Electrochemical study of ultrathin silica films supported on a platinum substrate

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The aqueous electrochemistry of ultrathin silica films supported on metal substrates has been investigated in an apparatus that combines an ultrahigh vacuum analysis chamber with an electrochemical cell. The silica films were prepared in vacuum by evaporating silicon in oxygen ambient onto a platinum substrate. It is established that the silica films completely cover the substrate and isolates it from the solution. The silica films on platinum are stable under electrochemical conditions of cycling. It is shown that the thin silica films (15–100 Å) are electrically conductive, with a conductivity several orders of magnitude larger than bulk silica. The silica/Pt electrodes behave over a wide range of potentials as ideally polarizable, which facilitate electrochemical studies of supported metal particles of Pd and Pt. The under-potential deposition of copper onto silica-supported palladium particles and methanol oxidation on platinum particles have also been demonstrated.

I. INTRODUCTION

Metal electrodes modified by self-assembled monolayers and Langmuir–Blodgett or polymeric films are known to exhibit improvements in the stability of their electrochemical activity and response.¹ These modifiers can serve as useful barriers to mass or charge transport between the metal electrode and the electrolyte solution, and thus can be used to inhibit certain undesirable electrode processes. Virtually all of the electrode modifiers utilized to date have been organic, likely because of the ease of their preparation and utilization.² To date, little work has addressed the corresponding properties of inorganic-derived electrode modifiers.

Recent work in these laboratories has demonstrated that ultrathin films of silica,³ magnesia,⁴ nickel oxide,⁵ and alumina,⁶ can be prepared on metal substrates. These films have been shown to be extremely homogeneous, continuous, and smooth, and thus offer new opportunities for studying thin dielectric coatings on conducting substrates. Because of the intense current interest in the modification of electrodes and the relative paucity of data now available regarding metal oxide modifiers, this work was undertaken to establish the electrochemical properties of ultrathin silica films deposited on a platinum electrode. This work was extended to include the electrochemical characterization of palladium and platinum particles deposited onto the thin silica films. This latter part of the study has implications regarding the role of metal particle size in electrocatalytic processes.

II. EXPERIMENT

These experiments were carried out using an apparatus that combines an ultrahigh vacuum (UHV) chamber with an electrochemical cell (EC).⁷ There are three principle subsystems: the UHV surface analysis chamber, the antechamber, and the electrochemical chamber. The UHV chamber is equipped with a U11-100C quadrupole mass spectrometer, electron optics for low energy electron diffraction (LEED), an Auger electron spectrometer, and an ion sputtering gun. The samples were mounted on a long-through sample translator with capabilities for 360° rotation with respect to the horizontal axis. The antechamber is located between the UHV surface analytical chamber and the EC, and is isolated from the main UHV chamber by a pair of differentially pumped, spring-loaded Teflon seals. The antechamber is also completely isolated from the EC chamber by a gate valve, and can be pressurized with ultra-pure N₂ prior to opening the gate valve and translating the sample to the EC chamber. The details of this apparatus can be found in Ref. 7.

The electrochemical cell consists of a cylindrical Pyrex tube (1.0 cm i.d.) and contains a platinum counterelectrode, an Ag/AgCl reference electrode, and the sample, only the front face of which contacts the solution. The cyclic voltammetry and transient impulse measurements were performed using an EG&G M270 potentiostat–galvanostat.

The Pt[111] sample was cleaned with cycles of annealing and sputtering and the surface cleanliness monitored with Auger electron spectroscopy. The silica thin films were prepared by a procedure that has been described in detail previously.⁷ This synthesis includes the evaporation of silicon onto a metal substrate in ~1×10⁻⁵ Torr oxygen, followed by an anneal to 1000 K. The annealed silica films have been shown to exhibit structural properties of vitreous silica and are stable to temperatures in excess of 1000 K.⁸ The thicknesses of the thin silica films were estimated using the attenuation of the substrate Auger electron signals; the dimensions of the thicker films were extrapolated from the growth rates of the thin films.

III. RESULTS AND DISCUSSION

A. Silica/Pt[111]

Figure 1 shows the cyclic voltammograms for a clean Pt[111] and silica-covered Pt[111] in 0.1M H₂SO₄ solution. The dashed line shows the characteristic hydrogen reduction waves at a potential below 0 mV and the platinum oxidation wave above 400 mV. For silica-covered platinum, both the hydrogen and oxygen adsorption features are absent, demonstrating that the platinum surface is completely covered with
silica and isolated from the solution. The solid line shows the current for hydrogen evolution at potentials below \(-300\) mV for two silica film preparations. With an increase in the thickness of the silica film, the rate of hydrogen evolution for a given potential decreases. Above \(-200\) mV, only double-layer charging is observed. In particular, the oxidation wave of platinum above 400 mV is not present for the silica-coated Pt electrode. The measured currents for hydrogen evolution below \(-300\) mV suggest that the silica thin films are conductive and that charge transport is sufficient to facilitate the reduction of \(\text{H}_2\text{O}^+\) ions.

