Preparation of graphene/nickel-iron hexacyanoferrate coordination polymer nanocomposite for electrochemical energy storage

Shahram Ghasemi [a,b,*], Sayed Reza Hosseini [b], Parvin Asen [b]

[a] Faculty of chemistry, University of Mazandaran, Babolsar, Iran
[b] Nanochemistry Research Laboratory, Faculty of Chemistry, University of Mazandaran, 47416-95447 Babolsar, Iran

A B S T R A C T

A new graphene/nickel-iron-hexacyanoferrate (graphene/Ni-Fe-HCF) nanocomposite was constructed and its electrochemical behavior was investigated. First, graphene oxide (GO) was deposited by electrophoretic deposition (EPD) technique onto stainless steel (SS). Then, it was electrochemically reduced to graphene (ERGO/SS) by applying constant potential at -1.1 V in NaNO$_3$. Finally, Ni-Fe-HCF hybrid was formed onto ERGO/SS from solution containing NiCl$_2$, FeCl$_3$ and K$_3$Fe(CN)$_6$ by chronoamperometry. The surface morphology of constructed electrode was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM indicates the formation of nanoparticles in the range of 20–60 nm. Also, crystal structure of nanocomposite was characterized by using X-ray diffraction. The performance of prepared electrode was investigated by various electrochemical methods using cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS). Results show that Ni-Fe-HCF hybrid has characteristics of battery-type materials. Ni-Fe-HCF/ERGO nanocomposite has higher capacity (67.77 mAh g^{-1}) than ERGO (32.5 mAh g^{-1}) or Ni-Fe-HCF (20.97 mAh g^{-1}) at 0.5 Ag^{-1}. Also, its capacity is higher than that of Ni-HCF/ERGO (44.58 mAh g^{-1}) or Fe-HCF/ERGO (44.72 mAh g^{-1}) at same current density. In addition, EIS results show Ni-Fe-HCF/ERGO has the lowest charge transfer resistance. Cycle life studies resolve that Ni-Fe-HCF/ERGO shows good stability in 0.5 M KNO$_3$ at pH = 5.

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1. Introduction

The formation of thin film of $Fe_4\left[Fe(CN)_6\right]_3$ (PB) on platinum foil was first reported by Neff [1]. It is recognized as the first synthetic coordination polymer compound which has general formula $M^A_{\ k}\left[M^B(CN)_6\right]$ where M^A and M^B are transition metals with different formal oxidation numbers [2]. Coordination polymers are a family of materials composed of 1D chain, 2D sheet and 3D network, containing organic ligands and inorganic metal ions connected to each other via strong bonds. Metal hexacyanoferrates (MHCFs, M: Ni, Co, Cu and Zn) known as PB analogues are coordination polymers because of the ability of polymerization and formation 3D structure. PB analogues have various applications in different research area such as chemical sensor and biosensor, electrocatalyst and charge storage [3–8].

There are three categories of samples which can be used in the energy storage systems: capacitor-type materials (EDLC), battery-type materials (such as Ni(OH)$_2$ and NiHCF), and pseudocapacitive materials (such as MnO$_2$ and RuO$_2$). MHCFs are battery type materials that can be used as active materials in batteries and hybrid supercapacitor [9–11]. PB analogues are desirable for use as battery electrodes because of tunable open channels that allow insertion of both molecular and ionic species. In battery-type materials, the energy density is generally twice that stored in capacitor-type materials [10]. Cyclic voltammograms of MHCFs show characteristic peaks due to their redox reactions.

The main drawback of PB analogues is gradual dissolution during potential cycling [8]. In order to overcome this problem, several strategies such as application of conducting polymer [8,12] and preparation of hybrid MHCFs [8] have been introduced. Kulesza et al. [13,14] reported the synthesis of hybrid Ni-Co-HCF and Ni-Pd-HCF with good stability.

