained with special measures to enhance the mass transport, such as in the case of gas-diffusion electrodes [6,8,9] and ultramicroelectrodes [11,12]. Without specially enhanced mass transport, the j_0 values were always underestimated and some researchers simply reported that the j_0 was too large to be measured [16]. Because of the fast kinetics, the mass transport in the usual version of RDE is not sufficient for a reliable determination of the j_0 of hydrogen electrode reactions at Pt in acidic media. As a result, the j_0 values obtained from Pt RDE measurements were usually lower than they should be.

The situation with Pt/C coated RDE is more complicated than the planar Pt RDE. For the coating electrodes, not only the limited mass transport in the liquid phase near the RDE but also the mass transport within the coating would affect the j_0 determination. Because of the limited solubility of molecular hydrogen, a shortage of hydrogen supply would easily develop inside the coating, resulting in a lowered utilization of the catalyst and reduced j_0. Obviously, for a high utilization of catalyst, the coating should be made as thin as possible [23]. In preliminary tests, we attempted such ultra-thin coatings by successive diluting the ink with ethanol. Unfortunately, the results were disappointing. As shown by the scanning electron microscopy (SEM) image in Fig. 1, the deposits were Pt/C agglomerates with diameters ranging from sub-micrometer to micrometers,

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Table 1
j_0 values reported in the literature.

Year [reference]	Sample	Electrolyte and temperature	Experimental technique	j_0 (mA cm^{-2} Pt)
1970 [2]	Pt disk	1 M H$_2$SO$_4$, 25 °C	Steady state polarization	1.9
1973 [10]	Pt microdisk	0.5–1 M H$_2$SO$_4$, 25 °C	Microelectrode with thin liquid film	>50
1975 [19]	Smooth Pt Pt black Pt/C	2 M H$_2$SO$_4$, 22 °C	CV, polarization, H$_2$–D$_2$ exchange	27 (smooth Pt) 21(Pt black) 18 (Pt/C)
1997 [3]	Pt(1 1 0)disk	0.05 M H$_2$SO$_4$ 1, 30, 60 °C	RDE	0.65(1 °C) 0.98(30 °C) 1.35(60 °C)
1998 [14]	Pt nanoparticles	0.5 M H$_2$SO$_4$, 25 °C	RDE, Pt/PAN	0.025~1.9 changed with rotating rate and Pt loading
1998 [4]	Pt disk	0.1 M HClO$_4$, *RT*	RDE	1.35 (no Nafion) 1.62 (Nafion coated)
2003 [11]	Pt microelectrode	0.01 M HClO$_4$ + 0.10 M NaClO$_4$, *RT*	SECM[a]	~42
2003 [5]	Pt deposited on Ru	0.5 M H$_2$SO$_4$, 25 °C	RDE	1–2
2004 [12]	Pt nano- and microelectrode	0.1 M H$_2$SO$_4$, 23 °C	Nano- and microelectrode	20–23
2004 [6]	47 wt% Pt/C (~5 nm)	Nafion 112, 60 °C	PEMFC	~27
2006 [13]	20 wt% Pt/C (3.4 nm), 20 wt% Pt/Cryogel (2.65 nm)	0.5 M H$_2$SO$_4$, 20 °C	RDE	0.15 (Pt/XC-72) 0.16 (Pt/Cryogel)
2006 [16]	Pt black(~9 nm)	0.5 M H$_2$SO$_4$, 25 °C	RDE	diffusion control
2007 [7]	20 wt% Pt/C (E-tek)	Nafion 112, 23 °C	PEMFC	1.73
2007 [8]	5 wt% Pt/C (3 nm)	Nafion 112, 80 °C	PEMFC	235–600
2007 [15]	20 wt% Pt/XC-72 (2.5 nm)	0.5 M H$_2$SO$_4$, 25 °C	RDE	0.16 (Pt/XC-72)
2008 [9]	Pt black (10.4 nm), 20 wt% Pt/C (3.1 nm)	Nafion 117, 50 °C	GDE[b]	22 (Pt black) 26 (Pt/C)
2009 [17]	16.6 wt% Pt/C (2.48 nm)	0.5 M HClO$_4$, 22 °C	RDE	~0.22
2009 [18]	20 wt% Pt/C (E-tek)	0.5 M H$_2$SO$_4$, 25 °C	RDE	0.27

