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High performance hybrid supercapacitor based on NiMoO4 nanoparticles embedded carbon nanofiber

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High performance hybrid supercapacitor based on $NiMoO_4$ nanoparticles embedded carbon nanofiber

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Abstract

In this article, a highly flexible electrochemical supercapacitor was developed based on a novel metal oxide-carbon nanofiber composite electrode. $NiMoO_4$-Carbon nanofiber composite electrodes were synthesized by a solution-based electrospinning technique. Results showed that the electrospinning process leads to formation of uniform structured nanofibers, without any beads or agglomerations. The synthesized composites were used as electrode in symmetric supercapacitors. According to the electrochemical studies the supercapacitor with the composite electrode containing 75% (wt.) $NiMoO_4$ displayed a high specific capacity of 122.5 Fg^{-1} at 1 Ag^{-1}.

Keywords*:* Carbon nanofiber, $NiMoO_4$, Electrospinning, Supercapacitor.

1- Introduction

Nowadays, utilizing renewable energies is increasing dramatically due to lack of fuel resources and also environmental concerns [1,2]. Increasing the rate of renewable energies has resulted in more attention to energy storage systems to generate power in emergency situations [3]. In the last decade, in order to store energy, electrochemical systems have developed such as flywheels, solar cells, batteries, and supercapacitors [4]. Supercapacitors have been expanded as a new technology with high potential in energy storage in comparison with the other ones [5]. Although supercapacitors cannot store energy like batteries, they are more efficient than Li-ion batteries due to excellent power density, long-term cycling stability, charge-discharge ability in a short time, and also working in extensive temperature ranges [6,7]. However, increasing energy density, while power density is constant, is necessary to extend practical supercapacitors.

Supercapacitors are categorized into three genera, electrical double-layer capacitor (EDLC), pseudo-supercapacitors, and hybrid supercapacitors [8,9]. Hybrid supercapacitors show better function in comparison with others [10].

Electrodes are one of the most important parts of a supercapacitor. Carbon electrodes can be nominated as conventional electrodes in energy storage systems, especially electrical double-

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layer capacitors. Recently, carbon nanofibers have been adverted as a suitable alternative to other materials for electrodes because of their superior features and facility of the fabrication process. On the other hand, most of the metal oxides, using pseudo-supercapacitors, have a high specific capacitance (more than carbon materials). However, these electrodes have not been fabricated in the form of commercial due to low electronic conduction, and also short lifespan compares to carbon stuff [11,12]. Two main approaches have been developed for the fabrication of CNFs, namely chemical vapor deposition (CVD) and spinning (including conventional spinning and electrospinning) of polymer precursor. The electrospinning technique is the most effective method to produce CNFs with diameters ranging from tens of nanometers to several hundred nanometers which have been widely used in electrochemical storage devices with multi-functionalities [12]. This is because of low production cost, high production efficiency, and fabrication of nanofibers at commercial scales.

Nowadays, transition metal oxides (TMOs) and hydroxides (TMHs) such as MnO_2 [13], Co_3O_4 [14], $CuCo_2O_4$ [15], CuO [16], NiO [17], and RuO_2 [18] are widely used as material electrodes of supercapacitors due to their high theoretical specific capacity, and also rapid redox reactions. The molybdenum trioxide (MoO_3) is an attractive option for supercapacitor applications because of the unique layer structure, and high electrical conductivity [19]. Moreover, although utilizing nickel oxide nanostructure as electrode material offers some advantages; for example, high theoretical specific capacity, low cost, and being environmentally friendly, its low electrical conductivity and poor cyclic stability lead to a dramatic reduction of using that for the supercapacitor devices [19–21]. The binary metal oxides such as $CoMoO_4$, $NiMoO_4$, and $MnMoO_4$ display higher capacity than the other metal oxides as they occur in multiple oxidation states and illustrate higher electrical conductivity [22–24]. Amongst the aforesaid binary metal oxides, NiMoO4 has been extremely noticed as the high electrical conductivity of Mo, coupled with the high electrochemical activity of Ni that result in the high capacity [25,26].

The aim of this research is the structural study of carbon nanofibers reinforced by NiMoO4 nanoparticles, and also performance evaluation of the hybrid symmetric supercapacitor.