MHCFs are attractive candidate to construct various composites, which can be used in charge storage systems. Safavi et al. prepared stable hybrid Ni-Co-HCF on stainless steel (SS) and investigated its application in supercapacitor [8]. Poly(3,4-

* Corresponding author at: University of Mazandaran, Faculty of Chemistry, Babolsar 47416-95447 Iran. Tel.: +98 1135302397; fax: +98 1135302350.
E-mail addresses: sghasemimir@yahoo.com, sghasemi@umz.ac.ir (S. Ghasemi).

ethylenedioxythiophene)/MHCF (Ni-Co-Fe) [15], FeOOH@CoHCF [16], MnHCF/MnO$_2$ [17], CuHCF [18], MnO$_2$/NiHCF [10] and hybrid Ni-CoHCF [8] are some reported HCF-based energy storage systems.

Carbon-based materials such as activated carbon, carbon nanotube, carbon aerogel and graphene employed as the most promising materials for supercapacitor. Among them, graphene is attractive candidate due to its large surface area (2675 m^2 g^{-1}) and high electrical conductivity [19,20]. However, the conductivity of graphene film is mainly limited by agglomeration of graphene nanosheets because of the Van der Waals attraction between neighboring sheets [21]. It is believed that the agglomeration reduces the effective surface area of the graphene and thus can't reflect the capacitance of an individual graphene sheet [20–23]. However, various parameters such as preparation method and degree of reduction can influence on the capacitance of graphene.

The electrophoretic deposition (EPD) is an economical method in the preparation of thin film of graphene [24] which is done in two steps. In the first step, when electric field is applied, charged particles in suspension move toward the electrode with opposite charge and in the second step, they deposit on the electrode surface and form a coherent film. Various oxygen functional groups such as hydroxyl and carboxyl are formed on graphene oxide (GO) nanosheets during the chemical exfoliation and allow the formation of stable aqueous suspension used in EPD [25–27]. By applying voltage between electrodes, GO nanosheets with negative charge, immigrate toward the positive electrode and form a thin film on it. The deposition rate, thickness and uniformity of GO film can be controlled by varying the time of deposition and passed current during EPD method [24]. To date, different substrate such as nickel foam, carbon fiber, carbon paper, carbon cloth and etc. have been used to deposit graphene. Moreover, SS has been considered in the electrode fabrication due to its availability and corrosion resistance.

It was reported that GO film presents lower capacitance than reduced graphene oxide (RGO). Elimination of oxygen groups can increase the conductivity of GO film; consequently, capacitive behavior increases [28]. Electrochemical reduction of graphene oxide (ERGO) is one of the proposed methods to remove the functional groups. In comparison to chemical treatment method, which use hazard material such as N$_2$H$_4$ and KOH, electrochemical reduction is simple, cost effective and eco-friendly technique to obtain ERGO film [29].

Composites of RGO with various materials including conducting polymer [30], metal oxide such as Co$_3$O$_4$ and SnO$_2$ [31,32] have been prepared to improve the electrochemical performance of energy storage device. Composites display better energy and power density in comparision with carbon materials.

Scholz and Reddy [33] prepared hybrid of nickel-iron-hexacyanoferrate (Ni-Fe-HCF) by chemical precipitation in 1996. Also, Kumar et al. [34] synthesized electrochemically hybrid thin film of Ni$_x$-Fe$_{(1-x)}$Fe(CN)$_6$ on glassy carbon electrode and used it as electrocatalyst for H$_2$O$_2$. To the best of our knowledge, there is no report on the use of Ni-Fe-HCF/graphene (Ni-Fe-HCF/ERGO) nanocomposite in the energy storage systems. Herein, Ni-Fe-HCF/ERGO was constructed and its electrochemical behavior was investigated by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Chemicals and apparatus

