

Oxygen Reduction on Thin-Film Gold Electrodes

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The electrochemical reduction of oxygen has been studied more extensively on platinum than on gold electrodes due to the excellent electrocatalytic properties for oxygen reduction [1]. Gold electrodes are of interest, however, since reduction process proceeds on an oxide-free surface in acid electrolyte [2]. The purpose of the present work was to study the reduction of oxygen on thin-film gold electrodes in order to investigate size effects on electrode kinetics.

Thin Au films were prepared by vacuum evaporation onto glassy carbon (GC) and highly oriented pyrolytic graphite (HOPG) substrates. The thickness was varied between 0.5 and 50 nm. The surface morphology of the gold films was examined by atomic force microscopy (AFM). Electrochemical measurements were carried out by using the rotating disk electrode technique.

The AFM images revealed that relatively large gold islands were formed on HOPG. For the 2 nm-thick film the substrate surface was completely covered by gold deposit. However, the deposit was not dense and the adhesion of gold to HOPG was found to be rather poor. The root-mean-square roughness of the samples increased only slightly for films thicker than 5 nm.

Repeated cyclic voltammetry in 0.5 M H₂SO₄ was used to stabilize the gold film on GC. The area under the gold surface oxide reduction peak decreased gradually for thinner films indicating a change in surface morphology of the film. The roughness factor of the Au film electrodes varied only slightly in the thickness range between 5 and 50 nm. This is in agreement with the AFM data for greater film thickness.

Typical oxygen reduction curves for thin-film Au electrodes are presented in Fig. 1. The reduction current gradually increased up to the potential of H₂ evolution. The half-wave potential of O₂ reduction ($E_{1/2}$) was almost independent of film thickness for values greater than 5 nm.

The number of electrons consumed per O₂ molecule was higher than two at potential $E < E_{1/2}$ indicating that the hydrogen peroxide formed is further reduced. The reduction of H₂O₂ commences at ca 0 V vs. SCE (Fig. 1, curve 7). This confirms that the reduction of O₂ stops at the H₂O₂ stage at the start of the polarization curve.

The kinetic parameters of O₂ reduction were determined from the mass-transfer-corrected Tafel plots shown in Fig. 2. The Tafel lines were linear in a large potential window showing a slope of -115 mV/dec for thin-film and bulk gold electrodes corresponding to slow first electron transfer kinetics to the O₂ molecule.

It was of special interest to study the influence of film thickness on the specific activity (SA) for O₂ reduction. The SA value was constant for films thicker than 2 nm and agreed well with the value for bulk Au.

Thin Au films and finely divided Au particles can be regarded as potential catalysts for hydrogen peroxide production since the reduction of oxygen stops at the

stage of H₂O₂ formation in a large potential window. However, the O₂ reduction overpotential at a gold electrode is rather large in acid electrolyte. Work is in progress to study O₂ reduction on thin-film Au electrodes in alkaline solution.

References

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2. R. Adzic, in: J. Lipkowski, P.N. Ross (Eds.), *Electrocatalysis*, Wiley-VCH, New York, 1998, pp. 197-242.

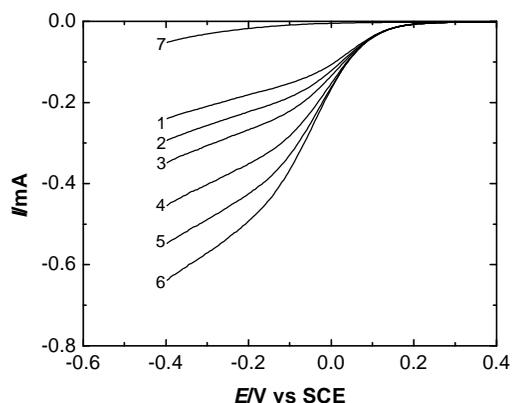


Fig. 1. Voltammetry curves for oxygen reduction on a 2 nm-thick Au film electrode in O₂-saturated 0.5 M H₂SO₄ at a scan rate of 10 mV/s. Electrode area 0.132 cm², rotation rate: 1) 360, 2) 610, 3) 960, 4) 1900, 5) 3100 and 6) 4600 rpm. Curve 7 was recorded in Ar-saturated 0.5 M H₂SO₄ containing 1 mM H₂O₂, $\omega=1900$ rpm.

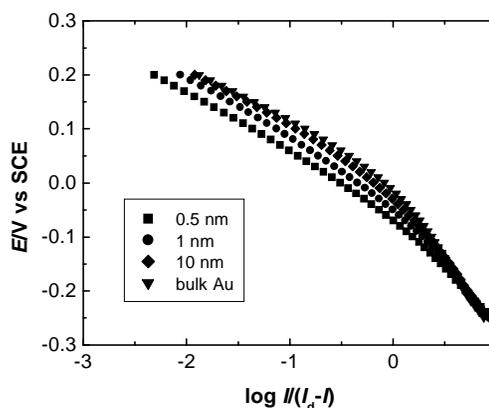


Fig. 2. Comparison of the mass-transfer-corrected Tafel plots for oxygen reduction on thin-film and bulk gold electrodes in 0.5 M H₂SO₄. Rotation rate: 1900 rpm.