Catalysis Today 174 (2011) 2–9

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Mass transfer effects on kinetics of the hydrogen oxidation reaction at Nafion film covered Pt/C rotating disk electrodes☆

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ARTICLE INFO

Article history:
Received 26 October 2010
Received in revised form 22 March 2011
Accepted 13 April 2011
Available online 24 May 2011

Keywords:
Electrocatalysis
Platinum
Hydrogen oxidation
Mass transfer
Fuel cells

ABSTRACT

The effects of mass transfer on the kinetics of the hydrogen oxidation reaction at the Nafion covered Pt/C electrodes immersed in 0.5 M H_2SO_4 was investigated using a rotating disk electrode configuration. The hydrodynamic voltammograms were analyzed to determine the kinetic parameters using the modified Koutecky–Levich equation. The permeability of H_2 in the Nafion film was determined to be 2.0×10^{-5} mM cm^2 s^{-1}, which is close to that in 0.5 M H_2SO_4. Due to the fast intrinsic reaction rate of H_2 oxidation on the Pt catalyst, the diffusion of H_2 in the catalyst layer affected the overall reaction rate to a higher extent when the Pt loading or the overpotential increased. The effect of H_2 diffusion in the catalyst layer on the overall reaction rate was accounted for using the effectiveness factor. The corrected exchange current density for the 20 wt% Pt/C catalyst was determined to be about 0.96 mA cm^{-2}, based on the real Pt surface area. The results of this work may contribute to the measurement on the intrinsic electrocatalytic activity of a high surface area catalyst used in proton exchange membrane fuel cells.

1. Introduction

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 [1]. Particularly, proton exchange membrane fuel cells (PEMFCs) have recently received more attention due to their high power density at relatively low temperatures and zero emission of air pollutants [2]. The fuel (H_2) and oxidant gases (O_2 or air) flow past the backside of the anode and cathode, respectively, and react in the zone of the three-phase boundary established at gas/electrolyte/catalyst interface within the electrodes, which are porous structures that have a large interfacial contact area to achieve practical current densities.

Platinum (Pt) is the most widely used electrocatalyst in low-temperature fuel cells [1,3]. Such a Pt catalyst, however, is very expensive. Lowering precious metal loading is desired to reduce the cost and to facilitate the market entry of fuel cells. Accordingly, electrodes were prepared consisting mainly of highly dispersed Pt particles supported on carbon (Pt/C), optimizing their active surface area for the electrocatalytical reaction. This cost requirement also led to the ionomer phases (e.g. Nafion) incorporating into the catalyst layer, forming the effective three-phase reaction zone [4–7]. So far, a lot of efforts were made to investigate the influences of the active layer compositions on the fuel cell performance. Most efforts were focused on optimization as a function of Nafion content [8–11]. Nevertheless, Pt catalysts loaded on carbon might not totally serve to electrochemical reactions. Probably half of Pt particles do work as electrocatalysts [12]. This may be related to the nature of the interface between ion-exchange polymer electrolyte and carbon particles with Pt catalysts [13,14]. Since the performance of a fuel cell is affected by the mass transfer, a better understanding of these effects is necessary in order to quantitatively determine the intrinsic activity of a catalyst and to devise such an efficient electrode for the practical operation.

In the present work, the commercial 20 wt% Pt/C catalyst was used and its activity for the H_2 oxidation reaction (HOR) when it was covered with a Nafion film was studied by the rotating disk electrode (RDE) methodology. The kinetic parameters for the H_2 oxidation reaction at the Nafion covered Pt/C electrodes were evaluated with the aim to investigate the mass transfer effects on the reaction kinetics and thus determine the intrinsic activity of the catalyst. Similar study has been carried out by Schmidt et al. [15], but the effect of the Pt loading was not reported and the theoretical description of the rotating thin-film method for the determination of the intrinsic activity of a high surface area catalyst was not discussed in detail.

☆ The manuscript had been presented at The 13th Asia Pacific Confederation of Chemical Engineering Congress (APCChE 2010), October 5–8, 2010, Taipei, Taiwan.

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doi:10.1016/j.cattod.2011.04.037

Nomenclature

Acronyms

CV	cyclic voltammetry
GC	glassy carbon
GPES	general purpose electrochemical system
HOR	hydrogen oxidation reaction
PEMFC	proton exchange membrane fuel cell
RDE	rotating disk electrode
RHE	reversible hydrogen electrode
SCE	saturated calomel electrode
XRD	X-ray diffraction

