This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Electrochemical preparation and characterization of polypyrrole/nickel–cobalt hexacyanoferrate nanocomposite for supercapacitor application

Ali Asghar Ensafi*, Najmeh Ahmadi and Behzad Rezaei

Department of Chemistry, Isfahan University of Technology, Isfahan, 84156–83111, Iran

Abstract

Polypyrrole/nickel-cobalt hexacyanoferrate (PPy/NiCoHCF) nanocomposite is synthesized using a fast and facile electrochemical approach on a low cost stainless steel substrate. The prepared nanocomposite is characterized in terms of composition and morphology using X–ray diffraction spectroscopy, energy dispersive X–ray spectroscopy, FT–IR spectroscopy and scanning electron microscopy. The capacitive behavior of the nanocomposite is investigated by means of cyclic voltammetry, galvanostatic charge/discharge technique and electrochemical impedance spectroscopy, in an aqueous electrolyte of 0.5 mol L⁻¹ K₂SO₄ and in a non-aqueous electrolyte of 0.5 mol L⁻¹ LiClO₄/ethylene carbonate: dimethyl carbonate (EC:DMC). The results showed that incorporation of NiCoHCF with PPy improves the capacitance properties of PPy in both aqueous and non-aqueous media. Maximum capacitance of 529 F g⁻¹ and 668 F g⁻¹ at the current density of 1.0 Ag⁻¹ are achieved for the proposed nanocomposite in aqueous and non-aqueous electrolytes, respectively using galvanostatic charge-discharge technique. Moreover, the nanocomposite showed an excellent stability (less than 10% drop after 1000 cycles), high specific power density (5600 W kg⁻¹) and high specific energy density (87 Wh kg⁻¹) at a current density of 10 Ag⁻¹. Based on the obtained results, the proposed nanocomposite is a potential candidate for electrode material in electrochemical supercapacitor.

* Correspondence author. Fax: +98–311–3912350; Tel.: +98–311–3912351. E–mail: Ensafi@cc.iut.ac.ir; aaensafi@gmail.com; ensafi@yahoo.com.
Keywords: Polypyrrole; Nickel-cobalt hexacyanoferrate; Nanocomposite; Electrochemical supercapacitor.

1. Introduction

Energy storage in supercapacitors is based on electrical double layer capacitance or pseudo-capacitance (based on the fast reversible oxidation-reduction reactions).¹ High-surface carbons, redox metal/metal oxides and conducting polymers are the main groups of electrode materials being studied for energy storage application in electrochemical supercapacitors.² Progress in the energy storage devices largely depends on the development of highly efficient electrode materials. In recent years, there is a growing interest in combination of different kinds of active materials to construct new hybrid electrode materials. One of popular approaches is combination of an electrical conductive organic polymer with an inorganic redox active material such as Prussian blue (PB) analogue compounds.³

PB analogues or transition metal/hexacyanometalates (MHCM) represent an important groups of mixed-valence compounds with a general formula of AₘMₖ[M(CN)$_6$]ₙ·mH₂O (h, k, l, and m are stoichiometric coefficients, A is alkali metal action and M is transition metal ion) while PB or iron/hexacyanoferrate (with A=K and M=Fe in the above general formula) is the most famous prototype.⁴ These materials are precisely suitable for fast insertion/removal of alkali cations such as Li⁺, Na⁺ and K⁺ with very little crystallographic lattice strain due to their open-framework crystal structure, which contains large interstitial sites.⁵ Simple and complex hybrid of PB analogues can be prepared using different transition metal ions. The MHCM hybrids such as NiCoHCF, NiPdHCF, FeNiHCF, and CuCoHCF have more stability and show special electrochemical and electrochromic characteristics in comparison with single MHCM components.⁶⁻¹⁰ Recently, NiCoHCF hybrid
has been used as an electrode material in energy storage devices, which shows higher performance in comparison with simple NiHCF and CoHCF.\textsuperscript{7, 11, 12}

Polypyrrole (PPy) is currently under intensive investigation as alternative materials in supercapacitor application. The interest in this conductive polymer is attributed to its high charge storage ability, high electrical conductivity, easy preparation procedure plus the low cost.\textsuperscript{13-16} Recently, different types of new PPy based nanocomposites, including CNT/PPy nanostructure,\textsuperscript{17} graphene nanoribbon/PPy,\textsuperscript{18} MnO\textsubscript{2}@graphene/PPy nanocomposite\textsuperscript{19} and PPy/ZnO/graphene oxide\textsuperscript{20}, have been utilized as electrode materials to improve the charge storage capacity and long term stability of PPy-based capacitors.

