

Electrodeposition of Reactive Metals and Metal Chalcogenides for Energy Generation

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Coating and deposition of metals such as Ti, Ta, Mo, and W and semiconductors (e.g. Ge and Si) has great worth to technology sectors and industry. Similarly, metal chalcogenides (e.g. MoS₂, MoSe₂) are of significant interest for industrial catalysis and electrocatalysts and optical & microelectronic devices. Current methods for preparation of these materials require energy intensive multistep deposition processes, the use of high temperature conditions (e.g. molten salts) and/or corrosive gases along with lengthy processing procedures. Electrodeposition offers a potential and low cost solution. However, it is not possible to deposit reactive metals in aqueous based electrolytes due to their reduction potential lying outside the electrochemical potential window of stability for water. Recently, ionic liquids have attracted the interest of electrochemists as a solvent for electrodeposition because they possess large electrochemical potential windows, good chemical and thermal stability, and low volatility. These characteristics make ionic liquids a great replacement for aqueous solvents in the electrodeposition of reactive metals and metal chalcogenides. In this presentation we describe facile room temperature electrodeposition method to produce thin films of reactive metals (Ge, Si, Se, Mo and W) and metal chalcogenides (GeS_x and MoS_x).

Selenium is used in optoelectric applications, including advanced solar cells, IR detectors and solid-state lasers. Electrodeposition of Se from ionic liquid is limited by the availability of soluble Se precursors in ionic liquid. Here we have developed ionic liquid soluble Se precursor by reaction of selenous acid with ethanol to form diethylselenite. Cyclic voltammetry of diethylselenite in ionic liquid shows reduction peak at -1.6 V vs Pt (Fig. 1A). Chronoamperometric deposition at -1.6 V vs Pt was performed for 600s shows formation of amorphous Se confirmed by presence of Raman peak at 252 cm⁻¹ (Fig. 1B).

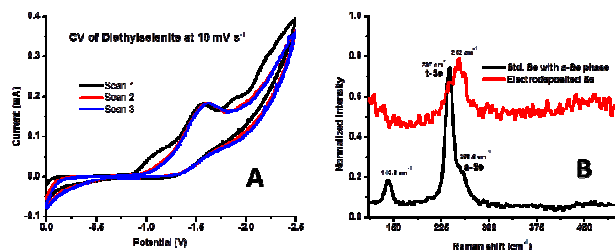


Figure 1. A. Cyclic voltammetry of diethylselenite (0.174 mol/L) in PP₁₃-TFSI ionic liquid at 10 mV/s scan rate. B. Raman spectrum of chronoamperometrically deposited at -1.6 V vs. Pt for 600s compared with standard Se.

MoS₂ have very important applications in electronics, field-effect transistors, amplifier, solid lubricants, hydrogen storage, hydrodesulfurization catalysts, electrochemical intercalation and Li batteries. MoS₂ is currently being produced through high

temperature, high pressure, low oxygen, and other varying conditions, and, even then, the yields of MoS₂ are often contaminated with oxides. Here, we have developed an electrochemical method using ionic liquids as an electrolyte. Reaction of Molyglycolate and 1,4 butanedithiol in PP₁₃-TFSI ionic liquid deposits thin film of MoS₂. The crystallinity of MoS₂ was increased with increase in temperature from 25 to 100 °C (Fig 2.A). Two sharp Raman modes, E_{2g} (375 cm⁻¹) and A_{1g} (401 cm⁻¹) confirms presence of MoS₂.

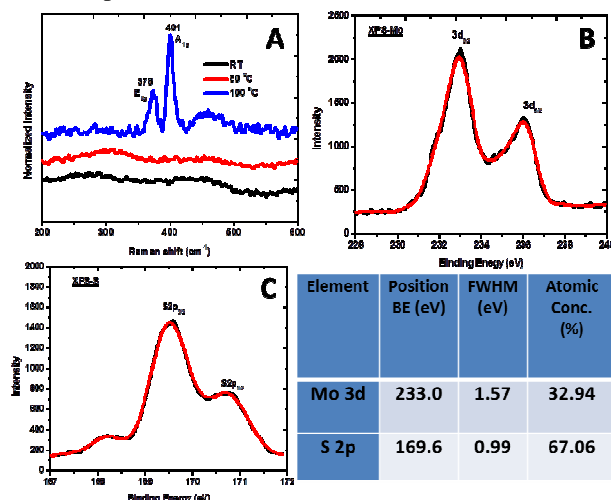


Figure 2. A. Raman spectrum of electrodeposited MoS₂ at various temperatures. B. XPS of Mo of electrodeposited MoS₂. C. XPS of S of electrodeposited MoS₂. **Table 1.** shows the atomic concentration of Mo and S of electrodeposited MoS₂ from high resolution XPS peak integration.

MoS₂ formation was further confirmed and quantified by XPS. The electrodeposited MoS_x films displayed the Mo 3d_{5/2} peak at 233 eV (Fig. 2B) confirming the presence of +4 oxidation state of Mo. Further presence of XPS S 2p_{3/2} peak at 169.6 eV (Fig. 2C), confirms the MoS₂ formation. Quantitative elemental analysis from high resolution XPS peak integration is presented in Table 1. Shows the atomic concentration Mo 32.94% and S 67.06% this further confirms the electrodeposited films are MoS₂.

This electrodeposition process offers promise for reducing and/or eliminating several energy-intensive processing steps and the corrosive materials currently required. The electrodeposited MS_x films where M= Mo and Ge are characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy (SEM-EDS), Raman and X-ray photoelectron spectroscopy (XPS). In addition, we will demonstrated that these metal chalcogenides films can be used for lithium ion storage and hydrogen generation applications.

[1] Murugesan, S.; Kearns, P.; Stevenson, K. J. *Langmuir* **2012**, *28* (13), 5513–5517.

[2] Non-Provisional U.S. Patent Application n. 61/537,366, "Chemical and Electrochemical Synthesis of Metal Chalcogenides in Ionic Liquids," P. Kearns, S. Murugesan, A. Akkineni and K. J. Stevenson.

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