Changes in Surface Stress of Gold Electrode during Underpotential Deposition of Lead

Masahiro Seo and Makiko Yamazaki
Graduate School of Engineering, Hokkaido University
Kita-13 Jo, Nishi-8 Chome, Kita-ku, Sapporo 060-8628,
Japan

There were many studies of the underpotential deposition (UPD) of foreign metals on single crystal metal electrodes. Scanning tunnel spectroscopy (STM) and atomic force microscopy (AFM) were recognized as powerful tools for investigating atomistic pictures of the UPD adlayers. Moreover, the recent development of in-situ surface X-ray scattering (SXS) technique has succeeded in determining more exactly two-dimensional (2D) structures of the UPD adlayers. It has been often reported that 2D phase of adlayer changes at a certain surface coverage of UPD metal. However, there are few studies on phase change in adlayer from the viewpoint of surface thermodynamics. In this study, the changes in surface stress of gold electrode during UPD of Pb were measured by a bending beam method to discuss surface energetics of the phase change in Pb-adlayer.

A gold film with a thickness of 210 nm was evaporated on one side of a thin glass plate (140 μm x 5mm x 60 mm). The evaporated gold film usually consists of fine crystals mainly oriented to (111) plane. A titanium film with a thickness of 50 nm was pre-coated to keep a good adhesion between gold film and the substrate glass plate. The electrolyte solutions used for experiments were pH 2.85, 0.5 M $NaClO_4$ + 10^{-3} M $HClO_4$ solutions with and without 10^{-4} M $PbCl_2$ or $Pb(NO_3)_2$, which were deaerated with pure argon gas before and during experiments. The principle and apparatus of a bending beam method was described elsewhere [1-2]. The potential sweep or potential step method was employed for measurement of the changes in surface stress, Δg, in the potential region between –0.24 V and 0.8 V (SHE). The cathodic limit of –0.24 V corresponds to the equilibrium potential of Pb-bulk deposition.

Figure 1 shows the cyclic voltammogram (CV) and changes in surface stress, Δg, vs. potential, E, curve for the gold electrode in pH 2.85, 0.5 M $NaClO_4$ + 10^{-3} M $HClO_4$ solution with 10^{-4} M $PbCl_2$. The potential sweep (10 mV s^{-1}) was started from the anodic limit of 0.8 V (SHE). The values of Δg were referred to zero at 0.8 V, and their positive and negative signs were taken for the tensile and compressive directions of Δg, respectively. The maxima of Δg appeared near the adsorption and desorption current peaks of Pb, A_1 and D_1, in the CV. Moreover, the shoulders of Δg emerged near the adsorption and desorption current peaks of Pb, A_3 and D_3, in the CV. Figure 2 shows the relation between Δg and cathodic charge density, q_c, obtained with the cathodic potential sweep from the anodic limit. The cathodic charge density, q_c, was obtained from the CV, referred to $q_c = 0$ at 0.8 V It is seen from Fig. 2 that there are three domains of linear relationships between Δg and q_c. The domain a) is in the range of anion adsorption on gold, while the domains b) and c) are responsible for the different UPD phases of Pb. It is expected that the UPD phase of Pb on gold changes in the plateau region between the domains b) and c) in Fig. 2.

References

1. K. Ueno and M. Seo, J. Electrochem. Soc.,**146**, 1496 (1999).
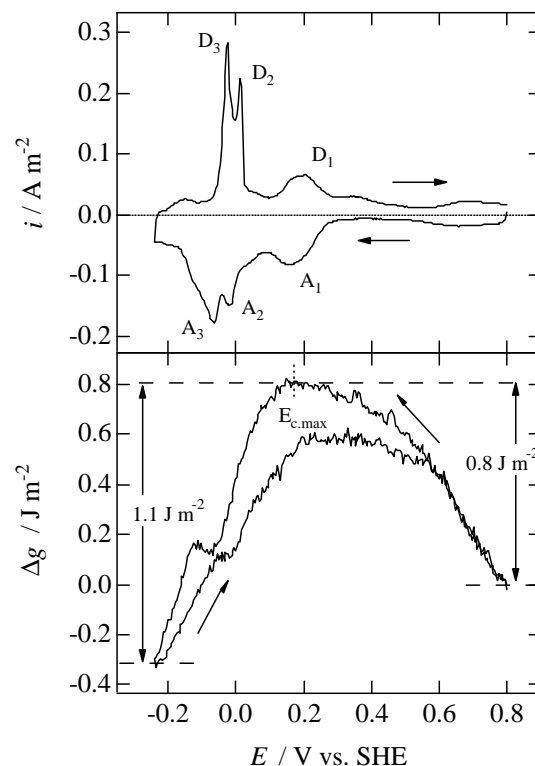2. G. G. Láng and M. Seo, J. Electroanal. Chem., **490**, 98 (2000).

Fig. 1 Cyclic voltammogram and Δg vs. E curve for UPD of Pb on Au electrode in pH 2.85, 0.5 M $NaClO_4$ containing 10^{-4} M $PbCl_2$. Sweep rate : 10 mV s^{-1}
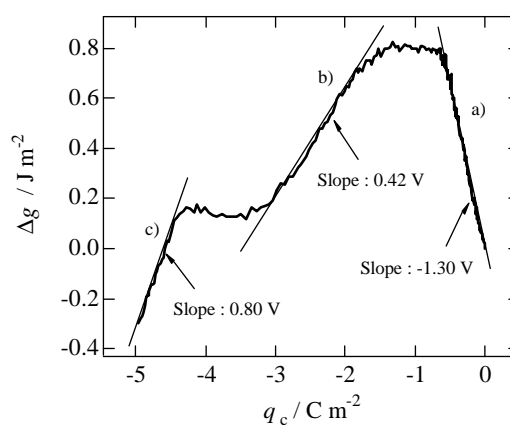

Fig. 2 Relation between Δg and q_c for the gold electrode in pH 2.85, 0.5 M $NaClO_4$ containing 10^{-4} M $PbCl_2$. Sweep rate : 10 mV s^{-1}