The goal of our work is to develop new hybrid organic/inorganic nanocomposite materials for supercapacitor application by combination of PPy (as an organic conductive polymer) and NiCoHCF (as a poly-nuclear inorganic compound) to obtain some reinforcement and/or their synergetic effect. In this way, incorporation of NiCoHCF into PPy matrix is performed using anodic polymerization of pyrrole in colloid solution of NiCoHCF. Stainless steel is chosen as a substrate due to its high corrosion resistance, good conductivity and the low cost. The charge storage properties of the obtained nanocomposite were investigated using different electrochemical methods in both organic and aqueous electrolytes.

2. Experimental

2.1. Chemicals and Apparatus

K\textsubscript{3}Fe(CN)\textsubscript{6}.H\textsubscript{2}O, Ni(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O, Co(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O, K\textsubscript{2}SO\textsubscript{4} and sulfuric acid were purchased from Merck. All chemicals were of analytical grade and used as received. Double distilled water was used throughout. Pyrrole (Fluka Corp., 99%) was distilled under vacuum
prior to use and stored in refrigerator. Stainless steel (SS), type 304, was purchased from local market.

The surface morphologies of the nanocomposites were investigated by Hitachi S4160 field emission scanning electron microscope (FE–SEM, Tokyo, Japan) at an accelerating voltage of 20 kV. X–ray diffraction (Bruker D/Advance X–ray, Germany) with Cu–Kα radiation (λ = 1.54 Å) and Fourier transform infrared spectroscopy (JASCO FT–IR, 680 plus, Japan) were used to survey characteristics of the electrode materials. Energy dispersive X–ray spectra (EDS) of the nanocomposites were recorded using a Philips XLS instrument (The Netherlands). An elemental analyzer (LECO CHNS-932/USA) was used for CHNS elemental analysis. Specific surface area and pore characteristics of the active materials were measured using a BELSORP MINI-II analyzer (JP. BEL Co. Ltd.), based on the nitrogen adsorption/desorption isotherms at 77 K.

Cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) experiments were performed with an Ivium potentiostat/galvanostat instrument (pocket STAT Model) in a three-electrode cell system incorporating a working electrode, a saturated Ag/AgCl reference electrode in aqueous medium or a Ag/Ag⁺ pseudo-reference electrode in organic solution and a Pt-wire counter electrode. Electrochemical impedance experiments were carried out by applying a sinusoidal potential perturbation of 10 mV at the open circuit potential with a frequency spectrum of 100 kHz to 10 mHz, using a computer controlled Autolab (PGSTAT302N, Eco–Chemie, The Netherlands) with NOVA 1.10 software. Mass loading was measured by analytical electronic balance (Sartorius–CPA2P, d = 0.001 mg).

2.2. Electrode preparation

A 304 type SS rod (with a diameter of 6.0 mm) was enclosed with Teflon to obtain an electrode with a geometric surface area of 0.28 cm². Before deposition of the active materials
on the SS surface, the electrode was successively polished with emery paper followed by 0.3 
µm alumina slurry and cleaned ultrasonically in 1:1 water/ethanol, to obtain a mirror like 
surface.

Fiorito et al.\textsuperscript{21} method was used to deposit PPy/NiCoHCF, PPy/NiHCF and 
PPy/CoHCF nanocomposites on the SS substrate with a little modification. Briefly, for 
PPy/NiCoHCF preparation, the SS electrode was cycled 25 times at a scan rate of 50 mV s\textsuperscript{−1} 
between potential of −0.10 to +0.90 V (vs. Ag/AgCl) in a solution containing 0.10 mol L\textsuperscript{−1} 
K\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}SO\textsubscript{4} as an electrolyte and 0.10 mol L\textsuperscript{−1} of pyrrole and different concentration of 
K\textsubscript{3}Fe(CN)\textsubscript{6}/Ni(NO\textsubscript{3})\textsubscript{2}/Co(NO\textsubscript{3})\textsubscript{2}. The synthesis process of PPy/NiHCF and PPy/CoHCF 
nanocomposites were similar to that of PPy/NiCoHCF by changing of 
K\textsubscript{3}Fe(CN)\textsubscript{6}/Ni(NO\textsubscript{3})\textsubscript{2}/Co(NO\textsubscript{3})\textsubscript{2} with K\textsubscript{3}Fe(CN)\textsubscript{6}/Ni(NO\textsubscript{3})\textsubscript{2} or K\textsubscript{3}Fe(CN)\textsubscript{6}/Co(NO\textsubscript{3})\textsubscript{2}, 
respectively. The PPy film without MHCF was prepared in a solution of 0.10 mol L\textsuperscript{−1} pyrrole 
containing 0.1 mol L\textsuperscript{−1} K\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}SO\textsubscript{4}, using the same electrochemical conditions. The 
prepared electrodes were washed with water and dried in a nitrogen stream. Table 1 shows 
the initial concentrations of pyrrole, K\textsubscript{3}Fe(CN)\textsubscript{6}, Ni(NO\textsubscript{3})\textsubscript{2} and Co(NO\textsubscript{3})\textsubscript{2} in the 
electrodeposition solution and also MHCF content of the prepared nanostructures 
(Determined by EDS and CHNS techniques) under the described synthesis conditions.

