A STUDY OF THE MECHANISM OF ELECTRODEPOSITION OF SELENIUM FROM LIQUID HYDROGEN CHLORIDE

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ABSTRACT

Elemental selenium has been electrodeposited onto a gold substrate from a solution of phenyl selenyl chloride in liquid hydrogen chloride at temperatures between $-85°$ and $-105°C$. The mechanism of selenium deposition has been studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). At constant electrolyte composition and in the absence of any form of forced circulation, the mechanism of deposition of selenium appears to change between $-95°$ and $-105°C$ from mass-transfer control at high temperatures to control by an interfacial process, possibly charge transfer, at low temperatures. SEM micrographs of selenium electrodeposits and EIS data provide evidence of **thermally mediated control of morphology.**

INTRODUCTION

Almost ten years ago Rose and Sadoway began conducting experiments demonstrating that it is possible to electrodeposit metals at cryogenic temperatures from solutions comprising liquefied hydrogen halides or interhalogens (1). The process was dubbed "cryoelectrodeposition" and offers a number of distinct advantages over competitive techniques. Owing to the low temperature of the process, cryogenic electrolysis minimizes thermal damage to the substrate, permits the formation of sharp interfaces and has the potential to generate smooth, uniform deposits. In connection with this last point, Figure 1 shows schematically how temperature affects the rate constants associated with two of the major kinetic processes in electrodeposition, mass transport of the electroactive ion from the bulk to the electrode and charge transfer at the electrode-electrolyte interface. For dimensional similarity, the relevant constants are, respectively, D/λ, where D is the diffusion coefficient of the electroactive ion in the electrolyte solution and λ is a characteristic diffusion distance, and k is the specific heterogeneous rate constant for the discharge step. At ambient and elevated temperatures D is smaller than k, and electrochemical processes are mass transfer controlled. To avoid the undesirable morphological consequences of mass transfer control, it is necessary to shift the mechanism to an interfacial step by, for example, the addition of leveling agents to the electrolyte. As depicted in Figure 1, owing to the fact that k is much more sensitive to temperature than D, it may be possible to promote this same shift in mechanism away from mass transfer control by decreasing temperature to a value low enough that charge transfer (or some other interfacial process, for that matter) is rate limiting.

The purpose of this study was to conduct a systematic investigation of cryogenic electrodeposition to determine the mechanism of reaction. The specific chemistry of this investigation was selenium deposition from liquid hydrogen chloride, as this was the first part of a broader effort aimed at the cryogenic electrosynthesis of selenide compounds such as nickel selenide, useful as an anti-corrosion film in IC packaging, and zinc selenide, a II-VI compound semiconductor.

EXPERIMENTAL

Figure 2 shows the cell which consisted of a closed-one-end borosilicate glass tube covered with a glass cap by means of a fluorocarbon plastic fitting. Compression fittings provided gas tight access for the electrodes. The working electrode (WE) consisted of 1.0 mm diameter gold wire, insulated from the electrolyte solution by a Teflon® coating and exposed at the tip. The counter electrode (CE) was made of a 1" square of platinum foil, 0.02" thick. Platinum wire leads were spot welded to the electrode and coated with Teflon®. The Ag/AgCl reference electrode (RE) consisted of silver wire, 1.0 mm in dia., onto which a porous deposit of silver chloride had been anodically electrodeposited. This was housed in a glass compartment which established electrical contact with the main cell by a microcrack glass junction (2). This junction was positioned just below the working electrode. Details of the electrode placement are revealed in Figure 3.

The cell was baked at $120°C$ for 1 hour in vacuum to prepare the glass. The selenium bearing solute, phenyl selenyl chloride (C_6H_5SeCl, 99.99%, Johnson Matthey, Ward Hill, MA) (3,4), was charged without treatment into the cell. Tetramethyl ammonium chloride (($CH_3)_4NCl$, 98^+%, MTM Lancaster Synthesis, Windham Hill, NH), which had been recrystallized in methyl alcohol, was added to the reference electrode compartment to make a saturated solution. This fixed the activity of the chloride ion and, in turn, the potential of the Ag/AgCl couple. Charging the cell and positioning the electrodes were done in a glove bag filled with argon in order to avoid moisture contamination.

