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SYNTHESIS AND CHARACTERIZATION OF FLEXIBLE CARBON FIBERS COATED WITH POLYANILINE/MANGANESE HEXACYANOFERRATE NANOPARTICLES FOR SUPERCAPACITORS

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Abstract. *The growing technological advances bring the search for renewable energy sources, as well as electronic devices ever-smaller, flexible, more efficient and sustainable. The electrochemical capacitors, also called supercapacitors, comply with all previous requirements, as they are capable to store and release an amount of electrical load better than conventional electrolytic capacitors and faster than batteries, which are most frequently used. Conventional capacitors store energy in the electrostatic form through the separation of the electrode and the dielectric, which can be made of ceramic, insulating plastic films, polypropylene film, aluminum oxide, etc. On the other hand, batteries are made of metals and/or acids and store energy through an electrochemical process, in which occurs the transfer of ions between the electrode and the electrolyte. Supercapacitors can storage energy from both types separately (electrochemical double layer capacitor – EDLC or pseudocapacitor) or at the same time (hybrid capacitor), which turns them into a potential device to replace batteries and conventional capacitors. Carbonaceous materials are highlighted in the study of supercapacitors due to its morphology and good electrical conductivity. However, besides carbon, metals, metal oxides, metal hexacyanoferrates and conducting polymers have also been used because of their chemical properties, such as reduction and oxidation (redox) reactions. The aim of this work is to develop flexible carbon fiber electrodes with manganese hexacyanoferrate and polyaniline electrodeposition, being as a low-cost, long-term and flexible alternative in the supercapacitors' composition. To accomplish that, physical and electrochemical characterizations of electrodes were employed to testify their good performance.*

Keywords: *polyaniline, manganese hexacyanoferrate, supercapacitors, energy storage.*

1. INTRODUCTION

Among various type of energy storage devices, supercapacitors (SCs) have higher power density, longer cycling stability, faster charge/discharge rates and safer operation conditions than lithium ion batteries and thus are considered as the most promising energy storage devices (Kotz and Carlen, 2000). The supercapacitor is formed by a dielectric material (electrolyte), which works as a separator between two conducting plates (electrodes).

Recently, numerous supercapacitor electrode materials have been studied, such as EDLCs based on carbonaceous materials (Pandolfo and Hollenkamp, 2006), which assurance a high surface area with smaller pores, hybrid capacitors based on the combined carbonaceous and redox materials (Maier, *et al*., 2017), and pseudocapacitors based on redox materials such as metal oxides/hydroxides (Chen and Dai, 2013), metal hexacyanoferrates (Pang, *et al*., 2015) and conducting polymers (Wang, *et al*., 2010). Pseudocapacitor materials can provide a huge specific capacitance, which far exceeds EDLCs based materials, because of their electrochemical reversible redox properties on the electrode/electrolyte surface. However, each type of material has its own unique advantages and disadvantages (Simon

and Gogotsi, 2008). Polyaniline (PANI) is a popular candidate for practical applications in supercapacitors due to its good processability, environmental stability, low cost and reversible control of electrical properties by both charge-transfer doping and protonation (Wang, *et al*., 2010).

In the present work, the electrodeposition of polyaniline with manganese hexacyanoferrate (MnHCF) on carbon fiber electrode is proposed to compose a hybrid supercapacitor. To accomplish that, physical and electrochemical characterizations of the PANI/MnHCF nanocomposite film electrode were employed, through Fourier infrared spectroscopy (FTIR), Atomic force microscopy (AFM), Field emission scanning electron microscopy (FESEM), galvanostatic charge/discharge and cyclic voltammetry tests, to testify it good performance.

2. EXPERIMENTAL PROCEDURE

In the Fig. 1 is showed the flexible carbon fiber (CF) electrode. The carbon fiber electrode is a good electrical conductor, flexible, mechanically strong and black in color. Through one-step electrodeposition method (Kulesza, 2001; Maier, *et al*., 2017; Wang, *et al*., 2015) was fabricated PANI/MnHCF nanoparticles electrode using CF as the substrate.