“Here Table 1”

The weights of the loaded active materials on the electrodes were calculated by 
subtraction of the weight of the SS electrode, before and after deposition of the active 
materials on the electrode surface, by six digit analytical electronic balance. The results 
showed that about 30 µg of the active materials were loaded on the electrodes surface, in each 
experiment.

3. Results and discussion
3.1. Characterization of the electrode materials

To determine the weight ratio between PPy and NiCoHCF and the stoichiometry of the metals (K, Ni, Co and Fe) in electrochemically prepared nanocomposites, EDS and CHNS techniques were used (Table 1). The results showed that increasing K₃Fe(CN)₆, Ni(NO₃)₂ and Co(NO₃)₂ concentrations in the electrodepositing solution cause increasing the MHCF contents of PPy/MHCF nanocomposites. Figs. 1A and 1B show the EDS spectra of PPy and PPy/NiCoHCF (sample 1 and 4) and their elemental compositions. As can be seen, EDS spectra of PPy shows presence of carbon, nitrogen, oxygen and sulfur, which confirms the sulfate doped PPy structure, while EDS spectra of PPy/NiCoHCF shows presence of iron, nickel, cobalt and potassium as well as carbon, nitrogen, oxygen and sulfur. In the EDS data (insets of Figs. 1A and 1B) all elements except hydrogen were listed, so to get the exact percent contribution of MHCF in PPy/MHCF, the hydrogen contents of the nanocomposites (which can be determined by CHNS analysis) have been considered. The following stoichiometric formulas for MHCF part of PPy/MHCF nanostructures were obtained from the EDS data: K₁Ni₀.₅Co₀.₅[Fe(CN)₆] (sample 2-5), K₁Co₁[Fe(CN)₆] (sample 6), and K₁Ni₁[Fe(CN)₆] (sample 7). The above results confirm that NiHCF, CoHCF and NiCoHCF were successfully incorporated into the PPy matrix.

XRD technique was used to determine the crystalline structures of the nanocomposites. The test was performed by scanning in steps of 0.02(2θ) with fixed counting time of 5 s per step in the 2θ range from 10 to 60 (Figs. 1C). The main diffraction peak in PPy (sample 1) pattern at 2θ of 20.2º corresponds to pyrrole counter ion or inter-counter ion interaction scattering, while the other main peak at 2θ of 26.4º is assigned to the PPy chain that is close to the inter-planar Van der Waals distance from the aromatic groups.¹⁹, ²² The diffraction peaks at 2θ about 17.1º, 35.3º, 39.2º, 43.6º, 51.0º, 53.9 and 57.8º, in PPy/NiCoHCF (sample 4), PPy/CoHCF (sample 6) and PPy/NiHCF (sample 7) are indexed
as the planes of 200, 400, 420, 422, 440, 600 and 620 in PB analogues.\textsuperscript{5,23} The obtained data from XRD analysis indicates that PPy and PPy/MHCF were successfully synthesized.

For IR spectroscopy characterization, the prepared films were peeled off from the SS substrate. FT–IR spectra were recorded using KBr diluted pellets of the nanostructures. FT–IR spectra (Figs.1D) of all of the nanocomposites show the characteristic peaks of pyrrole ring including C=C stretching vibration at 1548 and 1441 cm\(^{-1}\), C–N stretching vibration at 1269 cm\(^{-1}\), C–H in plane bending at 1283 cm\(^{-1}\), N–H in plane bending at 1042 cm\(^{-1}\) and C–H out of plane bending at 764 cm\(^{-1}\).\textsuperscript{24} PPy/CoHCF, PPy/NiHCF and PPy/NiCoHCF show absorption band at 2065 cm\(^{-1}\) (C≡N groups vibration) as well as PPy characteristic bands.\textsuperscript{25}

Presence of C≡N band in PPy/MHCF indicates that MHCF incorporated in the polymer matrix and the PPy/MHCF nanocomposites were successfully synthesized. \textit{“Here Fig. 1”}

The morphology of PPy/MHCF nanostructure (sample 4) was checked by FE–SEM. As can be seen in Fig. 2, the prepared nanostructure exhibited nanowire like morphology. Such structure would be proper as an electrode material for supercapacitor application because they have a suitable surface area, which is ideal for the electrochemical charge storage. \textit{“Here Fig. 2”}

