

Underpotential deposition (upd) of zinc on Au(111) in phosphate solution: Anomalous effect of phosphate co-adsorption on Zn upd

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Introduction

Underpotential deposition (upd) process of metal ions M^{n+} on a foreign single crystal metal substrate M' has been extensively studied for elucidation of the electrodeposition process at an atomic level. We have investigated the process of Zn upd on polycrystalline and single crystalline Pt electrodes in term of the effect of adsorbed anion [1-5]. Induced adsorption of phosphate and sulfate species by upd Zn was observed on polycrystalline Pt electrode by radiotracer technique [6]. However, there have been only a few studies of zinc upd on Au(111) surface [7]. The STM image of $(\sqrt{3} \times \sqrt{3}) R30^\circ$ structure was observed on upd-Zn/Au(111) in phosphate solution [7]. The upd occurs in the potential region between anion adsorption / desorption and hydrogen evolution on Au(111); adsorbed anions are not present on Au(111) surface at the upd onset potentials. In the present report, we investigated the voltammetric behavior of Zn upd on Au(111) in several acidic solutions in terms of the effect of anions: the effect of perchlorate, sulfate, phosphate, and halide species was investigated. It is known that the order of anion adsorption strength on Au(111) without upd metal is $\Gamma > Br^- > Cl^- > H_2PO_4^- \approx HSO_4^- > ClO_4^-$. It should be noted that Zn upd markedly induce adsorption of phosphate species on Au(111) in these anions.

Experimental

Au(111) was prepared by Clavilier's method in our laboratory. Before each measurement, the electrode was annealed in a gas + oxygen flame and then introduced into an electrolytic cell. The detailed procedure are found elsewhere [3]. A saturated calomel electrode (SCE) was used as the reference electrode, and a Pt foil was used as the counter electrode. The electrolyte solutions were prepared from reagents of ultra pure grade and Millipore Milli-Q water. The solutions were deaerated by Ar gas of 5N purity. Cyclic voltammograms were taken with ordinary electrochemical apparatus at room temperature.

Results and discussion

Fig.1 shows voltammograms of Zn upd at Au(111) in phosphate, sulfate, and perchlorate solutions. The onset potential of Zn upd was the same at -0.35 V in all solutions. However, the feature of Zn upd voltammogram in phosphate solution differs from that in sulfate solution, although sulfate anion as well as phosphate anion is known as specifically adsorbable anion. In phosphate solution, the very sharp peak was observed at -0.42 V at the negative going sweep, while the upd peak was observed at -0.725 V in sulfate solution. These results suggest that the co-adsorption of phosphate anion facilitates the Zn upd on Au(111) in comparison with that of sulfate anion, by analogy with the radiotracer method for the case of phosphate and sulfate induced adsorption on upd Zn at a polycrystalline Pt electrode [6]. In perchlorate solution, no sharp upd peak was observed at $-0.6V < E < -0.35V$, where the predominant reaction at $E < -0.6V$ was hydrogen evolution.

Fig.2(A) shows the effect of bromide ion to Zn upd voltammograms at Au(111) in perchlorate solution. The feature of Zn upd waves at $E < -0.35V$ with KBr is similar to that without KBr. This result indicates that the presence of bromide ions has no effect on the upd process; no induced adsorption of Br^- occurs with Zn upd. Fig.2(B) shows voltammograms at Au(111) in $0.1M KClO_4 + 10^{-4}M HClO_4 + 10^{-3}M KBr + 10^{-3}M KH_2PO_4$ with and without $10^{-3}M Zn^{2+}$, where KH_2PO_4 was added to the solution of Fig.2(A) with KBr. In contrast to the case of Fig.2(A), the sharp current peak of Zn upd was observed at around -0.55V with Zn^{2+} ions; the presence of phosphate ions in the solution facilitates the Zn upd. This result suggests that co-adsorption of upd Zn and phosphate species occurs regardless of the presence of Br^- ion, which is more strongly adsorbed than phosphate species on Au(111).

