ELECTROCHROMIC BEHAVIOR OF PRUSSIAN BLUE FILMS

Brief Introduction

Prussian Blue (PB) is a bright blue compound that has been an important pigment in paints, inks, etc. for hundreds of years. Thin solid films of PB can be grown on many different electrodes with the (nominal) composition KFe^{III}Fe^{II}(CN)₆. Electrochemical oxidation or reduction of the iron centers in PB compound requires cations (in this case K⁺) to enter or leave the structure to maintain charge neutrality in the solid (this processes is called ion intercalation/deintercalation). The electronic transitions in these materials change depending upon the oxidation states of the two different irons, and this translates into a color change in PB when both irons in oxidized (green) or both irons are reduced (transparent). Thus, PB films are electrochromic--they change color upon electrochemical modulation--leading to their potential use in video displays and smart windows.

Relevant Background Reading

- J. Appl. Phys. 53, pp 804-805 (1982).
- J. Chem Soc. Dalton Trans., pp. 2059-2061 (1984).
- J. Am. Chem. Soc. 104, pp. 4767-4772 (1982).

Experiment

You have access to a potentiostat, computer, optically transparent electrodes, and spectrophotometer for measuring the film's optical absorption spectra in the visible range. Using these facilities, along with pre-made solutions, you should characterize the film electrochemically and spectroscopically. Electrochemical measurements will include deposition of films by cyclic voltammetery, and characterization in potassium nitrate using cyclic voltammetry. Try a number of different sweep rates to see the influence. Optical chaacterization should begin with "eyeball" spectroscopy...what color is the film at various potentials? Then, determine the optical absorption spectra when the PB is fully reduced, in a mixed valence state, and fully oxidized. Pick one or two wavelengths where there is appreciable oxidation-state-dependence, and monitor them as a function of potential. The spectroscopy is most easily done by hand, not using the computer interface. Your report should discuss these results and compare them with similar results published in the literature. Also make certain to consider the technological implications of your results when writing the report.