Nitrogen adsorption-desorption isotherm was used to measure the specific surface area and the porous features of the PPy based active materials. It is now well established that the specific surface area and the porosity of PPy is related to different factors such as the anionic dopant, incorporation of inorganic nanoparticles and the polymerization solvent.\textsuperscript{26} Therefore, different surface area (ranging from 15 m\(^2\) g\(^{-1}\) to 400 m\(^2\) g\(^{-1}\)) have been reported in the literature for PPy based nanocomposites.\textsuperscript{26} The surface area of 22.80 and 18.35 m\(^2\) g\(^{-1}\) were calculated for PPy (sample 1) and PPy/NiCoHCF (sample 4), respectively based on Brunauer-Emmett-Teller method. Also, the pore sizes distribution of PPy and PPy/NiCoHCF were derived from the adsorption data and calculated from the isotherm using the BJH model.
The results revealed that most of the PPy pores fall into the size range of 2-18 nm with an average pore size of 5.13 nm, while PPy/NiCoHCF shows the pore size distribution of 2-20 nm with an average pore size of 6.06 nm. Although the specific surface area of PPy/NiCoHCF is a little lower than PPy, the higher specific capacitance of PPy/NiCoHCF (as shown in section 3.2) revealed that the charge storage properties of the PPy/NiCoHCF is mainly resulted from the redox properties of PPy/NiCoHCF and the specific surface area plays a less significant role.

3.2. Electrochemical behavior of PPy/NiCoHCF

Figs. 3A and 3B compares the voltammograms of the different electrode materials in the potential range of -0.10 to +1.10 V in 0.50 mol L\(^{-1}\) LiClO\(_4\)/EC:DMC and in the potential range of -0.20 to +0.80 in 0.50 mol L\(^{-1}\) K\(_2\)SO\(_4\), at a scan rate of 50 mV s\(^{-1}\). As can be seen, the shapes of the cyclic voltammograms are different from an ideal rectangular shape, which indicate that capacitance mainly resulted from pseudo-capacitance due to the faradaic redox reactions of the electroactive materials. The specific capacitance \(C_s\) was calculated according to the following equation:\(^{27}\)

\[
C_s = \frac{\int \text{d}V}{2 \times m \times v \times \Delta V}
\]  

(1)

Where \(\int \text{d}V\) is the integrated area of the CV curve, \(m\) (g) the mass of the active material, \(\Delta V\) (V) the width of the potential window and \(v\) (V s\(^{-1}\)) the potential scan rate. The obtained capacitances for the different electrode materials are given in Table 2. As can be seen in Table 2, PPy/MHCF electrode has a higher specific capacitance rather than PPy, due to the combination of the electrochemical capacity of organic (PPy) and inorganic components (MHCF). In addition, PPy/NiCoHCF has higher capacitance vs. PPy/NiHCF and PPy/CoHCF, due to the synergistic effect between nickel and cobalt in PPy/NiCoHCF.
Cyclic voltammograms of PPy/NiCoHCF in 0.5 mol L\(^{-1}\) LiClO\(_4\)/EC:DMC and 0.5 mol L\(^{-1}\) K\(_2\)SO\(_4\) were recorded at different scan rates (Figs. 3C and 3D). The results show that the specific capacitance of PPy/NiCoHCF in both electrolytes decreases with increasing the scan rate (insets of Figs. 3C and 3D). This behavior is due to decreasing in the degree of utilization of the nanostructure active sites at higher scan rates. In another word, at higher scan rates, as a result of an inadequate response time for the electrolyte ions to reach the surface of the electrode, the nanostructure–electrolyte interaction would be limited. Thus, the capacitance of the electrode will decrease due to the limitation of the diffusion of the electrolyte ions to the electrode surface.\(^{28}\)  

“For better comparison, the electrochemical behavior of different prepared PPy/NiCoHCF nanostructures (sample 2-5) with different MHCF contents were investigated using cyclic voltammetry. The results (Fig. 4) show that by increasing MHCF content in the samples leads to increasing the specific capacitance of PPy/MHCF (317, 374 and 453 F g\(^{-1}\) for sample No. of 2, 3 and 4, respectively) while the specific capacitance decreased at higher MHCF content (423 F g\(^{-1}\) for sample 5) of PPy/MHCF. Therefore, the nanostructures with MHCF content of 9.6% were chosen for the rest of the study. “Here Fig. 4”