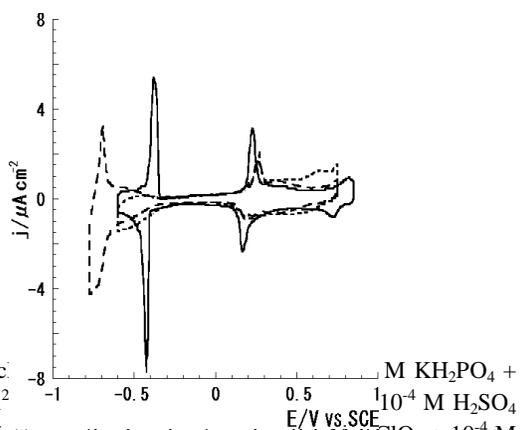


Fig. 1 Cyclic voltammograms of Zn upd at Au(111) in phosphate, sulfate, and perchlorate solutions. The onset potential of Zn upd was the same at -0.35 V in all solutions. However, the feature of Zn upd voltammogram in phosphate solution differs from that in sulfate solution, although sulfate anion as well as phosphate anion is known as specifically adsorbable anion. In phosphate solution, the very sharp peak was observed at -0.42 V at the negative going sweep, while the upd peak was observed at -0.725 V in sulfate solution. These results suggest that the co-adsorption of phosphate anion facilitates the Zn upd on Au(111) in comparison with that of sulfate anion, by analogy with the radiotracer method for the case of phosphate and sulfate induced adsorption on upd Zn at a polycrystalline Pt electrode [6]. In perchlorate solution, no sharp upd peak was observed at $-0.6V < E < -0.35V$, where the predominant reaction at $E < -0.6V$ was hydrogen evolution.

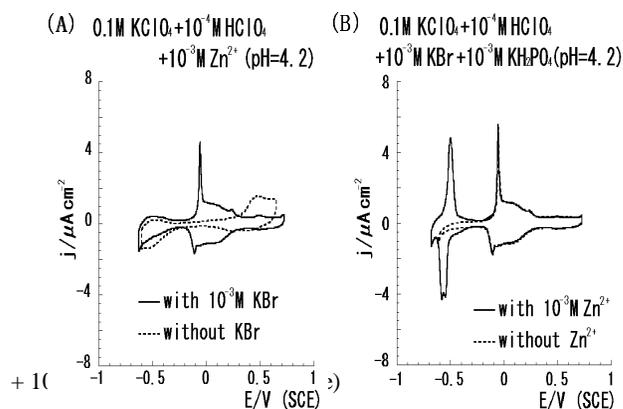


Fig. 2 Cyclic voltammograms of Au(111), (A) in $0.1 M KClO_4 + 10^{-4} M HClO_4 + 10^{-3} M Zn^{2+}$ (pH=4.2), and (B) in $0.1 M KClO_4 + 10^{-4} M HClO_4 + 10^{-3} M KBr + 10^{-3} M KH_2PO_4$ (pH=4.2) with (solid line) and without (broken line) $10^{-3} M Zn^{2+}$ ions, at $5 mV s^{-1}$.

References

1. Aramata, A.; Quaiyyum, M. A.; Balais, W. A.; Atoguchi, T.; Enyo, M. *J. Electroanal. Chem.* **1992**, 338, 367.
2. Taguchi, S.; Aramata, A.; Quaiyyum, M. A.; Enyo, M. *J. Electroanal. Chem.* **1994**, 374, 275.
3. Taguchi, S.; Aramata, A. *J. Electroanal. Chem.* **1995**, 396, 131.
4. Taguchi, S.; Fukuda, T.; Aramata, A. *J. Electroanal. Chem.* **1997**, 435, 55.
5. Taguchi, S.; Aramata, A. *J. Electroanal. Chem.* **1998**, 457, 73.
6. Horanyi, G.; Aramata, A. *J. Electroanal. Chem.* **1997**, 437, 259.
7. Nakamura, M.; Aramata, A.; Yamagishi, A.; Taniguchi, M. *J. Electroanal. Chem.* **1998**, 446, 227.