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Materials

Electrochemical characterization of ion selectivity in electrodeposited nickel hexacyanoferrate thin films

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Abstract: The ion selectivity of electrodeposited nickel hexacyanoferrate (NiHCF) thin films was investigated using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). NiHCF thin films were prepared by cathodic deposition on Pt and Al substrates. EIS and CV curves were determined in 1 mol/L (KNO_3+$CsNO_3$) and 1 mol/L ($NaNO_3$+$CsNO_3$) mixture solutions, which were sensitive to the concentration of Cs^+ in the electrolytes. Experimental results show that all Nyquist impedance plots show depressed semicircles in the high-frequency range changing over into straight lines at lower frequencies. With increasing amounts of Cs^+, the redox potentials in CV curves shift toward more positive values and the redox peaks broaden; the semicircle radius in corresponding EIS curves and the charge transfer resistance also increase. EIS combining CV is able to provide valuable insights into the ion selectivity of NiHCF thin films.

Key words: NiHCF thin films; ion selectivity; electrochemical deposition; cyclic voltammetry; electrochemical impedance spectra

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1. Introduction

Electrochemically switched ion exchange (ESIX) is an environmentally benign way to separate ions from solution using the selectivity of an ion exchange film [1-3]. By electrochemical modulation of the reduced and oxidized states of the film, target ions are reversibly intercalated and deintercalated from the solution. Effective ESIX processes depend on the ion exchange matrix that shows selectivity for a target ion. Nickel hexacyanoferrate (NiHCF), an inorganic coordination compound in the Prussian blue family, is being studied as a candidate for ESIX separation of alkali cations because of its unique structural attributes and electrochemical properties [4-5].

NiHCF can be made as a thin film by either anodization of nickel substrate in ferricyanide solutions [6-7] or by cathodic deposition onto a conductive substrate from electrolytes containing divalent nickel and ferricyanide [5, 8]. Both cathodically deposited and anodically derivatized films display excellent selectivity for Cs^+ in the presence of other alkali cations. But ion-exchange capacities for cathodically deposited films are normally much greater than those for derivatized films [5]. Direct evaluation with X-ray methods (XRD, EXAFS, and EDS), as well as indirect evidence such as voltammetry and molecular simulation suggest that the electroactive NiHCF thin films are quite diverse [9-13], and we have recently shown that processing conditions can be used to tune the stoichiometry and structure of NiHCF film [14]. For ESIX process, details of ion selectivity of thin films are of central importance. The selectivity of electrochemically prepared films has been measured quantitatively using different methods [2, 5]. However, further mechanistic information is still lacking on the NiHCF thin films in mixture alkaline electrolytes.

Electrochemical impedance spectroscopy (EIS) is a powerful nondestructive steady-state technique that is capable of studying the ion selective electrodes (ISE)

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[15-19]. In this article, EIS and cyclic voltammetry (CV) were used to study the characteristics of ion selectivity of NiHCF films deposited on Pt and Al substrates. The results show that EIS and CV behaviors are sensitive to the concentration of Cs^+ in mixed solution and thus can be a useful diagnostic of ion selectivity. These diagnostics may provide helpful insights to understand the mechanism of ion selectivity, which is an essential step in the design of more selective, higher performing alkali sensor and separation material.

2. Experimental

2.1. Experiment instrument and reagents

All reagents were analytical grade and water was Millipore water (18.2 MΩ·cm). All electrochemical experiments were carried out using a VMP2 Potentiostat (Princeton USA) controlled with EC-Lab software. A three-electrode cell, consisting of platinum or aluminum sheet as the working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode, was used.

2.2. NiHCF deposition and electrochemistry

NiHCF films were deposited onto the polished platinum and aluminum electrodes of 10 mm×10 mm surface area and 0.2 mm thickness by cycling the potential from 850 to 0 mV *vs.* SCE at 25 mV/s in a freshly mixed solution of 0.002 mol/L $NiSO_4$, 0.002 mol/L $K_3Fe(CN)_6$, and 0.25 mol/L $NaSO_4$. Before the deposition of a NiHCF film, the electrode surfaces were electrochemically cleaned in 1 mol/L H_2SO_4 by cyclic voltammetry.