CD curves of PPy, PPy/NiHCF, PPy/CoHCF and PPy/NiCoHCF at a current density of 2.0 A g\(^{-1}\), in 0.5 mol L\(^{-1}\) LiClO\(_4\)/EC:DMC and 0.5 mol L\(^{-1}\) K\(_2\)SO\(_4\), are shown in Figs. 5A and 5B, respectively. The CD curves are consisting of an initial voltage loss due to the internal resistance and a gradual linear voltage drop based on reversible redox reaction of the active materials. Generally, the capacitance properties of the present electrode materials could be explained using the following reversible reactions:\(^{11,29}\)

\[
[\text{PPy}^+]A^- + e^- \leftrightarrow [\text{PPy}] + A^- \quad (2)
\]

\[
\text{KNiCoFe}^{\text{III}}(\text{CN})_6 + M^+ + e^- \leftrightarrow \text{KMNiCoFe}^{\text{II}}(\text{CN})_6. \quad (3)
\]
Where $A^-$ is an anion ($SO_4^{2-}$, $ClO_4^-$) and M is an alkali ion ($Li^+$, $K^+$). Equation 3 is also used for a single MHCF. The following equation was used to calculate the specific capacitance of the proposed electrode materials: $^{30}$

$$\text{Specific capacitance} = \frac{I.t}{\Delta V.m}$$  \tag{4}

Where $I$(A) and $t$(s) are the discharge current and time, respectively, $\Delta V$(V) is the potential range, and $m$(g) is the mass loading of the films on the SS electrode. The obtained capacitances of PPy, PPy/NiHCF, PPy/CoHCF and PPy/NiCoHCF, using CD technique, are given in Table 2, which is in agreement with the obtained capacitance values by the CVs.

To further evaluate the application potential of PPy/NiCoHCF as an electrode material for supercapacitor, CD measurements were carried out at various current densities (ranging from 1.0 to 10.0 A g$^{-1}$), as shown in Figs. 5C and 5D. The results (Table 3) revealed that the specific capacitance decreases with increasing the discharge current density. This behavior can be attributed to more utilization of the nanocomposite active sites at lower current densities in comparison with the higher current densities. Actually, at higher current densities, some of the active sites of the nanostructures become inaccessible for charge storage because of limited migration of the electrolyte ions.$^{31}$ However, PPy/NiCoHCF retains about 60% of its capacitance in a current density of 10.0 A g$^{-1}$ (Table 3) in comparison with a current density of 1.0 A g$^{-1}$ (10 times higher), which indicates the good rate capability and consequently high power density of the proposed electrode materials.

"Here Fig. 5 & Table 3"

The specific power ($SP$, W kg$^{-1}$) and the specific energy ($SE$, W h kg$^{-1}$) can be calculated from CD using the following relationships:$^{11}$

$$SP = \frac{I \Delta V}{2m}$$  \tag{5}

$$SE = 0.5C_s\frac{\Delta V^2}{3.6}$$  \tag{6}
Where $I(A)$, $\Delta V(V)$ and $m(g)$ are the discharge current, operating potential window and mass of the electrode active materials, respectively. The overall operational characteristics of the PPy/NiCoHCF electrode material were demonstrated using the Ragone plot (Fig. 6) and are given in Table 3. The maximum power density of 5600 $W$ kg$^{-1}$ at energy density of 87 $W$ h kg$^{-1}$ and in discharge current of 10.0 $A$ g$^{-1}$ were achieved in 0.5 mol L$^{-1}$ LiClO$_4$/EC:DMC.

As can be seen in Table 3, PPy/NiCoHCF offer higher energy and power density in organic media in comparison with aqueous electrolyte, which is attributed to larger voltage window and specific capacitance in the organic electrolyte. $^{32}$ *Here Fig. 6*

### 3.3. Electrochemical impedance spectroscopy analysis of the electrode materials

Electrochemical impedance spectroscopy (EIS) was used to further verify the capacitance properties of the different electrode materials.$^{33}$ Fig. 7A shows the Nyquist plots for PPy, PPy/CoHCF, PPy/NiHCF and PPy/NiCoHCF electrodes in 0.5 mol L$^{-1}$ LiClO$_4$/EC:DMC and in a frequency range of 100 kHz to 10 mHz under open circuit condition. All the Nyquist plots are composed of two distinct parts, a semicircle in high-frequency region and a line in low-frequency region. Inset of Fig. 7A shows the equivalent electrical circuit model used for fitting of the EIS data of PPy/NiCoHCF electrode, based on Macdonald’s algorithm using ZView 2.3 (Scribner Associates, Inc.) software.

As can be seen, the equivalent circuit consists of the electrolyte resistance as well as substrate intrinsic resistance ($R_1$), the resistance due to the charge transfer ($R_2$), Warburg resistance ($W_1$) which is related to the ion diffusion, the double-layer capacitor ($CPE_1$) and the pseudo-capacitor ($C_1$). At the high frequencies, the intercept of the real axis ($R_1$) implies the solution resistance, which is almost equal for all of the electrode materials (Fig. 7A), while the radius of the semicircles in the Nyquist plots can be ascribe to the charge transfer resistance ($R_2$) between the active materials/electrolyte interface.$^{34}$ The smaller charge
transfer resistances of PPy/CoHCF, PPy/NiHCF and PPy/NiCoHCF in comparison with PPy should be attributed to the presence of an electroactive species of MHCF in the nanostructures network. In low frequency region, the imaginary parts of the Nyquist plots increase quickly and exhibits a nearly 90° angle with the real axis. This behavior can be attributed to the capacitive behavior of the active materials. The more vertical line (for PPy/MHCF rather than PPy) representing the lower diffusion resistance of the electrolyte ions to the structure of PPy/MHCF active material, which lead to the more ideal capacitance behavior.