[a] SECM—scanning electrochemical microscope.
[b] GDE—gas-diffusion electrode.

and scattered non-uniformly. On the edge of the disk electrode, the agglomerates are more concentrated than in the central part of the disk. Such a coating structure proved to be not ideal for the determination of j_0. For the smallest agglomerates (hardly visible in Fig. 1), the inside may be well utilized and local diffusion limiting current density is high (because of the spherical diffusion toward electrodes with small curvature radii); these features are favorable for j_0 determination. However, it is not likely the case for the larger agglomerates. Besides, it was found in practice that the reproducibility of this method was poor. Therefore it is imperative to find a new approach to uniformly disperse the Pt/C catalyst in extremely low loadings.

In this paper we report a new method of rational determination of j_0 for hydrogen electrode reactions at Pt/C in acidic media. The key feature of the new approach is to dilute the Pt/C sample of interest with a large amount of pristine carbon powder. In the coating made from such powder mixture, there is only a small amount of Pt-decorated carbon particles (denoted as Pt/C particles in the text

below) dispersed in excessive pristine carbon particles. As a result, all the Pt/C particles are under nearly identical and much enhanced mass transport conditions, which ensure a unity utilization of the catalyst and a reasonable rate ratio of mass transport to kinetics.

2. Experimental

Two Pt/C catalysts were tested in this work. One was 40 wt% Pt/C from Johnson Matthey and the other was home made 20 wt% Pt/C. In both samples, the carbon supports were Vulcan XC-72 (Cabot). The Pt particle sizes were calculated from X-ray diffraction (XRD) data using the Sherrer equation and turned out to be 2.1 and 2.5 nm, respectively. The original Pt/C powder was mixed with a required amount of pristine XC-72 carbon in a 0.05% Nafion solution (Nafion ionomer in mixed solvents) and sonicated for 1–2 h to make an ink of carbon-diluted Pt/C. Then a required volume of the ink was applied to the glassy carbon RDE (Autolab, Model ECO CHEMIE BV, disk diameter 4 mm). After solvent evaporation in air, the test coating was formed on the disk surface.

Cyclic voltammetry (CV) and RDE measurements were carried out using a CHI600 potentiostat (Chenghua, Shanghai) with a single compartment thermostatic cell. The electrolyte was 0.1 M HClO$_4$ (GR, Shanghai Jinlu Chemical Co., Ltd.). The purity of N$_2$ was 99.99% and the H$_2$ was 99.999%. All the solution was prepared by deionized water (18 MΩ cm). A Pt wire served as the counter electrode. The reference electrode was the reversible hydrogen electrode (RHE) in the same electrolyte and was connected to the cell through a Luggin capillary. The tip of Luggin capillary was positioned to the closest possible vicinity of the electrode surface and the uncompensated solution resistance was estimated by AC impedance, potential step and current step methods to be about 3 Ω. The IR drop was corrected for in the calculation of exchange current.

The contamination of electrode surfaces is a common problem in electrochemical experiments and it was encountered in this work too. In addition to serious measures taken in the preparation of the solution and the electrode, an electrochemical pretreatment of the electrode was adopted to depress the contamination to the lowest possible level. The working electrode was subjected to continuous
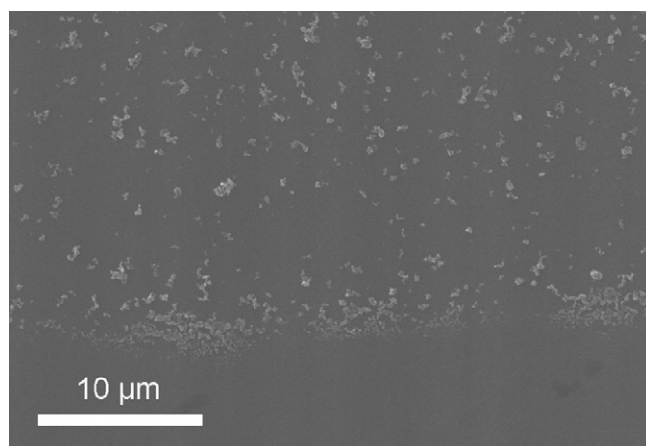

Fig. 1. SEM image of a Pt/C coating made from ethanol diluted 20% Pt/C for a 2 ng Pt loading on the glassy carbon disk of 4 mm diameter.