CV and EIS of thin films were carried out with VMP2 potentiostat in seven different Cs^+/K^+ (or Na^+) mixture solutions. These mixtures contained $CsNO_3$ in the amounts 0, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 0.1, and 1 mol/L, with KNO_3 (or $NaNO_3$) added to reach a total cation concentration of 1 mol/L. Impedance spectra were recorded in a frequency range from 100 to 0.1 Hz for Pt substrates and 100 to 100 Hz for Al substrates. The amplitude of the modulated signal was 10 mV. EIS were analyzed with matched ZsimpWin software and the corresponding equivalent circuit and electrochemical parameters were obtained.

3. Results and discussion

3.1. CV and EIS of NiHCF thin film on Al substrate

Cyclic voltammetry has been used to establish the qualitative selectivity order $Cs^+>K^+>Na^+$ for anodically derivatized NiHCF electrodes [1-2]. Fig. 1 shows the cyclic voltammograms of NiHCF film on Al substrate in 1.0 mol/L K^+/Cs^+ containing electrolytes. Positive currents correspond to the oxidation of iron centers in the film, with the corresponding elution of K^+ or Cs^+ from the matrix, whereas negative currents correspond to iron reduction and K^+ or Cs^+ loading. As the concentration of Cs^+ in solution is increased, the voltammetric peak shifts toward a higher potential and becomes broad. The CVs in Fig. 1 illustrate the transition from predominantly K^+ exchange to Cs^+ exchange and the NiHCF's Cs^+ selectivity is apparent.

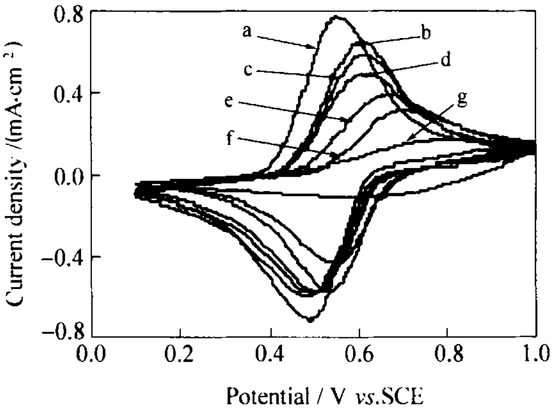

Fig. 1. Cyclic voltammograms of NiHCF film on Al substrate in a series of aqueous K^+ and Cs^+ nitrate mixtures. The total alkali content of $[Cs^+]+[K^+]$ is 1 mol/L. The Cs^+ concentration in each solution is (a) 0, (b) 10^{-5}, (c) 10^{-4}, (d) 10^{-3}, (e) 10^{-2}, (f) 10^{-1}, and (g) 1 mol/L.

Using impedance measurements, the films used for making ESIX electrodes can be studied satisfactorily. The analysis of changes of the various loops observed in the impedance diagrams with respect to the parameters which characterize the solution/electrode system allowed the role of the film substrate and various cation species contained in the film to be understood better. This should allow improvement in the ESIX material performances. Fig. 2 shows the EIS of NiHCF film on Al substrate for the same mixture solutions shown in Fig. 1. Z' is the real component of impedance and Z'' is the imaginary component of impedance in Fig. 2. It is evident in Figs. 2(a) and 2(b) that the diagram starts with a semicircle at high frequencies and it changes to the straight line as the frequency decreases. These indicate that the electrode process of thin films is controlled by kinetics and diffusion. The semicircle reflects the impedance of the electrochemical reaction, whereas the straight line indicates the diffusion of the ion or the electric charge.

With increasing amounts of Cs^+, the radius of semicircle increases, which indicates that the charge transfer reaction resistance increases. It also suggests that the corresponding rate of the ion loading and unloading is decreased and the NiHCF thin films have a higher af-