



Corrosion of carbon support for PEM fuel cells by electrochemical quartz crystal microbalance

Chih-Cheng Hung^a, Pau-Yee Lim^b, Jiann-Ruey Chen^a, Han C. Shih^{a,c,*}

^a Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

^b Material and Chemical Research Laboratories, Industrial Technology Research Institute, Bldg. 77.195, Sec. 4, Chung Hsing Rd., Chutung, Hsinchu 310, Taiwan

^c Institute of Materials Science and Nanotechnology, Chinese Culture University, Taipei 111, Taiwan

ARTICLE INFO

Article history:

Received 28 April 2010

Received in revised form 6 July 2010

Accepted 7 July 2010

Available online 13 July 2010

Keywords:

Corrosion

Electrochemical quartz crystal microbalance

Carbon support

Carbon black

PEMFC

Fuel cells

ABSTRACT

During the voltammetry of carbon supports for proton exchange membrane fuel cells (PEMFCs), including commercial carbon blacks, graphitized carbon black and multi-wall carbon nanotubes (MWNTs), in deaerated 0.5 M H₂SO₄ solution results in mass changes as observed by using in situ electrochemical quartz crystal microbalance (EQCM). The mass change and corrosion onset potential during electrochemical carbon corrosion indicate that oxides are formed and accumulated on the carbon surface, leading to an increase in mass. A decrease in the mass is associated with carbon loss from the gasification of carbon surface oxides into carbon dioxide. High BET surface area carbon blacks ECP600 and ECP 300 have a carbon loss of 0.0245 ng cm⁻² s⁻¹ and 0.0144 ng cm⁻² s⁻¹ and as compared to 0.0115 ng cm⁻² s⁻¹ for low surface area support XC-72 and so they are less resistant to corrosion. Graphitized XC-72 and MWNTs, with higher graphitization have higher carbon corrosion onset potential at 1.65 V and 1.62 V and appear to be more intrinsically resistant to corrosion.

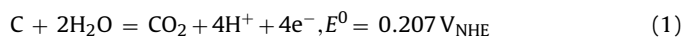
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1. Introduction

Carbon-supported platinum is the most commonly used catalyst in PEMFCs. Carbon black is widely used as a support material for nano-sized platinum particles due to its low cost and other favorable properties. It possesses good chemical stability, and when used as support material, it provides several desired functions, such as electronic continuity, a high surface area that enables a uniform dispersion of Pt nanoparticles, and a porous structure that facilitates the mass transportation of reactant and reaction products [1]. However, recent studies have reported that adverse effects arise from oxidation and corrosion of the carbon support in PEMFCs at the higher potential region near the open circuit voltage. It was observed that the surface groups that form during carbon oxidation change the surface properties of the carbon support. This may cause an increase in surface hydrophilicity, leading to the flooding effect, which could impede mass transport within the catalyst layer [2]. Furthermore, such surface oxidation can be accelerated due to the presence of the Pt catalyst. As a result, the Pt particles attached to the carbon surface eventually become detached due to loss of

carbon [3]. Loss of carbon could decrease the electronic continuity of the catalyst layer, aggravate aggregation of isolated Pt particles and reduces the electrochemically active surface area of Pt [4–6]. Consequently, carbon support corrosion is considered to be one of the most serious problems facing the performance and lifetime of PEMFCs.

From a thermodynamic perspective, carbon can be corroded to carbon dioxide at a potential above 0.207 V (vs. NHE) [7]. The electrochemical reaction is shown in Eq. (1).



In a PEMFC, the carbon support at the anode is comparatively more stable than cathode. The cathode side carbon support tends to corrode due to high oxygen concentration, low pH and a high operation potential between 0.6 V and 1 V. Some situations, such as during shutdown and restart, can cause the local potential at the cathode to be even higher than 1.5 V. These abnormal situations enhance carbon corrosion [8,9].

Carbon corrosion is generally analyzed by simple cyclic voltammetry (CV) measurements. The accumulation of surface oxide can then be estimated from the CV curves [10]. However, the results from CV are equivocal because the actual mass loss of carbon during corrosion is disregarded [11]. In some cases, studies on carbon corrosion for PEMFCs involve the use of mass spectrometry [12–14] or non-dispersive infrared spectroscopy [15] to monitor the gener-

* Corresponding author at: Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan. Tel.: +886 3 5715131x3845; fax: +886 3 5710290.

E-mail address: hcsih@mx.nthu.edu.tw (H.C. Shih).

ation of CO₂ under electrochemical oxidation conditions. However, complicated experimental tools are needed that allow the direct measurement of the CO₂ evolution rate from the membrane-electrode-assembly (MEA) sample, which is composed of not only the carbon support but also carbon cloth/paper.

The electrochemical quartz crystal microbalance (EQCM) is a sensitive instrument that allows measurements of mass changes in the nanogram range in electrochemical systems [16]. Yadav et al. [17] used EQCM combined with the CV method to investigate carbon oxidation of a sputtered carbon electrode. They observed mass loss during the CV positive scan. Dam et al. [18] used EQCM to evaluate the stability of XC-72 under several potentiostatic conditions at elevated temperatures and suggested that the sharp drop in mass at potentials higher than 1.15 V (vs. NHE) could be due to the formation of CO₂.

In this work, we investigate the carbon corrosion of various types of carbon support materials for PEMFCs, including the widely used commercial carbon blacks, graphitized carbon black and multi-wall carbon nanotubes. The EQCM method combined with CV in a three-electrode system was employed to investigate in situ mass change due to carbon corrosion during a positive CV scan between 0 V and 1.2 V. This work also demonstrates the influence of the BET surface area on carbon loss and on the inhibition of carbon corrosion at higher graphitization degrees.

