Novel hybrid materials with high stability for electrically switched ion exchange: carbon nanotube–polyaniline–nickel hexacyanoferrate nanocomposites

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A novel and stable carbon nanotube–polyaniline–nickel hexacyanoferrate nanocomposite film has been synthesized by the electrodeposition method, and the feasibility for removing radioactive caesium through an electrically switched ion exchange process using the nanocomposite film has been evaluated in a mixture containing $NaNO_3$ and $CsNO_3$.

It is well known that transition metal hexacyanoferrates (MHCFs) are an important class of polynuclear inorganic mixed-valence compounds because of their interesting properties such as electrocatalysis,[1] electrochromicity,[2] ion exchange selectivity,[3] sensing,[4] and magnetism.[5] The preparation and application of Prussian blue (PB)[6] and its analogous forms, such as samarium hexacyanoferrate,[7] nickel hexacyanoferrate (NiHCF),[8] and cobalt hexacyanoferrate,[9] have been extensively studied. Thin films of PB and related analogous complex salts are also promising candidates to prepare separating membranes capable of ion sieving[10] and electrochemical-controllable ion exchange because of their zeolitic structure.[11]

Caesium-137 is one of the important fission fragments present in a significant fraction of the radioactive liquid waste from the reprocessing of nuclear fuel by the Purex process. Removing this long-lived ($T_{½}$ = 32 y) radioisotope of caesium from the radioactive waste is a challenging project, and several techniques including ion exchange,[12] sorption,[13] solvent extraction,[14] and precipitation processes have been reported. Successful examples also include caustic-side solvent extraction using calixarene crown ether,[14b] developed in Argonne National Laboratory, and electrically switched ion exchange[12] using NiHCF, developed at Pacific Northwest National Laboratory (PNNL).

Previous studies demonstrated that MHCFs have high selectivity and affinity for ^{137}Cs in concentrated sodium solutions.[12,15] The previous studies at PNNL for NiHCFs, which were deposited on a surface by applying an anodic potential to a nickel substrate[12a] or on nickel foam[12c] revealed that the capacity and stability for uptake and elution can be improved by the preparation procedures. The surface area is one of the key factors to determine its ion exchange capacity. The stability or the ability to cycle through many loading/unloading cycles is very important in the development of a practical process. In this communication, we describe the development of novel nanocomposite materials by combining the high surface area of carbon nanotubes, the chemical stability of polyaniline (PANI), and the ion exchange properties of NiHCF. Fig. 1 illustrates the concept of electrically switched ion exchange based on carbon nanotube–PANI–NiHCF nanocomposites.

The synthesis of the nanocomposite films is described. Multi-walled carbon nanotubes (CNTs) were dispersed in *N,N*-dimethylformamide with the aid of ultrasonic agitation. The CNTs solution (10 μL, 5 mg mL^{-1}) was added onto the surface of a glassy carbon working electrode and dried at room temperature. The PANI thin-film was electrochemically deposited on the surface of the CNTs *via* cyclic voltammetry in a three-electrode cell containing an aqueous solution of 0.1 M H_2SO_4 and 0.1 M aniline of synthetic grade from Aldrich. The working electrode is the CNT modified glassy carbon electrode. A Pt wire is used as a counter electrode. The reference electrode is KCl saturated Ag/AgCl. The PANI films were deposited on the working electrode by cycling between −200 and +700 mV *versus* Ag/AgCl at a sweep rate of 100 mV s^{-1} with 15 cycles (30 segments). NiHCF nanoparticles were electrodeposited onto the CNT–PANI films from solutions containing 1 mM $Ni(NO_3)_2$, 1 mM $K_3[Fe(CN)_6]$, and 0.5 M $NaNO_3$. The solutions used to form the NiHCF nanoparticles were freshly prepared each time. Before electrodeposition of NiHCF, cyclic voltammograms were recorded in $K_3[Fe(CN)_6]$ at different scan rates in order to estimate the effective electrode area. Unless otherwise stated, the procedure involved 13 full voltammetric cycles (26 segments) at 25 mV s^{-1} in the potential range from 850 to 0 mV.

The formation of NiHCF nanoparticles on the surface of the CNTs was also confirmed by transmission electron microscopy (TEM). To obtain TEM images, the as-synthesized powder was detached from the electrode surface and dispersed on the copper–carbon grid. The TEM images of the nanocomposite indicate that NiHCF clusters were uniformly deposited on the surface of CNTs

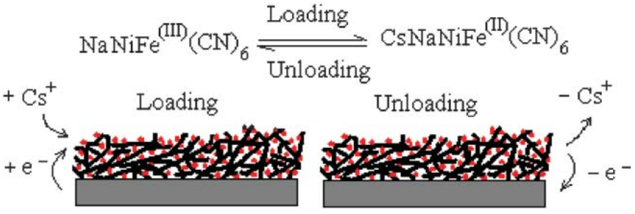

Fig. 1 Schematic illustration for electrically switched ion exchange based on carbon nanotubes, polyanline and nickel hexacyanoferrate nanocomposite.