The specific capacitances of the different active materials were calculated using the following equation:

\[ C_s (F g^{-1}) = \frac{-1}{2\pi f Z'' m} \]  

(7)

Where \( Z'' \) is imaginary part of the impedance, \( m \) is mass of active material and \( f \) is frequency. Fig. 7B shows the plots of the specific capacitances vs. frequency. As can be seen, in high frequencies, all the active materials behave like a pure resistance and the capacitance increases with decreasing the frequency. Among the different electrode materials, the hybrid electrode (PPy/NiCoHCF) exhibited a highest specific capacitance of 450 F g\(^{-1}\) at frequency of 0.01 Hz, which is in agreement with the results of the galvanostatic discharge curves and CV analysis. “Here Fig. 7”

3.4. Cycling stability of PPy/NiCoHCF

The cycling stability and capacitance retention of PPy/NiCoHCF were investigated in both organic and aqueous electrolytes, using CD test at a current density of 10.0 A g\(^{-1}\). The results revealed that PPy/NiCoHCF retains 93% of its original capacitance after 1000 cycles in organic electrolyte and 800 cycles in aqueous electrolyte (Fig. 8 A,B) indicating that only a minor degradation was occurred during the charge/discharge process. The more stability of
PPy/NiCoHCF during CD tests in organic media in comparison with the aqueous electrolyte may be attributed to the smaller size of Li$^+$, and consequently lower lattice strain and destruction due to insertion and extraction of the alkali ions.$^{38}$ Performance comparison of different PPy or MHCF based electrodes for supercapacitor application$^{39-46}$ vs. PPy/NiCoHCF are given in Table 4. As can be seen, the capacitance and long term stability of the proposed electrode material are comparable to, and even better than those recently obtained by other works. “Here Fig. 8 & Table 4”

4. Conclusion

In summary, the nanostructures of PPy, PPy/NiHCF, PPy/CoHCF and PPy/NiCoHCF were electrochemically deposited on SS and characterized with SEM, XRD and IR spectroscopy. The capacitance behaviors of the proposed materials in aqueous and non-aqueous electrolytes were studied. PPy/NiCoHCF showed highest capacitance in both media. The enhanced capacitance can be ascribed to synergy effect and combination of the electric capacity of organic-inorganic components. Also, the capacitance in organic electrolyte is higher than in aqueous electrolyte because of the smaller size of Li$^+$ rather than K$^+$ and more wettability of PPy in organic media and thereby this caused higher electrode-electrolyte interaction. Our study showed that PPy/NiCoHCF exhibited an excellent long-term cycling stability (93% capacitance remained after 1000 CD cycles), a large power density (5600 W kg$^{-1}$) and a high energy density (87 W h kg$^{-1}$). These results confirmed that PPy/NiCoHCF is a good candidate for electrode material in supercapacitors.
Acknowledgments

The authors wish to thank Iran National Science Foundation (INSF, project No. BN073) and Isfahan University of Technology Research Councils for financial support of this work.
References

20 W. K. Chee, H. N. Lim, I. Harrison, K. F. Chong, Z. Zainal, C. H. Ng, N. M. Huang, 


23 C. D. Wessells, M. T. McDowell, S. V. Peddada, M. Pasta, R. A. Huggins, Y. Cui, 
ACS Nano, 2012, 6, 1688.


Cells, 2010, 94, 1064.

26 F. Ghamouss, A. Brugère, A. C. Anbalagan, B. Schmaltz, E. Luais, F. Tran-Van, 


Chem. A, 2013, 1, 7709.

2013, 93, 93.


