

Electrochemical Deposition of Metal Chalcogenides for Electrocatalysis and Energy Storage

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Thin films of metal chalcogenides have unique properties that make them interesting for a variety of applications, including catalysis, sensing, energy storage and electronic devices such as field-effect transistors.¹ Methods currently used to prepare these materials are often energy intensive requiring multiple steps, high temperatures, and the use of toxic and corrosive gases, as well as, complicated processing procedures. Electrodeposition offers a facile, low-cost and scalable alternative to these methods. Traditionally electrodeposition is carried out in aqueous electrolytes, which can hinder the deposition of electropositive metals and metal chalcogenides whose reduction potential lies outside the electrochemical window of stability for water. Ionic liquids have been attracting interest in the electrochemical community as solvents for electrodeposition because they possess wide electrochemical windows of stability, high chemical and thermal stability, and low volatility. These make ionic liquids promising alternatives to aqueous and organic electrolytes. In this presentation we describe an electrodeposition procedure for thin film metal chalcogenides (e.g. MoSe_x and WSe_x).

MoSe_2 and WSe_2 are especially interesting metal chalcogenides due to their wide range of applications including photoelectrocatalysis, hydrosulfurization catalysts, electronics, solid lubricants, electrochemical intercalation and Li ion batteries.^{1,2} The methods currently used to produce these materials have many requirements such as high temperatures, high pressures, and minimal oxygen concentrations in addition to others. Even when these conditions are met the products contain oxide impurities. Recently, our group has developed a method to electrodeposit metal sulfides at mild temperatures in the presence of air.^{3,4} We are expanding on this work to include the electrodeposition of metal selenides. Finding suitable selenium precursors is highly dependent on their solubility in the ionic liquid. We have been investigating

the electrochemistry of two selenium precursors for this process: diethyl selenite and diphenyl diselenide in addition to the transition metal components for W and Mo. Below we show the cyclic voltammogram of diethyl selenite and diphenyl diselenide (Figure 1(A) and 1(B), respectively) representing the successful deposition of metallic selenium from an ionic liquid.

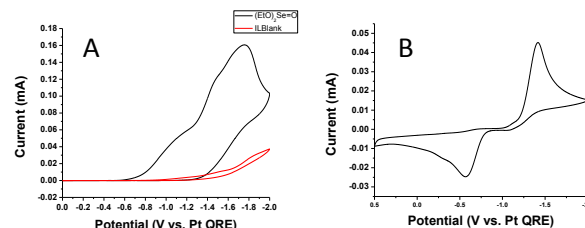


Figure 1: Cyclic voltammogram of (A) 0.1 M diethyl selenite + 0.6 M CH_3CN and (B) 0.1 M diphenyl diselenide in $\text{PP}_{13}\text{-TFSI}$. Scan rate was 10 mV/s for both.

Further work will describe the electrodeposition of metal selenide thin films for reducing and/or eliminating several energy-intensive processing steps and the corrosive materials currently required. In addition, we will show that these metal selenide films offer exceptional promise as electrocatalysts and Li ion storage.

References

- 1) Chhowalla, M.; Shin, H.S.; Eda, G.; Li, L.-J.; Loh, K.P.; Zhang, H. *Nature Chemistry* **2013**, *5*, 263–275.
- 2) Bouroushian, M. *Electrochemistry of Metal Chalcogenides*. Springer: Berlin, 2010.
- 3) Murugesan, S.; Kearns, P.; Stevenson, K. J. *Langmuir* **2012**, *28* (13), 5513–5517.
- 4) 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.