

EFFECT OF SOME PARAMETERS ON CYCLIC VOLTAMMETRY OF SELENIUM IN ETHALINE

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Abstract : Cyclic voltammetry (CV) studies were used to investigate the interaction behavior of selenium from a solution containing selenium chloride (SeCl₄) in choline chloride-ethylene glycol (EG) based ionic liquid called ethaline. The influences of various experimental conditions and some parameters on cyclic voltammetry have been investigated using a Hokudo Denko HAB-151 Potentiostat/Galvanostat, Tokyo, Japan, equipped with a potential sweeper. It is shown that the additions of 40 mL·L⁻¹ acetonitrile and 0.05 mol·L⁻¹ P₂O₅ cause significant changes in the shape and position of the voltammograms. The nature of cyclic voltammograms of Cu(II) has been changed dramatically in presence of the acetonitrile due to the strong interaction between metal ion and acetonitrile. The magnitude of the reduction current densities is significantly decreased on the addition of additives as compared with additive free IL. In this study, it was observed that an addition of acetonitrile as additive to solution containing Se(IV) with ethaline as supporting electrolyte caused an increase in the reduction current of Se(IV) by several factors and also with a slight cathodic shift in the reduction peak potential of Se(IV).

Key Words - Cyclic voltammetry, Selenium, Ethaline, Additives, Parameters.

I. INTRODUCTION

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. It offers a rapid location of redox potentials of the electro active species. It is possible to develop diagnostic criteria by correlating kinetic and experimental parameters so that unknown systems can be characterized by studying the variations of peak current, half-peak potentials, or ratio of anodic peak currents and cathodic peak currents as a function of rate of voltage scan. The effect of a chemical reaction on the voltammetric wave will depend on its rate, as compared with the time required to perform the experiment. The ratio of the rate constant to the rate of voltage scan appears in the kinetic parameter.

Selenium is an important element due to its many-fold applications including electrocatalysis [1], X-ray imaging [2], glass deoxidizing, grain refining [3], and so on. Especially, Se is an essential constituent of the materials for photovoltaic cells [4]. Various approaches including photodeposition [5], chemical bath deposition [6], and chemical vapour deposition [7] have been developed for preparation of selenium thin film.

Room-temperature ionic liquids (RTILs), especially the air- and water-stable ones, can be used for electrodeposition of selenium due to their advantageous properties, including wide electrochemical potential window, acceptable conductivity compared to non-aqueous electrolytes and negligible vapour pressure (up to 300 °C) [8-10]. In the past decade ionic liquids (ILs) have gained attention as an alternative electrolyte media for the electrodeposition of various semiconductors and reactive metals, such as Ge, Si, Ta and Al, due to their large electrochemical potential windows and low volatility [11]. Several groups have investigated electrodeposition of both amorphous and crystalline selenium using different ionic liquids and selenium species [4, 11-15]. However, information about the electrodeposition of selenium from ionic liquids is fairly limited [4]. The electrochemical behavior has been reported to be influenced by Se(IV) species in 1-ethyl-3-methylimidazolium tetrafluoroborate/chloride [13] and zinc chloride-1-ethyl-3-methylimidazolium chloride [16] ionic liquids. These ILs have been used in our laboratory for studying the cyclic voltammetry of Ag [17], Cu [18], Ni [19], Cr [20] and Co [21].

The electrochemical behavior of selenium ions has been studied in ionic liquid at different conditions to determine the deposition conditions of metallic selenium; the authors reported that both the ionic liquid and the deposition conditions influence strongly the quality and properties of the deposited layers.

This paper presents an electrochemical study of Se(IV) ions behaviour in a ionic liquid named ethaline in presence of surfactants at room temperature to 60°C temperature range on platinum electrode using cyclic voltammetric technique.