Liquid HCl was prepared from ULSI grade HCl gas (99.999%, Matheson Gas

Products, Gloucester, MA). This was first contacted with magnesium perchlorate and then condensed directly into the electrochemical cell. The cell was chilled by immersion in methylcyclohexane, which was cooled by liquid nitrogen flowing through copper tubing. Temperature was controlled by an automatic temperature controller (Model 330, Lakeshore Cryotronics, Westville, OH) between $-85°$ and $-105°C$ (5).

Cyclic voltammetry was conducted with a programmable potentiostat (Solartron 1286, Schlumberger Instruments, Burlington, MA). The voltage was varied between -0.7 and $+1.9$ V <u>versus</u> Ag/AgCl at linear sweep rates of 2, 6, and 18 V min^{-1}. The data were recorded on an X-Y recorder.

To investigate the kinetic processes at work in the electrodeposition of selenium, electrochemical impedance spectroscopy (EIS) was employed. Measurements were made with an impedance/gain-phase analyzer (Solartron 1260, Schlumberger Instruments, Burlington, MA) over a wide range of frequency: 1 mHz to 10 MHz. Data acquisition, storage, and analysis were controlled by a personal computer using the Z60 impedance program (Scribner Associates, Charlottesville, VA).

Selenium was deposited on gold by controlled potential electrolysis conducted at values of applied overpotential determined earlier in this study by voltammetry. The current density was typically on the order of 10 mA cm^{-2}. The chemistry and morphology of the deposits were investigated by Auger electron spectroscopy, X-ray photoelectron spectroscopy, x-ray diffraction, and scanning electron microscopy.

RESULTS AND DISCUSSION

Comparison of the cyclic voltammograms taken at a temperature of $-95°C$ in pure HCl and in binary solutions of C_6H_5SeCl dissolved in liquid HCl reveals that at cathodic potentials the voltammograms of the C_6H_5SeCl solutions exhibit a shoulder not present in the voltammograms measured in pure liquid HCl. The electrochemical reaction associated with this shoulder is not strictly reversible as evidenced by the shift to more cathodic potentials with increasing sweep rate (6). The peak current was found to scale with the square root of sweep rate.

To test the feasibility of electrodeposition of selenium, electrolysis was conducted at cathodic and anodic overpotentials: $\eta = -0.3$ V and $\eta = +0.3$ V. Analysis of the working electrode substrate by Auger electron spectroscopy (AES) revealed that selenium was electrodeposited only at potentials more cathodic than -0.3 V. X-ray photoelectron spectroscopy (XPS) showed the deposits to consist of pure elemental selenium.

SEM micrographs show that the morphology of the deposits was dependent upon temperature. At $-85°$ and $-95°C$ the deposits were uneven -- boulder-like features littered a base coat of selenium on the gold substrate. In contrast, at $-105°C$ the deposits were smooth and uniform. To help explain what seems to be a change in deposition mechanism between $-95°$ and $-105°C$ electrochemical impedance spectroscopy (EIS) was performed at the same value of applied d.c. potential at which the above mentioned deposits were produced, namely, $\eta = -0.3$ V. Figure 4 displays the results as plotted in the complex plane. At both temperatures there appear to be three reaction steps as evidenced by the three semi-circular features in both Figures 4 (a) and (b). As for the question of change of electrodeposition mechanism, it can be seen quite clearly in Figure 4 (b) that at $-105°C$ the characteristic feature of the Warburg impedance, i.e., Z_{Im} linear in Z_{Re} with a slope of $45°$, is not present. The behavior at $-105°C$ is a departure from what is observed at higher temperatures where all impedance spectra include the Warburg line, as in Figure 4 (a) for example. These observations are in conformity with the suggestion that between -95 and $-105°C$ there is a change of mechanism from mass transfer control at the higher temperatures to some kind of interfacial process at the lower temperature. Such a change of mechanism would be expected to produce the observed change in morphology in the resulting electrodeposits (7,8).

CONCLUSIONS

These results provide strong evidence for what must be the first reported observation of **thermally mediated control of morphology** in the context of electrochemical deposition. In other words, **without the aid of chemical additions to the electrolyte** it may be possible to control the morphology of the electrodeposit by controlling temperature alone. This also has profound implications for such engineering issues as cell design and scale-up.