31 D. Li, F. Meng, X. Yan, L. Yang, H. Heng, Y. Zhu, Nanoscale Res. Lett., 2013, 8, 
535.

32 A. Izadi-Najafabadi, T. Yamada, D. N. Futaba, M. Yudasaka, H. Takagi, H. Hatori, S. 


398 40  W. Lei, P. He, S. Zhang, F. Dong, Y. Ma, J. Power Sources, 2014, 266, 347.
400 42  J. Li, H. Xie, Y. Li, J. Power Sources, 2013, 241, 388.
Figure 1. EDS spectra of A) PPy, and B) PPy/NiCoHCF. C) XRD patterns of PPy (a), PPy/CoHCF (b), PPy/NiHCF (c) and PPy/NiCoHCF(d). D) FT–IR spectra of PPy (a), PPy/CoHCF (b), PPy/NiHCF (c) and PPy/NiCoHCF (d).
Figure 2. FE–SEM image of PPy/NiCoHCF nanostructure.
Figure 3. Cyclic voltammograms of (a) PPy, (b): PPy/CoHCF, (c): PPy/NiHCF and (d): PPy/NiCoHCF in A): non-aqueous electrolyte of 0.5 mol L$^{-1}$ LiClO$_4$/EC:DMC; and B): aqueous electrolyte of 0.5 mol L$^{-1}$ K$_2$SO$_4$ at a scan rate of 50 mV s$^{-1}$. Effect of different scan rates on PPy/NiCoHCF in 0.5 mol L$^{-1}$ LiClO$_4$/EC:DMC (C) and in 0.5 mol L$^{-1}$ K$_2$SO$_4$ (D).

Insets of C and D: Variation of the specific capacitance $\nu$s. scan rate.
Figure 4. Cyclic voltammograms of PPy/NiCoHCF with different NiCoHCF contents: (a) 4.9% (b) 7.3%, (c) 9.6%, and (d) 12.0% in 0.5 mol L$^{-1}$ LiClO$_4$/EC:DMC at a scan rate of 50 mV s$^{-1}$. 
Figure 5. Galvanostatic charge–discharge tests of (a) PPy, (b) PPy/CoHCF, (c): PPy/NiHCF and (d): PPy/NiCoHCF in A): 0.5 mol L\(^{-1}\) LiClO\(_4\)/EC:DMC, and B): in 0.5 mol L\(^{-1}\) K\(_2\)SO\(_4\) at a current density of 2.0 A g\(^{-1}\). Effect of different current densities on capacitance properties of PPy/NiCoHCF in 0.5 mol L\(^{-1}\) LiClO\(_4\)/EC:DMC (C) and in 0.5 mol L\(^{-1}\) K\(_2\)SO\(_4\) (D). Insets of C and D: Variation of the specific capacitance vs. the current density.
Figure 6. Ragone plots of PPy/NiCoHCF (a): in 0.5 mol L⁻¹ LiClO₄/EC:DMC, and (b): in 0.5 mol L⁻¹ K₂SO₄ at different current densities (1.0 – 10.0 A g⁻¹).
Figure 7. Nyquist plot (A) and the plot of $C_s$ vs. frequency (B) of PPy, PPy/CoHCF, PPy/NiHCF and PPy/NiCoHCF in 0.5 mol L$^{-1}$ LiClO$_4$/EC:DMC. Inset A): Equivalent electrical circuit comparable with Nyquist diagram of PPy/NiCoHCF.
Figure 8. Long-term cycle stability of PPy/NiCoHCF in 0.5 mol L\(^{-1}\) LiClO\(_4\)/EC:DMC (A), and in 0.5 mol L\(^{-1}\) K\(_2\)SO\(_4\) (B) at a current density of 10.0 A g\(^{-1}\). Insets A and B: First 10 cycles.
A new electrode material for supercapacitor application is introduced based on polypyrrole conductive polymer and nickel-cobalt hexacyanoferrate poly-nuclear inorganic compound.
Table 1. The initial concentration of Pyrrole, K₃Fe(CN)₆, Ni(NO₃)₂ and Co(NO₃)₂ in electrodepositing solution for preparation of different nanostructures (Electrolyte: K₂SO₄/H₂SO₄ 0.10 mol L⁻¹) and their corresponding MHCF content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyrrole/ mol L⁻¹</th>
<th>K₃Fe(CN)₆/mmol L⁻¹</th>
<th>Ni(NO₃)₂/mmol L⁻¹</th>
<th>Co(NO₃)₂/mmol L⁻¹</th>
<th>MHCF content of nanostructure *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0 %</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>4.9 %</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.75</td>
<td>0.38</td>
<td>0.38</td>
<td>7.3 %</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>1.00</td>
<td>0.50</td>
<td>0.50</td>
<td>9.6 %</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>1.25</td>
<td>0.63</td>
<td>0.63</td>
<td>12.0 %</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>1.00</td>
<td>0</td>
<td>1.00</td>
<td>9.7 %</td>
</tr>
<tr>
<td>7</td>
<td>0.1</td>
<td>1.00</td>
<td>1.00</td>
<td>0</td>
<td>9.7 %</td>
</tr>
</tbody>
</table>

* Determined by EDS and CHNS techniques.
Table 2. The specific capacitances of the different electrode materials in aqueous and organic electrolytes.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Capacitance (F g(^{-1})) using CV at 50 mV s(^{-1})</th>
<th>Capacitance (F g(^{-1})) using CD at 2 A g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 mol L(^{-1}) K(_2)SO(_4)</td>
<td>0.5 mol L(^{-1}) LiClO(_4)/EC:DMC</td>
</tr>
<tr>
<td>PPy</td>
<td>258</td>
<td>212</td>
</tr>
<tr>
<td>PPy/CoHCF</td>
<td>282</td>
<td>311</td>
</tr>
<tr>
<td>PPy/NiHCF</td>
<td>289</td>
<td>324</td>
</tr>
<tr>
<td>PPy/NiCoHCF</td>
<td>380</td>
<td>453</td>
</tr>
</tbody>
</table>
Table 3. The specific capacitance, specific energy and specific power of PPy/NiCoHCF (sample 4) electrode at various current densities.