2- Experimental methods

2-1- Materials

Polyacrylonitrile was received from Iran Polyacryle company. Polymethyl methacrylate, (PMMA, Mol wt: 120,000), Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and Nickel (II) acetate tetrahydrate ($(Ni\ (OCOCH_3)_2\cdot 4H_2O)$) were purchased from Sigma Aldrich. Potassium hydroxide (KOH), N, N-dimethyl formamide (DMF) were purchased from Merck. All chemicals were used as received without any further purification.

2-2- Synthesis of $NiMoO_4$/CNF composite

In a typical synthesis of the composite nanofibers, Nickel (II) acetate tetrahydrate and Ammonium molybdate tetrahydrate were dissolved in DMF. Then, PAN powder was added to this solution to obtain a PAN solution containing $NiMoO_4$ precursor salts. After that, the solution was electrospun using an electrospinner setup (HV35P) with an applied voltage of 17.0 kV. The electrospun fibers were stabilized in air at 260 ºC and then carbonized at 700 ºC in a nitrogen atmosphere.

2-3- Material Characterization

The microstructure and morphology of the $NiMoO_4$-CNF composite nanofibers were studied by Field emission scanning electron microscopy (TESCAN MIRA3 FE-SEM). Thermogravimetric analysis (TGA) was conducted (TGA/DTA 92 Setaram II testing system) in the air over a temperature range of 25−800 °C at a heating rate of 10 °C min^{-1}.

2-4- Electrochemical Measurements

To have an evaluation of the electrochemical performance, the two-electrode configuration cell was also assembled using the composite nanofiber as the electrodes directly. Two pieces of identical electrodes were separated by a filter paper as the separator, which was soaked in KOH 6M before the assembly of the symmetric cell. The prepared supercapacitor was tested using a cyclic voltammetry (CV) method and galvanostatic charge/discharge (GCD). These measurements were made at a potential window from 0 to 1.6 V at different scanning rates from 5 to 100 mV/s and current densities from 1 to 20 A g^{-1}. The specific capacitance (C), energy density (E), and power density (P) were calculated according to the following equations:

$$C=\frac{\int Idv}{\upsilon m\Delta V} \quad (1)$$

$$C=\frac{I\Delta t}{m\Delta V} \quad (2)$$

$$E=\frac{CV^2}{2} \quad (3)$$

$$P=\frac{E}{t} \quad (4)$$

Where C is the specific capacitance (Fg^{-1}), I is the constant discharge current (A), υ is the potential scan rate (mV/s), t is the discharge time (s), ΔV is the potential window (V), and m is the mass of the electrode (g).

3- Results and Discussion

3-1- Morphology and Structure characterization

Figure 1 displays the FESEM images of the electrospun $NiMoO_4$-CNF composite with different percentages of NiMo precursor salts. All electrospun composite nanofibers

represented uniform bead-free nanofibers with one-dimensional morphology and fortuitous oriented that result in creating an open and 3D structure. This macroscopically open structure leads to better achievement of the electrolyte. Moreover, the mean diameters of 250, 300, and 370 nm were obtained for different contents of 25, 50, and 75% of NiMo precursors. As can be seen in Figure 1, the number of $NiMoO_4$ nanoparticles, situated in/on the CNFs, developed with increasing the NiMo precursor percentage from 25 to 75 in the PAN.