II. EXPERIMENTAL DETAILS

2.1 CHEMICALS

Choline chloride (HOC₂H₄N⁺(CH₃)₃Cl⁻) ChCl (Aldrich 99%) was, when necessary, recrystallized from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (HOCH₂CH₂OH) (Aldrich >99%) was used as received. Selenium(IV)

chloride (SeCl_4) was obtained from PbSe alloy. PbSe alloy was dissolved in conc. nitric acid on heating with constant stirring for 3 to 4 hr. Lead was converted to lead nitrate and selenium was converted to selenious acid (H_2SeO_3). The solution was filtered in hot condition to remove the residue. Then the filtrate was again heated with conc. hydrochloric acid. Lead nitrate was converted to PbCl_2 and selenious acid was converted to SeCl_4 . The solution was filtered to remove PbCl_2 ppt. The filtrate was heated continuously with distilled water; acids were evaporated and finally pure SeCl_4 was obtained. Solutions were made so that a SeCl_4 concentration ranging from 0.025 to $0.20 \text{ mol}\cdot\text{L}^{-1}$ were obtained.

The additives di-phosphorus pentoxide (P_2O_5) (Merck >97%) and acetonitrile (CH_3CN) (Merck >99.9%) were used as received. Generally, the additives were added to the plating bath to a concentration of $0.10 \text{ g}\cdot\text{L}^{-1}$ polyethylene glycol and $40 \text{ mL}\cdot\text{L}^{-1}$ formic acid mixture or $0.05 \text{ mol}\cdot\text{L}^{-1}$ (P_2O_5) or $40 \text{ mL}\cdot\text{L}^{-1}$ acetonitrile. All other chemicals were used as received.

2.2 PREPARATION OF IONIC LIQUID

The eutectic mixture was formed by stirring the two components together, in the stated proportions, at 75°C until a homogeneous, colourless liquid formed. The molar ratio for the eutectic compositions was found to be 1:2 for choline chloride (ChCl) with ethylene glycol (EG). The ionic liquid, once formulated, was kept in a thermostatic oven at 30°C prior to use.

2.3 ELECTROCHEMICAL MEASUREMENTS

Electrochemical investigations including potential step chronoamperometry, chronopotentiometry and cyclic voltammetry were carried out using a Hokudo Denko HAB-151 Potentiostat/Galvanostat, Tokyo, Japan, equipped with a potential sweeper. Data were recorded in a computer through data acquisition system (USA) using WinDaq software. A three electrode system consisting of a platinum ($50 \times 5 \times 0.1 \text{ mm}^3$) working electrode, a platinum ($50 \times 5 \times 0.1 \text{ mm}^3$) counter electrode and a silver wire quasi-reference electrode were used in all electrochemical studies. The working and counter electrodes were cleaned electrochemically in $1.5 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ – $1.5 \text{ mol}\cdot\text{L}^{-1} \text{ H}_3\text{PO}_4$ mixtures, then rinsed with deionised water, and finally dried with acetone prior to use in all measurements. All voltammograms were obtained at 30°C with various scan rates ranging from 5 to $100 \text{ mV}\cdot\text{s}^{-1}$. A silver wire (immersed in ethaline) quasi-reference electrode was used in all electrochemical experiments which have been shown to have stable reference potential in chloride based eutectics. All potentials in this work are quoted with respect to this Ag|1:2 ChCl-EG reference electrode which will be written as Ag|Ag(I) (note the reference potential will change slightly with melts of different compositions). The overall instrumental cell set-up for the cyclic voltammetry experiment is shown in figure 1.



Fig. 1 The instrumental set-up of the three electrodes cell connected with the potentiostat/galvanostat via transducer with winDaq software installed computer system.

III. RESULT AND DISCUSSION

Cyclic voltammetry of Se(IV) in ChCl:2EG (ethaline) IL

The cyclic voltammogram recorded on a platinum electrode in 1:2:0.05 (mole ratio) ChCl:EG:SeCl₄ IL at 50°C with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ is shown in Fig. 2. The rest potential is $+0.38 \text{ V}$. The scan towards negative direction consists of first (C_1) and second (C_2) reduction waves with the current starting to increase at 0.02 V and -0.46 V , respectively. Additional reduction wave C_3 is observed with the current again starting to increase at -0.97 V . The reverse scan consists of first (P_{a1}) and second (P_{a2}) stripping peaks at 0.18 V and 0.69 V , respectively. Additional oxidation wave is observed with the current again starting to increase at 1.08 V .

