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Project Title: **Potential-Modulated Intercalation of Alkali Cations into Metal Hexacyanoferrate Coated Electrodes**

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POTENTIAL MODULATED INTERCALATION OF ALKALI CATIONS INTO METAL HEXACYANOFERRATE COATED ELECTRODES

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Research Objectives

This program is studying potential-driven cation intercalation and deintercalation in metal hexacyanoferrate compounds, with the eventual goal of creating materials with large ion exchange capacities, excellent selectivity for separating cesium, and good material stability. Ions intercalate or deintercalate into metal hexacyanoferrate to maintain charge neutrality when iron centers in the matrix are reduced or oxidized, respectively. Nickel hexacyanoferrrate is known to preferentially intercalate cesium over other alkali cations, thus providing a basis for separation. The separation of radiocesium from other benign cations has important cost and safety implications for the processing of various cesium contaminated wastes forms within the DOE complex.

Specific ojectives for the period of this report include:

(1) Verify the use of thin film energy dispersive x-ray spectroscopy for quantifying the alkali metal content of metal hexacyanoferrate coated electrodes.

(2) Assess cathodic electrodeposition methods for coating electrodes with nickel hexacyanoferrate that can improve the ion exchange capacity of anodic deposition processes.

(3) Compare the selectivity of electrodeposited nickel hexacyanoferrate to films made anodically.

Research Progress and Implications

(1) Energy dispersive x-ray spectroscopy (EDS) is a routine method for characterizing the composition of thick films (>2 μm) and bulk materials. Quantitative analysis of bulk materials can be accomplished by accounting for atomic density (Z), absorption (A), and fluorescence (F) effects within the sample (so-called ZAF corrections). With thin films (typically less than about 200 nm), backscattered electrons and x-ray fluorescence from the substrate can interact with the overlying film in such a manner that conventional ZAF corrections are no longer appropriate. During this research period, we have developed a

combined electrochemical and EDS method that permits the determination of quantitative values for the ionic selectivity and distribution coefficient in the film. We anticipate this combined electrochemical/EDS method to allow rapid and non-destructive assessment of the relationship between how we process the material and the properties of the coating that result.

(2) There are two common methods for growing thin films of nickel hexacyanoferrate thin films; anodic derivatization of nickel electrodes immersed in ferricyanide solution and cathodic electrodeposition of solutions of ferricyanide and divalent nickel. Anodized nickel hexacyanoferrate films are formed by holding a nickel substrate at +1.0 V vs. SCE for 300 s in a solution of 5 mM $K_3Fe(CN)_6$ and 100 mM KNO_3. The thin films that form have a typical ion intercalation capacity of about 2.5 mC/cm^2. The cathodic electrodeposition of nickel hexacyanoferrate is accomplished by cycling a platinum electrode between +850 and 0 mV vs. SCE for 25 times at a scan rate of 25 mV/S in freshly prepared solution of 2 mM $NiSO_4$, 2 mM $K_3(CN)_6$ and 250 mM Na_2SO_4. The resulting thin films can routinely be produced with ion intercalation capacities of 8 mC/cm^2 or greater.

(3) The main property we use to compare materials is the distribution coefficient for the ion exchange matrix is the distribution coefficient (K_d) for solution mixtures of Na^+ and Cs^+ nitrate. When comparing the performance of the anodically vs. cathodically deposited materials, we find that the selectivity of the two materials to be comparable. For example, in large excesses of sodium (10^{-5} to 10^{-6} M Cs^+ with 1 M Na^+) the maximum distribution coefficient (K_d) we have measured is approximately 4 x 10^4 ml/g for nickel hexacyanoferrate materials made by each method. It is worth noting that this K_d value neglects the weight of the substrate supporting the ion exchange matrix.

Planned Activities

During the next period, we intend to better understand and improve material stability in harsh environments such as highly alkaline media. Preliminary results show that one can make a conductive graphite/metal hexacyanoferrate/glass composite intercalation electrode using sol-gel technology. The composite electrode has substantial intercalation capacity and appears to have better stability in alkaline media than either of the alternative preparation methods described above. We also intend to study the mechanisms of cycle-life degradation in nickel hexacynaoferrate thin films. We have just brought on-line a 670 nm laser diode system for performing Raman spectroscopy of the nickel hexacyanoferrate thin films. This wavelength should be sufficiently long to be outside the optical absorption band of the material, leading to measurements that are free of photoelectrochemical effects.

Publications

S.M. Haight, D.T. Schwartz, and M.A. Lilga, In-situ oxidation state profiling of nickel hexacyanoferrate derivatized electrodes using line-imaging Raman spectroscopy and multivariate calibration, *J. Electrochem. Soc.* **146**, 1866 (1999).

K.M. Jeerage and D.T. Schwartz, Determining selectivity parameters for electrochemically switched ion exchangers using energy dispersive x-ray spectroscopy, in preparation.

Human Resource Development

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