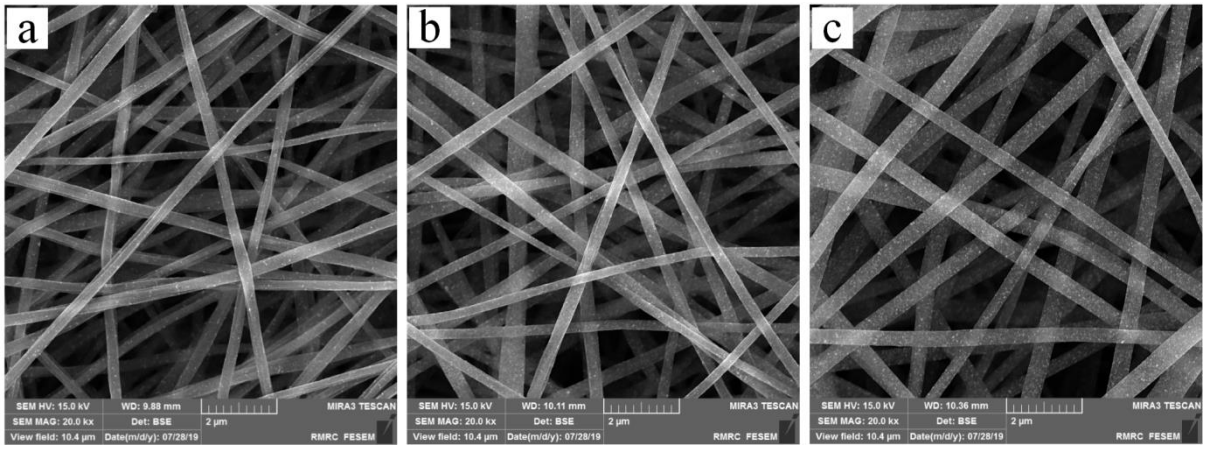

Figure 1. FESEM images of (a) $NiMoO_4$/CNF (0.25), (b) $NiMoO_4$/CNF (0.5) and (c) $NiMoO_4$/CNF (0.75).

The concentration of $NiMoO_4$ in the nanofiber composites after heat treatment was appointed by TGA as illustrated in Figure 2. A drastic weight loss was observed in all the samples at about ~400−580 °C which is due to the combustion of carbon. No weight loss was observed at temperatures higher than 580 °C. As can be seen in Figure 2, weight percent of $NiMoO_4$ was ~20, 44, and 71 wt. % in $NiMoO_4$/CNF (0.25), $NiMoO_4$/CNF (0.5), and $NiMoO_4$/CNF (0.75), respectively. The results are very close to the percentage of the precursor added to PAN in the synthesis step.

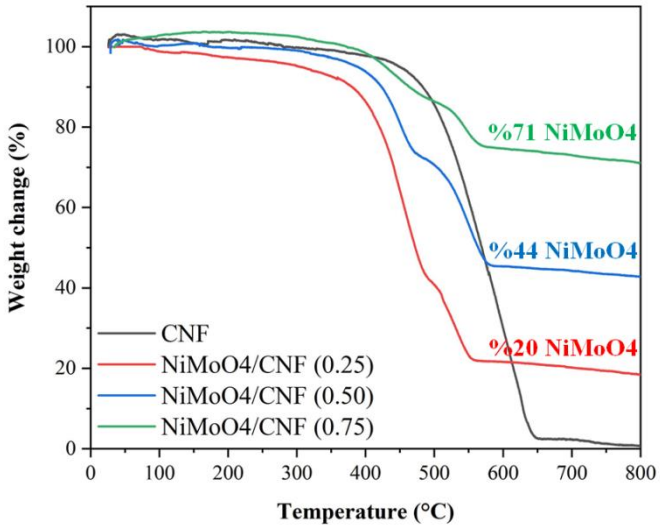

Figure 2. TGA curves for $NiMoO_4$/CNF composites provided with utilizing different precursor salts contents.

3-2- Electrochemical Investigation

A symmetric supercapacitor device was assembled by two freestanding $NiMoO_4$/CNF composite nanofiber electrodes. Figure 3 illustrates the CV curves of the supercapacitor at different scan rates in the voltage window 0–1.6 V. Two sharp redox peaks are observed in each cycle. This can be attributed to the Faradic reaction of $Ni^{2+} \leftrightarrow Ni^{3+} + e^-$ between electrolyte and electrode. It is to be noted; Mo preserves its initial form (MoO_4^{2-}) and does not participate in the redox reaction. It helps to increase specific capacity by reforming the conductivity of Nickel molybdate [27]. The CV curves exhibit that the curves keep their pattern with increasing scan rate portending the good rate capability of $NiMoO_4$/CNF (0.75) composite as the electrode [28]. However, increasing the scan rate leads to a decrease in the specific capacity of the supercapacitor. This is due to insufficient diffusion of ions from electrolyte to carbon material at the higher scan rates [29,30].