Comparison of the voltammogram obtained in the absence of SeCl_4 (dotted curve in Fig. 2), it is noticed that a reduction wave appeared at -0.87 V in ethaline corresponding to the reduction of cationic species (Cat^+) into this IL, while the oxidation wave appeared at 1.05 V in ethaline corresponds to the oxidation of chloride ions (anions) to molecular/gaseous chlorine [17].

Figure 3 shows the effect of cathodic sweeping potentials on the cyclic voltammogram recorded on a platinum electrode in 1:2:0.05 (mole ratio) ChCl:EG:SeCl₄ IL at 50°C with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. It is readily seen from the voltammogram that the first (C_1) and second (C_2) reduction waves correspond to the first (P_{a1}) and second (P_{a2}) oxidation peaks.

Pure selenium has been detected in the deposit obtained at a deposition potential of -0.30 V (C_1) and -0.60 V (C_2) by constant potential method. Therefore, the increase of the cathodic current in the first (C_1) and second (C_2) reduction waves are obviously associated with the reduction of selenium ion to metallic state according to the following reaction:

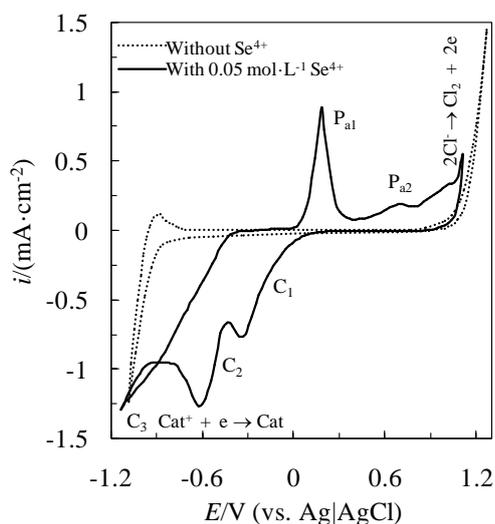


Fig. 2 Cyclic voltammograms recorded on a platinum electrode in ChCl:2EG containing 0.05 mol·L⁻¹ SeCl₄ at 50 °C with a scan rate of 10 mV·s⁻¹.

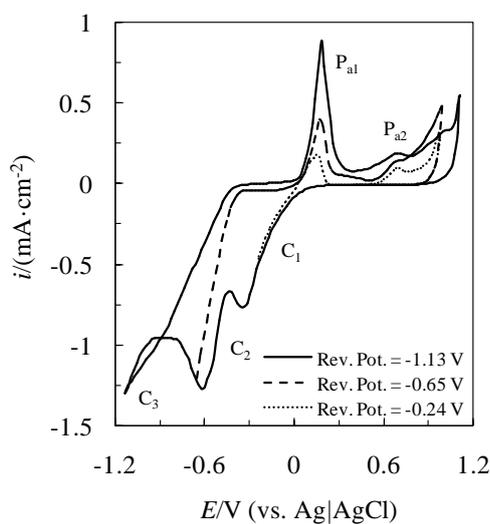


Fig. 3 Effect sweeping potential on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquids at 50 °C with a scan rate of 10 mV·s⁻¹.

This strongly suggests the presence of two energetically different phases/morphologies of selenium deposit. The two different morphologies must result from different growth mechanisms. One possibility could be the initial growth of a large number of nuclei on the surface where some of which stop growing giving a material with a different morphology. Alternatively, some aspect of the interfacial layer structure could neutralise the surface energy of the growing particle. Similar morphology has been reported by Abbott et al. [22] for the deposition of zinc from choline chloride based IL and Ali et al. [17] for the deposition of silver from reline.