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with a size around 20 nm. The results of EDS also confirmed the presence of Ni and Fe elements on the carbon nanotube surfaces.

The stability of the as-prepared films was characterized and demonstrated using the cyclic voltammetry method in 1 M $NaNO_3$ solution starting from 0 V scanning anodically to 0.85 V at a scan rate 25 mV s^{-1}. Fig. 2 indicates the response of NiHCF electrodes on a bare glassy electrode (A), CNTs (B), and on CNT–PANI films (C) in a 1 M $NaNO_3$ electrolyte as a function of cycling. Well-defined and reversible cyclic voltammetric responses were obtained in $NaNO_3$ electrolytes. The redox event observed around +0.38 V *vs.* Ag/AgCl has been associated with oxidation, and +0.37 V corresponds to the reduction of the surface-attached iron species. The reduction of the NiHCF films requires the uptake of cations into the films, while the oxidation on the hexacyanoferrate centers forces the release of the cations from the films. The cyclic voltammograms in Fig. 2 show that the process of oxidation and reduction are chemically reversible and that cation loading and unloading can be controlled by modulating the electrode potential. The substrates exert great influence on the ion exchange capacities and the redox cycling stability of the NiHCF films. The ion exchange capacities were estimated by the charge passed, *i.e.*, the area under the curve for each potential scan.[12] The loss of the ion exchange capacity occurs very quickly on repeated cycling for the NiHCF film deposited on a bare glassy carbon electrode (Fig. 2A). However, the stability of the NiHCF films can be improved on the porous CNT (Fig. 2B) and CNT–PANI (Fig. 2C) substrates. As can be seen from Fig. 2, the NiHCF films on porous CNT and CNT–PANI substrates have much higher ion exchange capacities than those on a bare glassy carbon electrode.

Fig. 3 shows the decay in the ion exchange capacity for numbers of segments for these three kinds of electrodes determined in 1000 segments (500 cycles) in 1.0 M $NaNO_3$ solution. The substrate of NiHCF is known to affect the redox cycling stability of the electroactive materials and this is further demonstrated in Fig. 3. The capacity values are normalized by their corresponding initial capacity, measured in the fifth cyclic voltammogram to allow for signal stabilization. As shown in Fig. 3, a better performance was observed on the electrode modified with CNTs, about 80% of the initial capacity is retained after about 500 cycles. The NiHCF nanoparticles on CNT–PANI have the highest stability for cation uptake and elution, showing dramatically improved cycling stability. The loss of capacity for the CNT–PANI–NiHCF films is the smallest after about 500 cycles, retaining 92% of the initial capacity.

The high affinity of MHCF in films for caesium has been demonstrated by many previous studies.[3,12,15] A series of cyclic voltammetry experiments were performed to quantify the preferential caesium ion selectivity over sodium ion for the

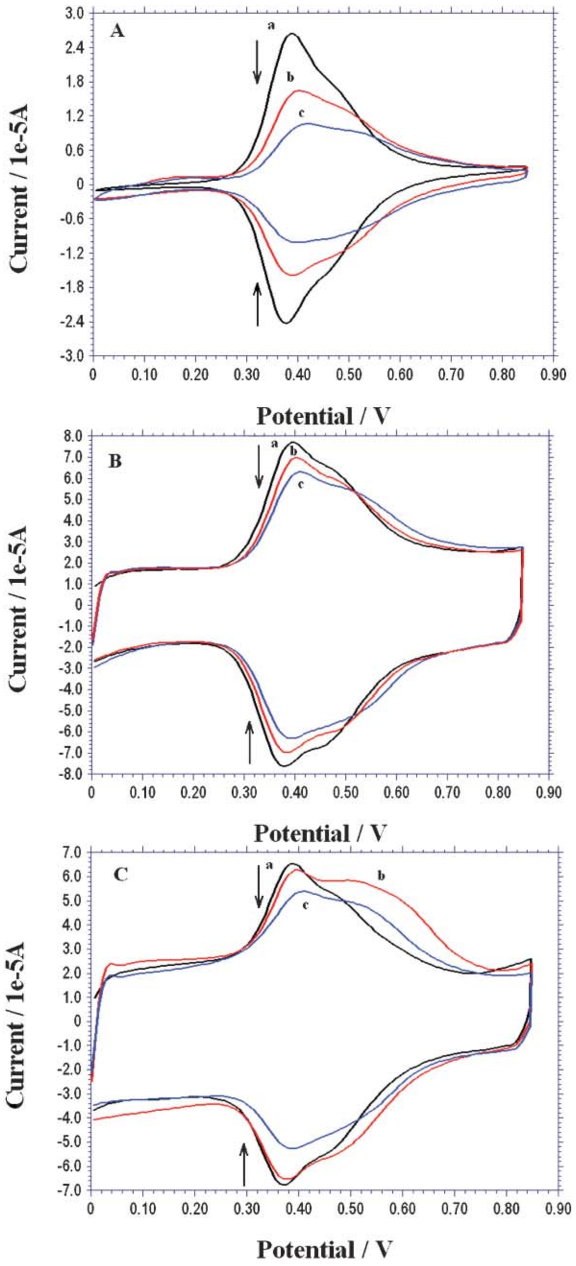

Fig. 2 Cyclic voltammograms showing the effect of redox cycling in a 1.0 M $NaNO_3$ solution on the ion exchange capacity of the NiHCF films deposited on bare glassy carbon electrode (A), and glassy carbon electrode modified with CNTs (B) and CNT–PANI (C). The cycle numbers are 1 (a), 100 (b), and 499 (c) respectively. The arrows indicate the decay of the capacity of the films.

