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Oxidation/reduction studies on nanoporous platinum films by electrical resistance measurements

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HIGHLIGHTS

- Synthesized nanoporous platinum films by co-sputtering Pt and carbon and burning off carbon.
- Investigated their oxidation kinetics at 80 °C in air by electrical resistance measurement.
- Assessed implications concerning degradation of proton exchange membrane fuel cell cathodes.

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ABSTRACT

Mechanisms and kinetics of surface reactions in nanoporous platinum films were investigated. Nanoporous films of platinum of ~250 nm thickness were deposited on glass slides by co-sputtering Pt and carbon followed by subsequently burning off carbon in air at 450 °C. Electrical resistance was measured in air and in 10% H_2 + nitrogen at 80 °C as a function of time. The change in electrical resistance was extremely fast when switched to the $H_2 + N_2$ atmosphere. When switched to air, the film resistance increased with time at a much slower rate. The increase in resistance in air was attributed to the formation of Pt-oxide on the internal surfaces of the nanoporous films. The kinetics of oxidation was described by a model which includes two surface kinetic steps and a diffusional step. The use of nanoporous films makes it possible to investigate mechanisms and kinetics of surface reactions by ensuring a large surface to volume ratio. Oxide scale thickness at 80 °C in air after several hours of oxidation was only sub-monolayer. Oxide scale thickness after 3 h at 450 °C was about 1 nm. Implications of the results for proton exchange membrane fuel cell (PEMFC) Pt catalyst degradation are discussed.

1. Introduction

Platinum (Pt) is one of the most widely used catalysts for numerous chemical and electrochemical processes. Nanosize Pt particles supported on high surface area carbon are used as both cathode and anode in proton exchange membrane fuel cells (PEMFC) [1]. To ensure a high catalytic activity, it is necessary that Pt catalyst exhibit a high surface area. Typical particle size of Pt in PEMFC electrodes is 2–5 nm. The high surface area necessary to ensure reasonable reaction rates also promotes other competing (often deleterious) reactions. These include for instance chemisorption of CO at the anode and oxidation of Pt (especially at high voltages) at the cathode. An oxidative atmosphere at the cathode can lead to Pt oxidation and dissolution into the aqueous medium and in the monomer [2–6]. This leads to two unwanted reactions: (a) Growth of Pt particles by dissolution/re-precipitation, thus lowering the catalytic activity [4]. (b) Dissolution of Pt at the cathode, transport into the membrane as Pt^{2+} ions, and precipitation of Pt inside the membrane [6]. This latter phenomenon not only lowers the catalytic activity (due to the loss of Pt from the cathode) but also causes membrane degradation. It is thus of great importance, both scientifically and technologically, to investigate the interaction of Pt with other species with which chemical reactions are expected. The two of greatest interest include: (a) Reaction with CO, which can drastically lower anode activity. (b) Reaction with oxygen which can result in the oxidation of Pt at the cathode. In PEMFC, the oxidized Pt can dissolve into the liquid and may participate in other unwanted reactions. A study of the interaction of Pt with oxygen in the absence of liquid water is of interest as it can potentially isolate the role of oxygen in catalyst

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degradation. Such results are also of interest in high temperature PEMFC which may operate at temperatures >100 °C such that no liquid water is present. Transport of ionized Pt, however, can occur through the ionomer and is expected to affect catalyst durability even in the absence of water.

One of the approaches to investigate the interaction of Pt with various gaseous species involves the study some property that changes as a chemical reaction or an interaction occurs with the gaseous atmosphere. One such property is the electrical conductance (or resistance) measured as a function of time. Any adsorption of gases on the surface of Pt or reaction to form another phase is expected to change the total electrical resistance. For example, Berry [7] investigated the oxidation of Pt wires by measuring the electrical resistance as a function of time in oxygen-containing atmospheres. Such an approach may also be used with dense Pt films deposited on some support, such as glass slides. If the film is relatively thick the reaction is limited only to the surface and the resulting change in electrical resistance is expected to be rather modest similar to the observations of Berry on platinum wires [7].

In the present work we investigated the kinetics of oxidation/reduction using nanoporous Pt films. The use of nanoporous films vastly increases the total surface area exposed to oxidizing/reducing environments compared to dense films thus increasing the net signal (change in electrical resistance). Also, the use of nanoporous films should drastically increase the kinetics thus facilitating studies of oxidation/reduction at relatively low temperatures in a reasonable period of time. By contrast, when bulk samples (wires) are used, experiments need to be conducted for weeks or months to observe any detectable response [7].

