Effect of sulfuric acid concentration on hydrous oxide film growth at Au electrodes

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Introduction

Hydrous oxide films (β–oxide) formed on noble metal surfaces have been the topic of a significant amount of interest over the last years [1-3], partly because of their many possible practical applications in areas such as electrocatalysis, batteries, and in electrochromic display devices. Previous studies of the electrochemical oxidation of noble metals have suggested that a thick, dispersed, hydrous oxide film (β–oxide) is located above a compact, uniform, anhydrous oxide (α–oxide) layer. The degree of hydration of the β–oxide film and its thickness depend on the anodizing conditions employed [4].

The properties of the hydrous β-oxide film formed on polycrystalline Au electrodes have been much less studied than at other metals, although it has been reported that this Au oxide film can become very thick when formed in 0.5 M H_2SO_4 solutions [5]. Many different compositions have been suggested for the Au β–oxide film, including Au_2O_3, hydrated Au_2O_3, $Au(OH)_3$ [5-6], and complex mixtures of $Au(OH)_3$, H_2O and trapped O_2 [7]. Clearly, additional techniques are required to establish the Au β–oxide film composition with more certainty.

In this work, both sensitive *in situ* mass measurements (quartz crystal microbalance (QCMB)) and the ellipsometric technique have been employed to establish the composition and the structure of the β–oxide film formed at polycrystalline Au electrodes in sulfuric acid solution. It was found that these properties as well as Au oxide growth rates can be controlled by varying the H_2SO_4 concentration in the growth solution.

Results and Discussion

Figure 1 shows a family of reduction profiles, at 10 mV/s, after oxide growth, achieved by holding at 2.1 V vs. RHE in 0.1, 0.25 and 0.5 M H_2SO_4 for 3 min. The oxide film reduced in peak C_1 has a mass to charge ratio (g/mol e⁻) of ca. 8, and is therefore either AuO or Au_2O_3. The charge density of this unhydrated α-oxide decreases with increasing H_2SO_4 concentration. However, the growth of this unhydrated oxide reaches a limit at 7 min in 0.1 M H_2SO_4, 3 min in 0.25 M H_2SO_4 and 2 min in 0.5 M H_2SO_4 solution.

The β-oxide film reduced in peak C_2 has a mass to charge ratio which is higher than 8 g/mol e-, i.e., in the range of 11 at short times (ca. 30 sec) of growth to 15 at longer times, e.g., 7 min. This is indicative of the partial hydration of the film, which is found to be independent of the sulfuric acid concentration. The composition of the β-oxide formed in various sulfuric acid concentrations is likely $Au_2O_3.H_2O$ at short times and $Au_2O_3.2H_2O$ at longer times of growth. The charge density of the β-oxide film increases with increasing growth time, with no limiting thickness observed.

Ellipsometric measurements were carried out on the Au electrode surface during polarization at 2.1 V in 0.1, 0.25 M and 0.5 M sulfuric acid solutions. The experimental Δ and Ψ plot, collected during α – and β-oxide growth over 25 min in 0.25 M sulfuric acid, is shown in Fig. 2 (solid squares). The ellipsometric data was fit to a multilayer model, showing clearly that the α–oxide grows to a limiting thickness of 2.2 nm at 7 min in 0.1 M, 1.5 nm at 3 min in 0.25 M and 1.3 nm at 2 min in 0.5 M sulfuric acid, consistent with the results obtained from the α-oxide stripping charges. The refractive index (n-ik) of the α–oxide film is found to be identical in the three acidic solutions, 3.3 – 0.7ii, while that of overlying β–oxide film depends on the growth time and sulfuric acid concentration employed. However, the n value of all of the β–oxide films is less than that of the α–oxide, indicating that the β–oxide is porous. In the first 20 min of growth, the β–oxide film formed in 0.1 M H_2SO_4 has the highest porosity, while the oxide formed in 0.25 and 0.5 M H2SO4 has a lower, but similar, degree of porosity, with the β–oxide formed in the 0.5 M solution being the least porous at still longer times of growth.

The rate of film thickening of the β–oxide film, based on the ellipsometric data, is 4.3, 2.7 and 3.3 nm/min in 0.1, 0.25 and 0.5 M sulfuric acid, respectively. The β–oxide film formed in 0.1 M H₂SO₄, which has the lowest charge density, has the

0.5 M solutions, the films are of similar porosity, and the higher charge density in 0.5 M sulfuric acid results in a greater film thickening rate.

References

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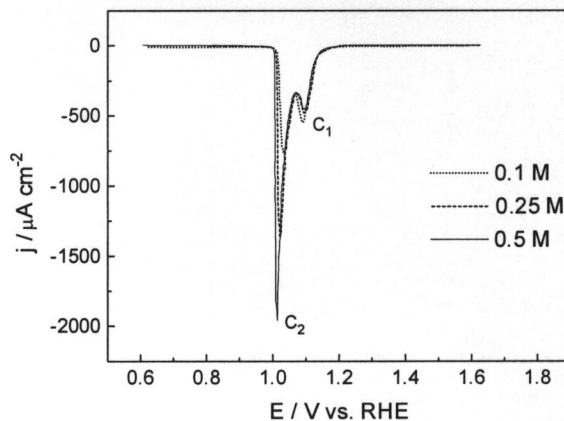7. M.E. Vela, J.O. Zerbino, A.J. Arvia, Thin Solid Films 233 (1993) 82.

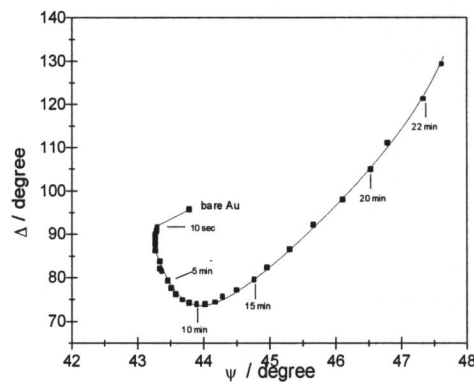Fig. 1 Reduction profiles (10 mV/s) of Au oxide formed at 2.1 V for 3 min in 0.1, 0.25 and 0.5 M H_2SO_4.

Fig.2. Experimental (solid dot) and theoretical (solid curve) ellipsometric data of Au oxide formed at 2.1 V vs. RHE in 0.1 M H2SO4 solution