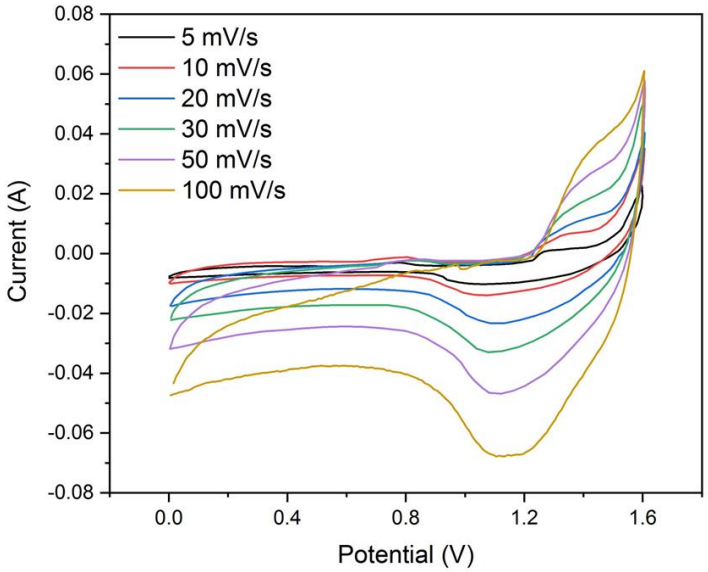

Figure 3. CV curves of hybrid symmetric supercapacitor at different scan rates.

Figure 4 illustrates galvanostatic charge-discharge profiles of the $NiMoO_4$/CNF (0.75) symmetric supercapacitor drawn at different current densities in the voltage window 0–1.6 V. This figure shows good electrochemical reversibility. A plateau is observed in all discharge curves, especially at low current densities, indicating the pseudocapacitive characteristics of the electrode material [31]. According to Figure 4, increasing the current density results in a graduate reduction in the discharge time. Moreover, the specific capacity values of the supercapacitor assembled with $NiMoO_4$/CNF (0.75) composite electrodes are 112.5, 105, 93.75, 87.5, and 50 Fg^{-1} at current densities of 1, 2, 5, 10, and 20 Ag^{-1} respectively. There is a definite link between increasing the current density and a decrease in the values of specific capacity because only a few percentages of inner active sites of the electrode material are involved in redox reaction at the high current density [32]. At the current density of 10 Ag^{-1}, the supercapacitor retains a specific capacity of about 78% of the specific capacity at 1 Ag^{-1}, implying the good rate capability of the supercapacitor.

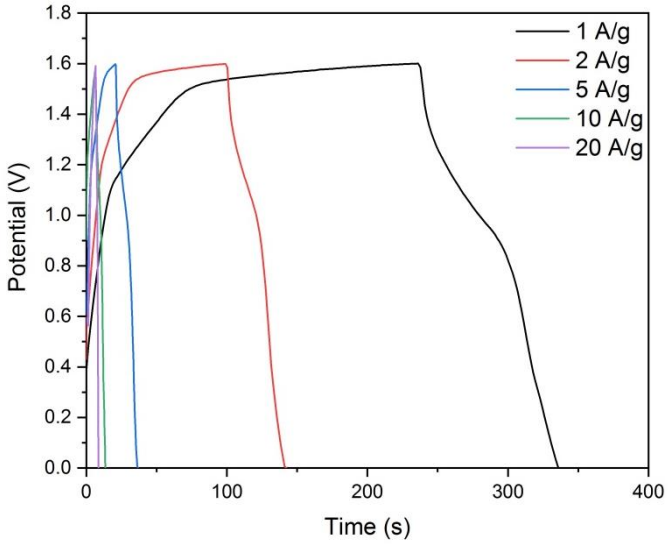

Figure 4. Galvanostatic charge-discharge curves of the hybrid symmetric supercapacitor at different current densities.

4- Conclusions

In summary, a facile and scalable electrospinning technique was utilized to embed $NiMoO_4$ particles in the carbon nanofiber membranes. The fabricated nanofiber reinforced with $NiMoO_4$ had a uniform structure in the case of morphology and particle dispersion. There was a great correspondence between the amount of $NiMoO_4$ nanoparticles in the composites and weight ratios of metal precursors in the polymer solution. The freestanding symmetric supercapacitor was assembled with $NiMoO_4$/CNF (0.75) composite membrane electrodes. The results showed that the high specific capacity of 112.5 Fg^{-1} was achieved at a current density of 1 Ag^{-1}. Also, it had a good rate performance at the higher current densities. We believe the developed supercapacitor is a high-efficiency and scalable energy storage device.

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