

## Underpotential Deposition of Cadmium onto Ag(111) from Chloride Containing Solution

V.D.Jovic, B.M.Jovic and G.R.Stafford

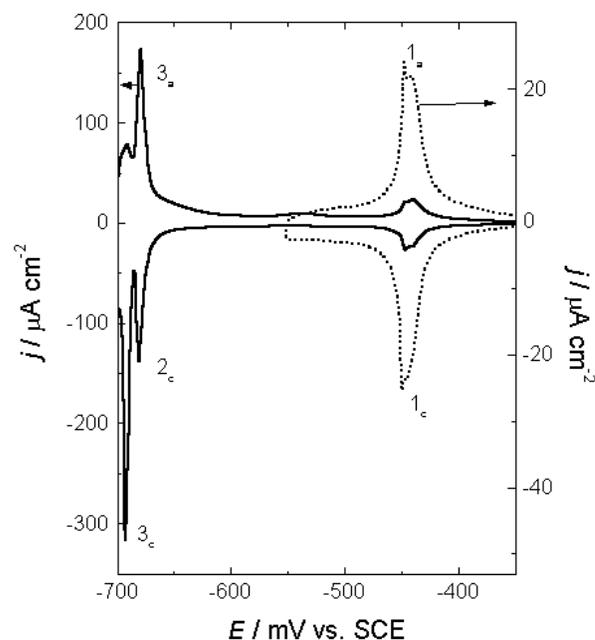
Materials Science and Engineering Laboratory  
National Institute of Standards and Technology  
Gaithersburg, MD 20899-8551, USA

UPD of cadmium onto silver single crystals has been the subject of only two papers. H. Bort et al. [1] investigated UPD alloy formation in the system Ag(hkl)/Cd<sup>2+</sup> from sulfate containing solution. They found that on the Ag(111) surface, the UPD of Cd commenced at a potential of about 300 mV vs. Cd by the formation of a ( $\sqrt{3}\times\sqrt{3}$ )R30° structure. The voltammetric waves associated with this process were reversible. A second cathodic peak, observed at about 70 mV vs. Cd, was reported to correspond to monolayer deposition of Cd while the charge associated with a third cathodic peak was consistent with that required for a second monolayer of Cd. Significant alloying of Ag with Cd was found to occur at potentials between 0 and 50 mV vs. Cd<sup>2+</sup>/Cd. The time dependence of the alloy formation process was described by a parabolic rate law, the rate constant of which was reported to be a function of both potential and temperature. In the paper of V.D. Jovic et al. [2] the influence of different anions (sulfate, perchlorate and citrate) on the UPD of Cd onto Ag(111) was investigated. It was found that both cyclic voltammograms and differential capacity curves were altered in the presence of different anions.

In this paper, we investigate the UPD of Cd onto Ag(111) as a function of CdCl<sub>2</sub> concentration in 0.1 mol L<sup>-1</sup> NaCl. The UPD process was examined by both linear sweep voltammetry and chronoamperometry. The alloying of Cd and Ag at underpotentials was examined by potentiostatic deposition followed by anodic stripping voltammetry. All experiments were carried out in a two-compartment electrochemical cell at 25 °C in an atmosphere of purified nitrogen. A solution of 0.1 mol L<sup>-1</sup> NaCl (pH 4.96) was used as the supporting electrolyte. Four concentrations of CdCl<sub>2</sub> were investigated, 0.0001, 0.005, 0.01, and 0.1 mol L<sup>-1</sup>. A saturated calomel electrode (SCE) was used as a reference electrode. All solutions were made from supra pure (99.999%) chemicals (Aldrich) and EASY pure UV water (Barnstead). After mechanical polishing, the single crystal surface was chemically polished in a solution containing sodium cyanide and hydrogen peroxide [2]. The counter electrode was a platinum sheet and was placed parallel to the working electrode. Cyclic voltammetry experiments were performed using a PAR M-175 universal programmer, PAR M-173 potentiostat, and an X-Y recorder (Houston Instrument 2000R). Potentiostatic *j-t* transients were recorded on a digital oscilloscope (Nicolet 4094A).

The cyclic voltammograms, from solutions containing varying amounts of CdCl<sub>2</sub>, were slightly different. All of the voltammograms were characterized by a pair of reversible peaks appearing between -400 mV and -500 mV and two pairs of peaks close to the reversible potential of Cd deposition. These peaks were found to be well defined only at sweep rates of 10 mV s<sup>-1</sup> and lower. A typical cyclic voltammogram, recorded in a solution containing 0.1 mol L<sup>-1</sup> CdCl<sub>2</sub> + 0.1 mol L<sup>-1</sup> NaCl, is shown in the figure. The charge associated with the

voltammetric peaks,  $1/1_a$ , was about 170 μCcm<sup>-2</sup>, while the charge obtained from pulse experiments (after correction for the double layer charge) was found to be 150 μCcm<sup>-2</sup>. Hence, these peaks correspond to an adsorption and desorption process which is consistent with the ( $\sqrt{3}\times\sqrt{3}$ )R30° structure of Cd on Ag(111) (nominally 149 μCcm<sup>-2</sup>, assuming complete charge transfer). One can therefore conclude that the chloride adatoms are not desorbed, but are replaced by Cd atoms, and remain adsorbed on the newly formed Cd surface. This is consistent with the findings of C.Schulmann et al. [3] for the UPD of Cd onto Cu(111).



The kinetics of alloy formation was examined by potentiostatic deposition for a given time (*t*) followed by anodic stripping voltammetry to reveal the Cd charge,  $\Delta q$ , associated with the alloy. In the potential region of peak 3<sub>c</sub>, linear  $\Delta q - t^{1/2}$  dependences were obtained for four different potentials ( $\Delta E$ ) indicating diffusion controlled surface alloying of Cd with Ag [1]. A rate constant *K*, defined as:

$$K = \left[ \frac{\partial \Delta q / 2F}{\partial t^{1/2}} \right]_{\Delta E, T}^2$$

was evaluated from the slope of the  $\Delta q - t^{1/2}$  curve. A linear log *K*- $\Delta E$  dependence [1] was obtained for 0.1 mol L<sup>-1</sup> and 0.01 mol L<sup>-1</sup> CdCl<sub>2</sub> solutions. The appearance of an additional stripping peak after the electrode was held for longer times in the potential region of peak 3<sub>c</sub> clearly indicated the presence of a Ag-Cd alloy. In the potential region of peak 2<sub>c</sub>,  $\Delta q$  was found to increase with hold time at a given potential, indicating that some degree of alloying does occur in this potential region. However, in this case, the corresponding  $\Delta q - t^{1/2}$  dependences were found to deviate from linearity, suggesting that a different alloying mechanism is operative.

- [1] H.Bort, K.Juttner, W.J.Lorenz, G.Staikov, *Electrochim.Acta*, 28, 993 (1983).
- [2] V.D.Jovic, B.M.Jovic, A.R.Despic, *J.Electroanal.Chem.*, 288, 229 (1990).
- [3] C.Schulmann, Z.Park, C.Bach, K.Wendelt, *Electrochim.Acta*, 44, 993 (1998).