<table>
<thead>
<tr>
<th>Current density (A g⁻¹)</th>
<th>0.5 mol L⁻¹ K₂SO₄</th>
<th>0.5 mol L⁻¹ LiClO₄ in EC:DMC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capacitance (F g⁻¹)</td>
<td>Specific energy (W h kg⁻¹)</td>
</tr>
<tr>
<td>1.0</td>
<td>529</td>
<td>73</td>
</tr>
<tr>
<td>2.0</td>
<td>457</td>
<td>64</td>
</tr>
<tr>
<td>3.0</td>
<td>403</td>
<td>56</td>
</tr>
<tr>
<td>4.0</td>
<td>373</td>
<td>52</td>
</tr>
<tr>
<td>5.0</td>
<td>340</td>
<td>47</td>
</tr>
<tr>
<td>7.0</td>
<td>313</td>
<td>43</td>
</tr>
<tr>
<td>10.0</td>
<td>289</td>
<td>40</td>
</tr>
</tbody>
</table>
Table 4. Capacitance comparison of different PPy or metal hexacyanoferrate based electrodes (three-electrode system) for supercapacitor application, reported in other works.

<table>
<thead>
<tr>
<th>Working electrode</th>
<th>Current density</th>
<th>Specific capacitance (F g(^{-1}))</th>
<th>Electrolyte</th>
<th>Capacitance retention</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/PPy/MWCNT</td>
<td>0.5 A g(^{-1})</td>
<td>407</td>
<td>1 M NaNO(_3)</td>
<td>92% after 1000 cycle</td>
<td>[39]</td>
</tr>
<tr>
<td>PPy/PANI</td>
<td>1.0 A g(^{-1})</td>
<td>380</td>
<td>1 M H(_2)SO(_4)</td>
<td>54% after 1000 cycle</td>
<td>[40]</td>
</tr>
<tr>
<td>MnO(_2)/PPy</td>
<td>0.5 A g(^{-1})</td>
<td>337</td>
<td>2 M KCl</td>
<td>90% after 1000 cycle</td>
<td>[41]</td>
</tr>
<tr>
<td>GO/PPy</td>
<td>1.0 A g(^{-1})</td>
<td>696</td>
<td>1 M KCl</td>
<td>93% after 1000 cycle</td>
<td>[42]</td>
</tr>
<tr>
<td>Gr/SnO(_2)/PPy</td>
<td>1.0 A g(^{-1})</td>
<td>616</td>
<td>1 M H(_2)SO(_4)</td>
<td>98% after 1000 cycle</td>
<td>[43]</td>
</tr>
<tr>
<td>MnHCF/MnO(_2)</td>
<td>0.5 A g(^{-1})</td>
<td>159</td>
<td>0.5 M Na(_2)SO(_4)</td>
<td>81% after 1000 cycle</td>
<td>[44]</td>
</tr>
<tr>
<td>CuHCF/GN/SS</td>
<td>1.0 A g(^{-1})</td>
<td>570</td>
<td>1 M KNO(_3)</td>
<td>96% after 1000 cycle</td>
<td>[45]</td>
</tr>
<tr>
<td>Gr/Ni-Fe-HCF</td>
<td>0.5 A g(^{-1})</td>
<td>244</td>
<td>0.5 M KNO(_3)</td>
<td>95% after 500 cycle</td>
<td>[46]</td>
</tr>
<tr>
<td>PPy/NiCoHCF</td>
<td>1.0 A g(^{-1})</td>
<td>529</td>
<td>0.5 M K(_2)SO(_4)</td>
<td>93% after 800 cycle</td>
<td>This work</td>
</tr>
<tr>
<td>PPy/NiCoHCF</td>
<td>1.0 A g(^{-1})</td>
<td>668</td>
<td>0.5 M LiClO(_4)/EC:DMC</td>
<td>93% after 1000 cycle</td>
<td>This work</td>
</tr>
</tbody>
</table>

A new electrode material for supercapacitor application is introduced based on polypyrrole conductive polymer and nickel-cobalt hexacyanoferrate poly-nuclear inorganic compound.