

Project ID Number 60123

POTENTIAL MODULATED INTERCALATION OF ALKALI CATIONS INTO METAL
HEXACYANOFERRATE COATED ELECTRODES

3/1/00

Principal Investigator

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Co-Investigator(s): None

Research Personnel Supported by Project

2 undergraduate students, 2 graduate students, 0 postdoctorate, 1 visiting professor

Specific DOE Problems Addressed by Project

The separation of radiocesium from other cations has important cost and safety implications for the processing of various cesium contaminated wastes forms such as basin waters and sludges (e.g., at Hanford and Savannah River sites), as well as groundwater and more acidic tank wastes (e.g. at the Idaho Site). The key feature of these sites being their cesium contamination in a moderate to low pH aqueous solvent. The current materials being used are not sufficiently stable to be viable for separations involving direct contact with highly alkaline aqueous wastes.

Research Objectives

Ions intercalate or deintercalate into metal hexacyanoferrate to maintain charge neutrality when iron centers in the matrix are reduced or oxidized, respectively. Nickel hexacyanoferrate (NiHCF) is known to preferentially intercalate cesium over other alkali cations, thus providing a basis for separation. This program is studying potential-driven cation intercalation and deintercalation in metal hexacyanoferrate compounds, with the goal of (1) quantifying the ion exchange selectivity properties for cation mixtures, (2) enhancing ion exchange capacities, and (3) improving the material stability.

Research Progress and Implications

After approximately 2.5 years, progress has been made on each of the research objectives. A combined electrochemical and energy dispersive x-ray spectroscopy method has been developed for analyzing the quantity and type of ion loaded into NiHCF films. In the third journal article cited below, we describe the methodology and show the range over which this technique can be used to quantify separation factors in NiHCF coated electrodes. We find that the distribution coefficient

for NiHCF coated electrodes can exceed 3×10^4 ml/g in a solution of 10^{-6} M Cs^+ with excess sodium nitrate (1 M Na^+). This value for the distribution coefficient, which excludes the weight of the substrate, is comparable to values reported for bulk metal hexacyanoferrate compounds used in conventional ion exchange processes.

To increase the ion exchange capacity, we have taken three approaches, namely, cathodic deposition, spontaneous reduction, and sol-gel NiHCF/carbon/silica composite electrodes. In the first approach, NiHCF is deposited cathodically by cycling a platinum electrode between +850 and 0 mV vs. SCE at a scan rate of 25 mV/S in freshly prepared solution of 4 mM NiSO_4 , 4 mM $\text{K}_4\text{Fe}(\text{CN})_6$ and 500 mM Na_2SO_4 . The resulting thin films can routinely be produced with ion intercalation capacities exceeding 8 mC/cm². Our normal anodic deposition scheme produces a typical capacity of 3 mC/cm², so cathodic deposition represents a roughly 3 fold improvement in capacity. In the same electrolyte, one can get films to form on a noble metal electrode by spontaneous reduction. If one places a noble metal in freshly prepared electrolyte overnight, the film that forms spontaneously normally has an ion exchange capacity in the range 5 to 20 mC/cm². A second layer will grow on the previous layer if fresh electrolyte is used. In this manner, through repeated spontaneous formation, we have made NiHCF films in excess of 33 mC/cm² of capacity (34.1 mC/cm² is our highest to date). This represents a ten-fold increase in capacity from the anodic films used at the beginning of this project. The third method, and the most immature, that has been developed to increase capacity is to make monolithic ceramic/carbon composite electrodes using sol-gel processing, followed by overnight soaking of the composite in a nickel sulfate/potassium ferrocyanide solution. This method, though not optimized at all, can also achieve greater than 20 mC/cm² of ion exchange capacity.

Finally, with regards to more stable materials, the sol-gel processed electrodes appear more stable in alkaline electrolytes than are normal NiHCF thin films made in any of the ways described above. Because the silica matrix of the sol-gel electrode is nano-porous and soluble in highly alkaline media, we find the electrode falls apart around pH 14, though some electrochemical activity was still displayed at that pH. Nonetheless, we are encouraged and believe this approach may work using other sol-gel ceramics that are less soluble at high pH.

Planned Activities

- Continue studies of selectivity, capacity, and the role of film processing.
- Assess cycle life characteristics of the various NiHCF electrode structures.
- Continue to characterize and optimize the material behavior and failure found in the sol-gel composite electrodes.

Information Access

- (1) 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).
- (2) D.T. Schwartz and S.M. Haight, Transport and chemistry at electroactive interfaces studied using line-imaging Raman spectroscopy, *Coll. Surf. A*, accepted.

(3) K.M. Jeerage and D.T. Schwartz, Characterization of cathodically deposited nickel hexacyanoferrate for electrochemically switched ion exchange, *Sep. Sci. Tech.*, submitted.