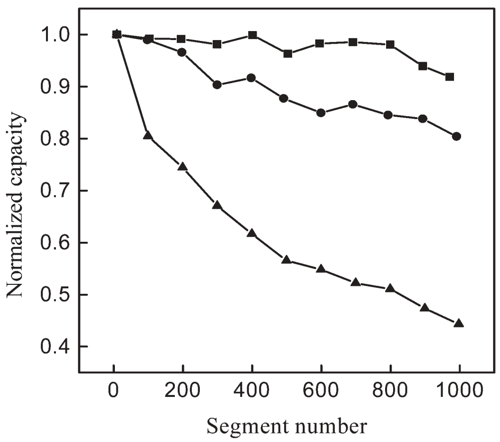

Fig. 3 Normalized capacity as a function of segment numbers showing film stability for three NiHCF films deposited on a bare glassy carbon electrode (▲), and glassy carbon electrodes after being modified by CNTs(●) and CNT–PANI(■) from cyclic voltammetry in 1 M $NaNO_3$ uptake/elution.

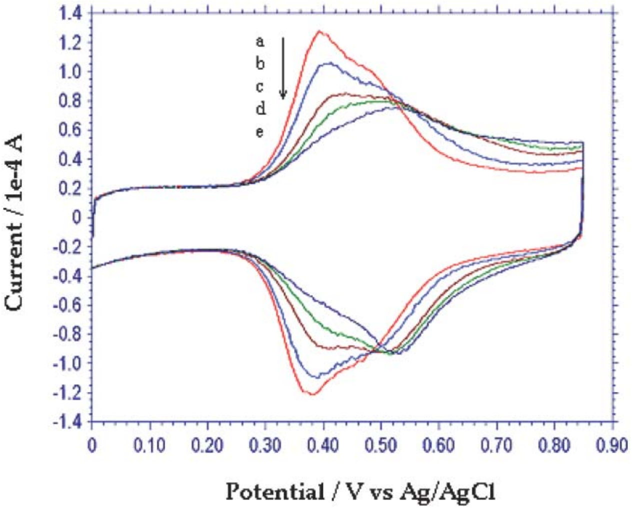

Fig. 4 Cyclic voltammograms indicating the sensitivity for Cs^+ of NiHCF films at the CNT surface in $NaNO_3$ with different concentrations of $CsNO_3$, $Na^+ : Cs^+$ 1 : 0 (a); 2000 : 1 (b); 400 : 1 (c); 100 : 1 (d); 20 : 1 (e).

NiHCF films deposited on different substrates. The results indicate that all three kinds of electrodes have good selectivity for Cs^+ over Na^+, which reflects the characteristics of NiHCF. Fig. 4 shows the typical cyclic voltammograms obtained with the NiHCF–CNT electrode for a solution with a series of mixtures containing $NaNO_3$ and $CsNO_3$. The shapes of the cyclic voltammetric responses shown in Fig. 4 are similar to those reported in the literature[12a,15] for such a film of NiHCF in contact with a solution mixture of Na^+ and Cs^+. The sensitivity of the NiHCF–CNT electrode to caesium in the presence of excess sodium is clearly noted in Fig. 4 for a 2000 : 1 [Na^+] : [Cs^+] solution. When the concentration of Cs^+ becomes larger and larger, the cyclic voltammogram peak becomes broader and broader. This has been attributed to multiwave behaviour in the film and a large NiHCF site–site interaction resulting from incorporation of relatively large Cs^+ into the zeolitic structure of the NiHCF film. The higher potential of the caesium cyclic voltammgram peak indicates the relative selectivity for this species over Na^+.

In summary, we have developed a method for preparing novel nanocomposites of CNT–NiHCF and CNT–PANI–NiHCF through the electrodeposition method. The high capacity and stability for ion exchange of the hybrid films was demonstrated, and the selectivity for caesium over sodium was examined for various sodium : caesium ratios. The high surface area and good conductivity of the porous CNT matrix provide an excellent substrate for loading NiHCF nanoparticles. High surface area of the porous CNT film leads to the high loading capacity for the NiHCF nanoparticles, which in turn leads to the high ion exchange capacity of the NiHCF–CNT nanocomposite film. The presence of the PANI polymer film further improve the stability of the nanocomposite film. The results presented in this paper may form the basis of a novel electrochemical ion exchange process for the treatment of nuclear waste and Cs-137 contaminated waters, while minimizing the production of secondary waste. More detailed studies are underway in this laboratory, and the results will be reported in due course.

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