Symbols

a	surface area per unit catalyst layer volume, cm^{-1}
B	Levich constant, $mC\,cm\,mol^{-1}$
b	$\exp(nF\eta/RT)$
C_0	H_2 solubility in electrolyte, $mol\,cm^{-3}$
C_f	H_2 solubility in polymer film, $mol\,cm^{-3}$
D	H_2 diffusivity in electrolyte, $cm^2\,s^{-1}$
D_e	effective diffusivity, $cm^2\,s^{-1}$
D_f	H_2 diffusivity in polymer film, $cm^2\,s^{-1}$
E	potential of an electrode versus a reference, V
F	Faraday constant, 96,485 $C\,mol^{-1}$
I	current of an electrode, mA
i_d	diffusion-limited current density, $mA\,cm^{-2}$
i_f	polymer film diffusion-limited current density, $mA\,cm^{-2}$
i_k	kinetic current density, $mA\,cm^{-2}$
$i_{k,0}$	intrinsic kinetic current density, $mA\,cm^{-2}$
i_m	measured current density, $mA\,cm^{-2}$
i_0	exchange current density, $mA\,cm^{-2}$
i_0^*	corrected exchange current density, $mA\,cm^{-2}$
k	rate constant for H_2 oxidation reaction, $cm\,s^{-1}$
L	polymer film thickness, μm
L_c	catalyst layer thickness, μm
n	number of electrons involved in the reaction
Q_H	hydrogen adsorption/desorption charge, $mC\,cm^{-2}$
Y_0	Levich intercept, $mA^{-1}\,cm^2$
R	gas constant, 8.314 $J\,mol^{-1}\,K^{-1}$
r_s	reaction rate, mole $cm^{-3}\,s^{-1}$
$r_{s,0}$	intrinsic reaction rate, mole $cm^{-3}\,s^{-1}$
S_g	specific surface area, $m^2\,g^{-1}$
T	temperature, K
W_l	Pt loading, $\mu g\,cm^{-2}$
α	transfer coefficient
η	overpotential, mV
η_e	effectiveness factor
δ	roughness factor of the electrode
ρ_b	bulk density of the catalyst layer, $cm^3\,g^{-1}$
ν	kinematic viscosity, $cm^2\,s^{-1}$
ω	rotation rate, rpm
ψ	Thiele modulus

2. Experimental

2.1. Materials

The Pt catalyst used was 20 wt% platinum on Vulcan XC-72R carbon black (HiSPEC^{TM} 3000, Johnson Matthey). For brevity, this catalyst was referred to as Pt/C catalyst in this study. The mean particle size of the carbon black, 4.0 μm, was measured by laser diffraction using a Coulter LS-230 analyzer. According to the manufacturer's data, the active Pt surface area was 110 $m^2\,g_{Pt}^{-1}$ determined by gas-phase CO chemisorption. The Pt crystal size was 2.6 nm determined by X-ray diffraction (XRD). 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 Nafion solution containing 5 wt% Nafion dissolved in a mixture of isopropanol and water (1100 equivalent weight, Ion Power) was used to recast the Nafion film. High purity H_2 gas (99.999%, San-Fu) was used. The electrolyte was 0.5 M H_2SO_4 solution prepared form concentrated sulfuric acid (J.T. Baker) and ultrapure water (18 MΩ, Millipore).

2.2. Electrode preparation

An aqueous catalyst suspension of 2 $mg\,mL^{-1}$ was prepared by mixing 50 mg of Pt/C catalyst and 25 mL of deionized water under ultrasonication for about 10 min. Diluter catalyst suspensions, which were necessary to form thinner catalyst layer, were prepared following a similar process with lower catalyst weights. About 10–20 μL of the catalyst suspension was pipetted onto the disk surface and dried under room temperature. After the catalyst layer was dry, a 20 μL of Nafion solution was put on the top of the catalyst layer. Subsequent annealing in a vacuum oven (70 °C) was made for at least 40 min to evaporate the residual solvent in the resulting thin-film electrode. This annealing renders the recast film insoluble and with sufficient strength to bind the catalyst particles [16]. The concentration of Nafion solution was varied by diluting the 5 wt% Nafion solution with isopropanol to yield the 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 $g\,cm^{-3}$ [8,16,17]. It was estimated that about 90% of the shroud surface area was covered, i.e. 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 difference between the measured and calculated values was about 6%. The fabrication procedure of the thin-film rotating disk electrode was similar to that described elsewhere [15,18,19].

2.3. Electrochemical measurements

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 behaviors of the thin-film rotating disk electrodes. Electrochemical measurements were conducted at room temperature (25 ± 1 °C) 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 the measurements, the electrode was well hydrated in deaerated 0.5 M H_2SO_4 solution, which exhibited a very similar pH value to that of the Nafion film. Characteristic cyclic voltammograms (CVs) were obtained after scanning the potential of the electrode between 0 and 1 V versus RHE for hundreds of cycles. This long run-in period was necessary to obtain stable and reproducible data. Experiments for H_2 oxidation on the Nafion film covered Pt/C rotating disk 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 0.15 V versus RHE at a scan rate of 5 $mV\,s^{-1}$.