The conductivity of the silica thin films was further studied with the homogeneous \(\text{Fe}^{3+}/\text{Fe}^{2+}\) reaction (Fig. 2), since this reaction is well known to involve the transfer of only a single electron through the double layer.\(^9\) The dashed line in Fig. 2 was obtained with a bare Pt(111) electrode, where the well-defined oxidation-reduction current maxima occur near the formal Nernst potential of this reaction. The peak currents are significantly reduced by the presence of the silica thin films, indicating that the charge transfer process is inhibited by the silica layers. This observation is consistent with minimal potential drop across the silica film.

The resistivity of the silica thin films was investigated by galvanostatic transient experiments where the double layer capacitance and the ohmic resistance were measured at different current densities.\(^10\) Figure 3 shows the resistance of the silica/Pt system as a function of the silica film thickness. As anticipated, the resistance of the silica films increases with film thickness and is approximately constant (\(~4\times 10^6\) \(\Omega\) m), for films with a thickness of 5, 14, 50, and 100 Å. This resistivity, however, is considerably smaller than values reported in the literature for bulk silica (\(~1\times 10^{12}\) \(\Omega\) m).\(^11\)

The higher conductivity of the silica thin films can be attributed to several effects: quantum tunneling, hydroxyl
formation, or to highly conducting defects at grain boundaries. Tunneling through oxide thin films is a well-known phenomenon in metal/oxide/metal sandwich structures.\textsuperscript{12} The formation of hydroxyl groups on the silica surface can also increase the lateral conductivity of silica films via hydrogen diffusion.\textsuperscript{13} Defects as well along grain boundaries could also increase markedly the conductivity of the silica thin films.\textsuperscript{14}

Figure 4 shows a scanning electron microscopy (SEM) micrograph of copper electrochemically deposited onto a silica film on Pt(111). This micrograph indicates that copper preferentially deposits onto extended defect sites. These local defect sites represent areas of relatively high conductivity and are likely to be the major contributing factor to the overall higher conductivity of the silica films compared to bulk silica.

B. Under-potential-deposition of copper onto palladium particles supported on silica/Pt(111)

The electrochemical properties of silica-supported metal particles have also been addressed. Figure 5 shows the cyclic voltammogram for palladium particles supported on silica/Pt in 1×10⁻³ M CuSO₄ solution in 0.1 M H₂SO₄. Monolayer copper was found to deposit on these particles at a potential corresponding to under-potential deposition (UPD). The UPD of Cu on the palladium particles is very similar to Cu UPD on polycrystalline palladium,\textsuperscript{11} consistent with the silica-supported Pd particles having multiple-faceted structures.

Finally, to demonstrate the potential for using supported metal particles on thin silica films for electrocatalytic applications,\textsuperscript{15} the oxidation of methanol on supported platinum particles was investigated. Figure 6 shows the cyclic voltammograms obtained for silica-supported platinum particles and for a bare Pt(111) electrode in a solution of 0.1 M methanol in 0.1 M H₂SO₄. The total surface area of the platinum particles for the data in Fig. 6 is ~60% of the flat Pt(111) substrate, as determined by hydrogen adsorption. The supported Pt particles are clearly active for methanol oxidation; however, it is noteworthy that the oxidative process on the Pt particles occurs at ~150 mV more anodic compared with Pt(111).

Fig. 3. The ohmic resistance as a function of the thickness of the silica film on Pt(111), determined electrochemically.

Fig. 4. A SEM micrograph of Cu electrochemically deposited onto silica (60 Å)/Pt.

Fig. 5. Under-potential deposition of Cu onto palladium particles (~400 Å in diameter) supported on silica(60 Å)/Pt in 1×10⁻³ M CuSO₄ +0.1 M H₂SO₄. The sweep rate was 50 mV/s.
The stability of the silica/Pt system and the passive electrochemical behavior of the silica/Pt electrode provide an opportunity to investigate the electrochemistry of silica-supported metal particles. Two examples are shown in this work: the under-potential deposition of copper onto silica-supported palladium particles; and methanol oxidation on silica-supported platinum particles.

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1 For a recent status report, see A. J. Bard et al., J. Phys. Chem. 97, 7147 (1993), and references therein.