Figure 4 shows the effect of SeCl₄ concentrations on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG IL at 50 °C with a scan rate of 10 mV·s⁻¹. It is readily seen from these voltammograms that the magnitude of the current density in the reduction waves (C₁) and (C₂), which are attributed to the reduction of Se(IV) to Se(0), increases with the increase of the SeCl₄ concentrations added into the IL. The same phenomenon is also observed with the stripping peaks (P_{a1}) and (P_{a2}), which shows also the increase of the current density with the increase of the SeCl₄ concentrations added into the IL. The increases in the magnitudes of Se(IV) reduction current densities with the increase of SeCl₄ concentrations added into the IL is due to increased mass transport, which would act to promote the diffusion of selenium ions to the electrode surface, encouraging bulk growth. Similar result has been reported in the previous studies for the deposition of Ag [17] and Cu [18] in this IL.

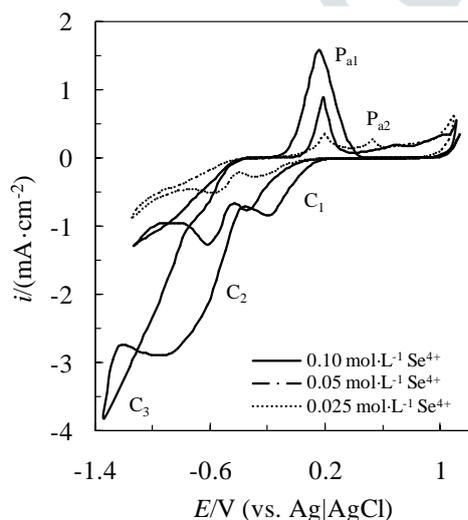


Fig. 4 Effect of SeCl₄ concentrations on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquids at 50°C with a scan rate of 10 mV·s⁻¹.

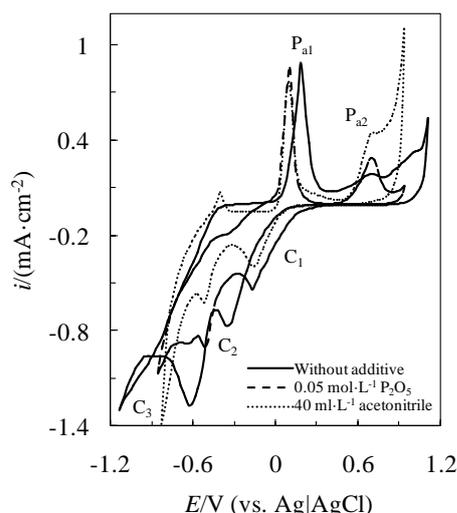


Fig. 5 Effect of additives on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquids at 50°C with a scan rate of 10 mV·s⁻¹. The additions and washed curves cause significant changes in the shape and position of the voltammograms.

This indicates that the presence of additives alters the deposition process of Se. It is interesting to note that the magnitude of the reduction current densities is significantly decreased on the addition of additives as compared with additive free IL. This

is likely to simply be an effect of decreased mass transport due to the addition of additives. Here the onset of Se reduction potential is unchanged but the first anodic peak potential (P_{a1}) is shifted cathodically by 80 mV. However, the first stripping current density (P_{a1}) is unchanged but the second stripping current density (P_{a2}) is little increased upon the addition of additives into the IL.

IV CONCLUSIONS

This research work reveals that choline chloride based IL specially ethaline can be used as electrochemical solvents. The reduction of Se(IV) to Se(0) increases with the increase of the SeCl₄ concentrations added into the IL. This is due to increased mass transport, which would act to promote the diffusion of selenium ions to the electrode surface, encouraging bulk growth. It is also observed that the additions of 40 mL·L⁻¹ acetonitrile and 0.05 mol·L⁻¹ P₂O₅ cause significant changes in the shape and position of the voltammograms. The magnitude of the reduction current densities is significantly decreased on the addition of additives as compared with additive free IL. This is likely to simply be an effect of decreased mass transport due to the addition of additives. Additive improves the grain sizes of the selenium crystals.

II. ACKNOWLEDGMENT

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