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Fabrication of nickel hexacyanoferrate film on carbon fibers by unipolar pulse electrodeposition method for electrochemically switched ion exchange application

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ABSTRACT

Nickel hexacyanoferrate (NiHCF) film was successfully deposited on carbon fibers by unipolar pulse electrodeposition (UPED) method. The effects of pulse potential and cycle number during the film deposition on the composition, regeneration ability and cycle stability of the film were investigated.The morphology, composition and electrochemical behavior of the as-fabricated NiHCF film were varied with the deposition conditions, and two structural analogues, i.e., soluble and insoluble NiHCFs, could be appeared together or alone in the finally obtained films. Especially, it is found that higher pulse potential was necessary to obtain high-quality NiHCF film on the carbon fiber than on metal electrode. In this study, when the pulse potential during the unipolar deposition of NiHCF film was set at a condition of 0.8 V with 0.5 s on-time, 0.5 s off-time and 3000 cycles, a film with insoluble structural analogue was obtained and it showed large ion exchange capacity, good regeneration ability and long-term cycle stability.

1. Introduction

Nickel hexacyanoferrate (NiHCF) is an excellent candidate for selective separation of alkali cations because it has different affinity for alkali cations ($Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$)[1–3]. When it is deposited on electrode, besides conventional ion exchange ability, more ion adsorption and desorption can be easily controlled by changing the redox states of redox-active Fe(II/III) centers bound to Ni(II) cations through applying negative and positive potentials on it. This kind of process is called electrochemically switched ion exchange (ESIX) process [4,5]. It is considered as an environmentally friendly way to separate and recover ions via reversible electrochemical adjustment of the matrix charge density. The advantage of this process is no secondary pollution generated. To date, NiHCF has been fabricated on various kinds of electrodes and used as the ESIX film [5–17]. However, the electrochemical properties and structures of obtained NiHCF thin films on different electrodes are strongly depended on the preparation method. NiHCF has two structural analogues, i.e., “soluble” one with the unit cell stoichiometry of $A^I{}_4Ni^{II}{}_4[Fe^{III}(CN)_6]_4$ and “insoluble” one with the unit cell stoichiometry of $A^I{}_{4-3n}Ni^{II}{}_4[Fe^{III}(CN)_6]_{4-n}$ (n = 1-4/3), which could be formed on the electrode together or alone when changing the preparation conditions[5,18,19]. Traditional chemical deposition of NiHCF usually produces non uniform and less stable films. Hao et al. developed unipolar pulse electrodeposition (UPED) method to prepare NiHCF film with controllable structure on different electrodes such as platinum, graphite and chitosan and/or carbon nanotubes modified electrodes[4,10,14]. In this method, the unipolar potential pulse waveform consists of an applied cathodic potential during the on-time period and the open-circuit potential during the off-period. It is found that the structure of the film can be modulated by tuning the pulse potential, pulse waveform, and pulse cycle and the obtained film with the insoluble form structure always exhibit good stability and high dynamics for charge transport.

Carbon fiber is a material consisting of fibers with a diameter of 5-10 μm and composed mostly of carbon atoms [20–23]. It has high stiffness, high tensile strength, high chemical resistance, high temperature tolerance, high specific surface area, and low electrical

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resistivity (10^{-2} Ωcm), low weight and low thermal expansion and thus can be used as a promising conductive substrate for supporting the NiHCF film. If NiHCF film can be well and strongly deposited on the single carbon fiber, a large amount of NiHCF-coated carbon fiber can be woven together into a fabric with a large-scale surface area for ESIX separation of harmful ions such as Cs^{137} ions from radioactive liquid wastes. However, to date, few studies were reported on deposition of electroactive film on carbon fiber [24]. In the present work, NiHCF was deposited on single carbon fiber by using UPED method. The effects of pulse potential and cycle number on the composition and electrochemical properties of the film were investigated. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) was used to characterize the morphology and composition of the obtained film. The electrochemical property, regeneration ability and the cycle stability were evaluated by cyclic voltammetry (CV). It is expected to produce stable NiHCF film on the single carbon fiber with excellent ESIX properties.

2. Experimental

2.1. Chemicals

Potassium haxacyanoferrate(III) (Wako, Japan), nickel(II) sulfate hexahydrate (Wako, Japan) and sodium sulfate (Wako, Japan) with analytical grade were used as chemicals for the preparation of NiHCF film. Potassium nitrate (Wako, Japan) and cesium nitrate (Wako, Japan) were dissolved in deionized water as electrolyte solutions in ESIX process for electrochemical characterization of films. Potassium hydroxide (Sigma-Aldrich, Japan) solution and 1 M sulfuric acid (Wako, Japan) was used for cleaning the electrodes. Carbon fiber (TORAYCA® T700SC) was provided by Toray, Japan.