2. Experimental

2.1. Sample preparation

Commercial carbon blacks: Vulcan XC-72 (Cabot), Ketjen black ECP300 (Akzo Nobel Chemicals), Ketjen black ECP600 (Akzo Nobel Chemicals), graphitized XC-72 and MWNTs were used to prepare carbon film quartz crystal electrodes (C-QCEs) for EQCM measurements. The commercial carbon blacks and MWNTs were used as received. The graphitized XC-72 was prepared by high-temperature heat treatment in a high-temperature furnace. The XC-72 was heated from an ambient temperature to 2200 °C and held at that temperature for 60 min. The furnace was purged with dry argon before and during the heating process. The carbons were ultrasonically mixed in isopropanol (IPA), with a carbon to IPA weight ratio of 1:200, to form well-dispersed carbon inks. A T-cut 7.995 MHz Au-coated quartz crystal electrode (Au-QCE) with an area of 0.196 cm² was used as a working electrode substrate. The C-QCE was prepared by spray coating a fixed amount of well-dispersed carbon inks to obtain about 10 μg of carbon on the Au-QCE. A Teflon mask that pre-covered the Au-QCE was used for the confined coating area. After the coating process, the C-QCE was oven-dried at 65 °C for 1 h.

2.2. Electrochemical experiment

Resonance frequencies were measured using an EG&G PAR model QCA917 to evaluate the mass change. The relation between the change in resonance frequency and the mass change on the quartz crystal electrode was calculated by the Sauerbrey equation:

$$\Delta f = \frac{-2nf^2}{\sqrt{\mu_q \rho_q}} \frac{\Delta m}{A}, \quad (2)$$

where Δf is the measured resonant frequency change (Hz), n is the fundamental mode of the crystal, f is the resonant frequency of the fundamental mode of the crystal, μ_q is the shear modulus of quartz (2.947×10^{11} g cm⁻¹ s⁻²), ρ_q is the density of quartz (2.684 g cm⁻³), Δm is the mass change, and A is the area of the gold disk coated on the crystal. This equation was used to calculate the mass change from the frequency change, neglecting the small viscous effects observed. In our measurements, a net change of 1 Hz

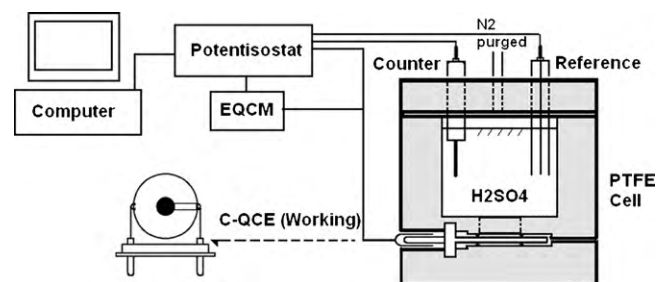


Fig. 1. Schematic of the EQCM system.

corresponds to 1.34 ng of mass change on the crystal surface area of 0.196 cm². QCE frequencies were measured before and after carbon spray coating to record the weight of the deposited carbon. The amount of deposited carbon was maintained at about 10 μg, less than 2% of the unloaded quartz crystal, so that the Sauerbrey equation could be used accurately [19]. The mass change response from EQCM data in this study was calculated and normalized to the initial carbon black's sample mass.

A standard, three-electrode cell, with a C-QCE as the working electrode, a hydrogen reference electrode and a platinum wire as the counter electrode, was used in an electrochemical experiment. The electrodes positioned in a Teflon-made cell were connected to the EG&G PAR model QCA917 and an EG&G PAR model 263A potentiostat for the EQCM measurements. The assembly is shown in Fig. 1. All tests were carried out at room temperature in a 0.5 M H₂SO₄ solution that was purged with nitrogen for 30 min to remove dissolved oxygen. Prior to the EQCM measurements, the C-QCE working electrode was pre-activated first by immersion in the deaerated 0.5 M H₂SO₄ solution for 24 h, and subsequently by electrochemical potential cycling between 0.05 V and 1.2 V at a scan rate of 50 mV s⁻¹ until the resultant CV curves became stable.

2.3. Physical characterization

The graphitization degree of the carbon materials was characterized with a Raman spectrometer (Renishaw system 2000) using a HeNe laser (632.8 nm excitation wavelength) as the light source. The specific surface area and pore volume of the carbon support was measured using a Brunauer–Emmett–Teller (BET) apparatus (Micromeritics ASAP 2010).

3. Results and discussion

3.1. EQCM measurement of XC-72

EQCM measurements of a bare Au-QCE were performed in deaerated 0.5 M H₂SO₄ at 298 K at a scan rate of 10 mV s⁻¹. Fig. 2 presents the CV and corresponding EQCM mass change data for the bare Au-QCE. Only a small mass change was observed below 0.6 V during the positive scan from 0.05 V. The notable mass gain at a potential from 0.6 V to 0.9 V could be attributed to the adsorption of sulfuric acid anions [17]. The mass increment was minimal at potentials above 0.9 V. These results were maintained until 1.4 V, at which point continuous mass gain again occurred. From this result, it was evident that the influence of mass change from the Au electrode background was negligible within the potential range of 1.0–1.4 V. Considering the possibility of oxygen evolution at the higher potential region and that carbon black may be detached mechanically from the C-QCE electrode, the upper potential range was limited to 1.2 V in subsequent CV experiments.

The XC-72 carbon film quartz crystal electrode (C-QCE) was similarly characterized by CV and EQCM in deaerated 0.5 M H₂SO₄ at a scan rate of 10 mV s⁻¹. Fig. 3 shows the CV and mass change

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