Graphite powder, NaNO$_3$, H$_2$SO$_4$, H$_2$O$_2$, KMnO$_4$, HCl, NiCl$_2$.6H$_2$O were purchased from Merck. KNO$_3$ and K$_3$Fe(CN)$_6$ was purchased from Fluka. FeCl$_3$·6H$_2$O was purchased from BDH. The electrochemical experiments were carried out using AUTOLAB 302N (Netherland) electrochemical analyzer with three-electrode cell. The employed electrodes were MHCF/ERGO/SS (M = Ni, Fe), platinum foil and Ag|AgCl (3 M KCl, Azar electrode, Iran) as working, auxiliary and reference electrode, respectively. The characterizations of electrodes were carried out with field-emission scanning electron microscopy (KYKY-EM 3200), X-ray diffraction (XRD) by X-ray diffractometer (GBC MMA) using Cu Kα irradiation. AFM was carried out in ambient conditions using Araresearch (0101/A, Iran), operating in non-contact mode. Fourier transform infrared (FT-IR) spectra were recorded with KBr pellet on a VECTOR- 22 (Bruker) spectrometer. UV–V is absorption spectrum was performed using UV–V is spectrometer PG Instruments Ltd.

2.2. Synthesis of graphite oxide

Graphite oxide was synthesized by modified Hummer's method [35]. Typically, 1 g graphite and 1 g NaNO$_3$ were mixed with 23 mL concentrated sulfuric acid in an ice bath. 4 g KMnO$_4$ was added gradually to yield a green-purple mixture. Then, the mixture was maintained at 0 °C for 1 h under stirring. Afterward, 180 mL double-distilled water was added slowly during 1 h. Temperature of mixture increased to 98 °C. After 15 min, 10 mL of H$_2$O$_2$ was transferred to the suspension in order to terminate the reaction. The color of suspension changed from brown to yellow. The resulting product was filtered and rinsed with 5% HCl solution and then washed several times with distilled water to adjust the pH~6. The obtained product was dried at room temperature.

2.3. Preparation of GO/SS

In order to obtain SS with mirror like-surface, SS substrate was polished galvanostatically by applying 5 A cm^{-2} for 2 min in a bath containing 50 vol.% phosphoric acid, 25 vol.% sulfuric acid, and balanced distilled water. After electropolishing, SS substrate was rinsed with water and then the area of 1 cm^2 was assigned by covering with polytetrafluoroethylene tape. The electrophoretic cell consisted of two electrodes; SS (grade 304, 1 cm^2) and platinum (Pt) foil as positive and negative electrode, respectively. These electrodes were placed vertically and immersed in suspension containing 1.5 mg mL^{-1} graphene oxide while the distance between them was kept 1 cm. GO nanosheets were deposited onto SS by applying a constant voltage of 5 V for 10 min. Afterward, GO/SS was dried at room temperature for 1 h.

2.4. Electrochemical reduction of GO/SS

Three-electrode cell was used in order to reduce GO to ERGO. ERGO/SS was prepared by applying potential of −1.1 V to GO/SS in 0.5 M NaNO$_3$ solution for 1000 s [29]. After reduction, ERGO/SS was washed with distilled water and then dried in the oven at 70 °C for 1 h.

2.5. Preparation of Ni-Fe-HCF/ERGO/SS

Electrochemical formation of Ni-Fe-HCF onto ERGO/SS and SS was carried out in cell containing 0.5 mM NiCl$_2$·6H$_2$O, 0.5 mM FeCl$_3$.6H$_2$O, 0.5 mM K$_3$Fe(CN)$_6$, 0.5 mM HCl and 0.1 M KNO$_3$ under constant potential of 0.35 V versus Ag|AgCl during 300 s. After electrodeposition, it was rinsed with distillated water and dried in oven at 70 °C for 1 h. In order to compare the electrochemical behavior of Ni-Fe-HCF/ERGO nanocomposite with single-metal HCF/ERGO (Ni or Fe), various electrodes were prepared at the same conditions and potential from solution containing NiCl$_2$ or FeCl$_3$, respectively.