2.2. Preparation of NiHCF film on single carbon fiber

Potentiostat (Princeton Applied Research, VersaSTAT 4 USA) operated with VersaStudio software was applied to controllably deposit the NiHCF film and characterize the electrochemical properties of the as-fabricated films. Three electrodes of platinum gauze (80 meshes, 25 × 35 mm, ALS, Japan), Ag/AgCl/saturated KCl reference (ALS, Japan) and carbon fiber substrate were used as counter electrode, reference electrode and working electrode, respectively. Carbon fibers were pretreated in ethanol to facilitate their hydrophilicity at first, and then they were homogeneously adhered on a platinum tablet with conductive carbon type and fixed on a slide glass (76 × 26 mm, Matsunami, Japan) as a working electrode for electrodeposition. Electrolyte solution for UPED was freshly prepared with a composition of 0.002 mol L^{-1} $NiSO_4$, 0.25 mol L^{-1} Na_2SO_4 and 0.002 mol L^{-1} $K_3Fe(CN)_6$. As shown in Fig. 1, only the part with carbon fibers on the working electrode was immersed in the solution with the counter and reference electrodes to form a three-electrode cell for the UPED process for the preparation of NiHCF film on the carbon fibers. Pulse cycle number varied from 500 to 4000 times and pulse potential from 0.5 to 0.8 V with both on-time and off-time periods of 0.5 s were chosen for the UPED process. The NiHCF film coated the carbon fibers were rinsed with water, dried at room temperature and applied for the further electrochemical studies. Scanning electron microscope (SEM) SU6600 (Hitachai, Japan) were used for the characterization of the morphology of the film.

2.3. Electrochemical characterization

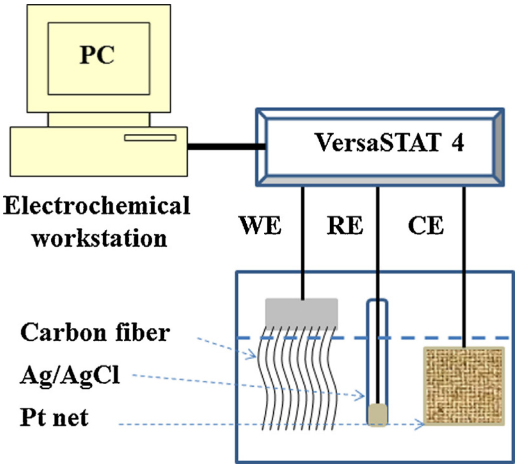

Fig. 1. Schematic diagram of the experimental set up used for UPED of film and CV measurements.

NiHCF film coated carbon fibers as the working electrode were immersed in 1 mol L^{-1} KNO_3 solution with the counter and reference electrodes to form a three-electrode cell. Cyclic voltammetry was performed at a potential range of -0.25 to 1 V with 25 cycles and a scan rate of 25 mVs^{-1} under quiescent condition. Electrochemical regeneration ability of the NiHCF film coated carbon fibers was verified by performing ESIX process alternately between the potassium-form and cesium-form: after the original K-form NiHCF film coated carbon fibers were immersed in a solution of 1 mol L^{-1} $CsNO_3$ solution for CV measurement, which also performed at a potential range of -0.25 to 1 V with 25 cycles and a scan rate of 25 mVs^{-1}, the film was converted to the Cs-form by immersing it in 1 M $CsNO_3$ solution and performing ESIX; then, the Cs-form NiHCF film coated carbon fibers were converted back to the K-form by immersing in a solution of 1 M KNO_3 and performing ESIX; and then, CV measurement was carried out again; this process was performed several times. In order to check the cycle stablity of the NiHCF film coated carbon fibers, CV measurement was performed up to 200 times in a solution of 1 mol L^{-1} KNO_3 at a potential range of -0.25 to 1 V with a scan rate of 25 mVs^{-1}.

3. Results and discussion

3.1. Potential-time and current-time transient curves during UPED of NiHCF film on carbon fibers

Fig. 2 shows typical potential-time and current-time transient curves corresponding to the first 20 s during UPED of NiHCF thin films on carbon fibers with 3000 pulse cycles at various on-potentials with both on-time and off-time periods of 0.5 s. As pulse deposition began, film started to be formed on the carbon fibers, and in this case, one can see that the open circuit potential measured during the off-time period increased with the increasing of the cycle number and was approaching to the applied potential, indicating that the film was becoming thicker and thicker. Herein, with the increase in the applied potential, the values of open circuit potential during off-period gradually increased from 0.47, 0.5, 0.53 and 0.57 V to 0.48, 0.53, 0.57 and 0.7 V at the initial 20 s of deposition process, respectively, when the on-potentials were set at 0.5, 0.6, 0.7, and 0.8 V, respectively. On the other hand, from the current-time transient curves, one can see that the peak currents during the on-time periods decreased rapidly during the first few cycles and then decreased gradually and finally became to a relatively stable value. As shown in the inset of Fig. 2 (d), during the end period of deposition process, the peak current was stabilized at stable value, indicating that only a trace amount of deposition occurred by the end of 3000 pulse cycles. This trend is a general