Nanoporous films of Pt of ~250 nm thickness were deposited on glass slides by sputtering using Pt and carbon targets. Porosity was formed in the films after burning off carbon in air. The electrical resistance of the film was measured as a function of time at 80 °C in oxidizing and reducing environments. All measurements were conducted under no applied voltage. A theoretical model was developed to describe the kinetics of oxidation.

2. Experimental procedure

2.1. Design and construction of the test system

The test chamber consisted of a fused silica glass cylinder clamped between two metallic plates with O-rings to ensure gas-tight seals. An electrical heater and a sample holder were inserted into the chamber. A thermocouple was introduced into the chamber to measure the sample temperature. Electrical feed-throughs were inserted from the end plates into the chamber. Also connected to the end plates were gas inlet/outlet fittings. The chamber was connected to a vacuum pump. A gas supply system consisting of flow meters and valves was used to introduce various atmospheres into the chamber. Electrical measurements were conducted using Keithley Model 2000 meter. Data acquisition was done using LabView software. Fig. 1 shows a schematic and a photograph of the testing stand.

2.2. Deposition of nanoporous platinum films on glass slides

For the formation of nanoporous Pt films, Pt and carbon were co-deposited using the two targets by RF and DC sputtering, respectively. The base chamber pressure was 2.4×10^{-6} Torr. Pt was sputtered using 50 W of RF power, while carbon was deposited using 300 W of power. After sputtering, the samples were heated in air at 450 °C for 3 h to burn off the deposited carbon and form platinum films with nanostructured porosity.

2.3. Measurement of electrical resistance in various atmospheres

The sample was inserted into the test chamber with electrical leads connected for a two-probe measurement, maintaining a distance of 8.5 mm between the probes. All measurements were conducted under no applied voltage. Initially, power to the heater was turned on, and the vacuum pump was turned on to evacuate the chamber to an end pressure of 7.5×10^{-3} Torr. The sample temperature and the electrical resistance of the sample were continuously recorded. After the temperature reached 80 °C, both the temperature and the resistance were recorded for several hours. An evacuation step in between changes of atmosphere ensured an almost instantaneous change of atmosphere inside the chamber. Direct change of atmosphere without an evacuation step was too sluggish, as to be expected, since such a situation resembles a continuously stirred tank reactor. A gas mixture containing 10% $H_2 + N_2$ was introduced into the chamber to reduce any platinum oxide(s) that may have formed during carbon burn off in air. After a short exposure to an H_2 containing atmosphere, all of the inlet and the outlet valves were closed once again and the chamber was evacuated. After achieving a vacuum of 7.5×10^{-3} Torr, flowing air was again introduced into the chamber and the electrical resistance of the sample was continuously measured for several hours. This procedure was repeated several times.

2.4. Characterization of the nanoporous platinum films

The as-formed Pt films and after exposure to various atmospheres were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM). The volume fraction of platinum (V_v) and the pore surface area per unit volume (S_v) were measured on SEM images using quantitative stereology [8]. The volume fraction of Pt was measured using the systematic point count method, where $V_v = P_{\mathrm{Pt}}$ in which P_{Pt} is the fraction of the grid points falling on Pt on the SEM images. The pore surface area per unit volume is given by $S_v = 2P_L$ where P_L denotes the number of intersections of Pt/pore boundaries with a test line applied to the SEM images [8].

3. Results and discussion

3.1. Microstructure of the nanoporous Pt film

Fig. 2 shows an SEM image of the nanoporous Pt film formed by co-sputtering Pt and C, followed by burning off carbon at 450 °C in air for 3 h. The micrograph shows that the individual particle size (feature) is on the order of a few nanometers and the pores are also on the order of a few nm in size. Thus, when exposed to various gaseous atmospheres, we expect rapid gaseous transport to occur into and/or out of the pore space of the film. An approximate estimate of the time needed for change of atmosphere to occur through the film of thickness l is given by $t \sim l^2\tau/D_K V_p$ where $D_K = 1/3\sqrt{8k_BT/\pi m}d_p$ is the Knudsen diffusivity, d_p is the pore diameter, m is the molecular mass of the diffusing gas, V_p is the volume fraction of porosity, and τ is the tortuosity factor. For $d_p = 10$ nm, assuming the diffusing gas to be oxygen (molecular mass of $32/N_A$ g where N_A is the Avogadro number), the $D_K \approx 0.016\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ at 80 °C. Assuming $V_p = 0.4$, a tortuosity factor of 3 [9], for $l = 250$ nm, the time needed for the change of atmosphere to occur through the thickness of the film is on the order of 0.3 μs. Indeed, extremely rapid exchange of atmosphere through the thickness of the film is expected. Thus, the slower step is actually the exchange of gaseous atmosphere inside the chamber upon switching of gases. It is for