Figure 1. Flexible carbon fiber electrode.

In the electrodeposition method to form PANI/MnHCF, the CF was immersed into the solution containing 0.18 ml of aniline monomer, 0.05 M (mol/l) $MnCl_2$ and 0.05 M $K_3(FeCN)_6$ with 0.25 M Na_2SO_4 and 0.5 M H_2SO_4 mixture of electrolytes. This mixture was kept in the electrochemical cell of IVIUM COMPACTSTAT® potentiostat, instrument composed by a three-electrode system.

Figure 2a shows the three-electrode system of the potentiostat instrument, with carbon fiber as the working electrode (WE), silver/silver chloride (Ag/AgCl) as the reference electrode (RE), and platinum as the counter electrode (CE). The instrument operation is based on the electrical potential control between the WE and the RE, through the current control between the WE and the CE, to deposit the material on the electrode surface.

The CF was electrochemically copolymerized in the cut off range from -0.2 to 1 V for 30 continuous cycles at the scan rate of $50mVs^{-1}$. In this range of potential, the PANI/MnHCF was electrodeposited on the carbon fiber surface as showed in Fig. 2b, where is notable that the curves were linearly increasing the peak current due to the uniform growth of PANI/MnHCF nanocomposites.

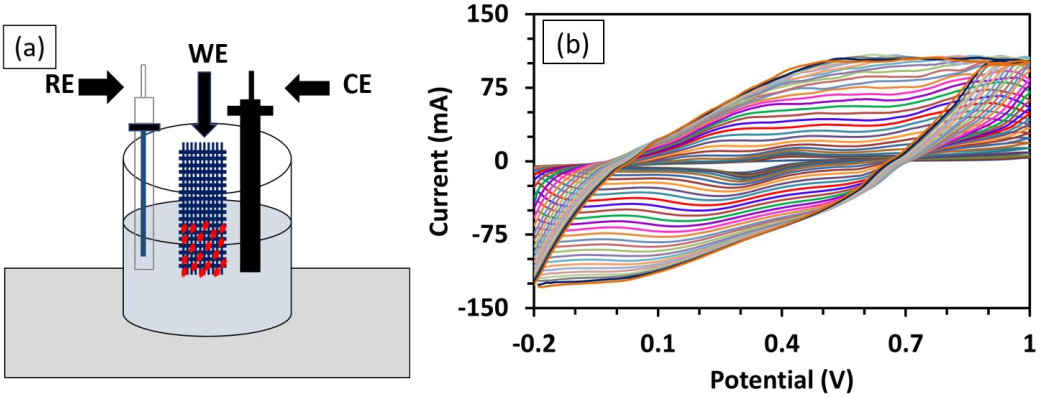

Figure 2. (a) Three-electrode system of the potentiostat instrument and (b) Current versus potential obtained by the electrodeposition of PANI/MnHCF.

After the electrodeposition process, the electrode was washed with double distilled water to remove the unbound materials from the electrode surface and dried in the air. The mass of the electrode before and after this process was

measured using an electronic weighing balance Marte BL320H. The mass of the active material on the electrode surface was optimized which is approximately 1.0 mgcm^{-2}.

3. RESULTS AND DISCUSSION

The fabricated CF/PANI/MnHCF nanoparticle electrode was characterized by AFM, FESEM and FTIR measuring the physical characterization. In order to analyze its electrochemical performance, the following techniques were included: cyclic voltammetry and galvanostatic charge/discharge test.

The AFM is a setting that allows the high-resolution observation of the material nanoscale physical structure. Two and three-dimensional AFM topographic images of the electrode before and after the process are shown in Fig. 3. The topographic images displayed the electrode surface which is rougher surface with irregular islands, and the roughness increased from bare CF (without coating) to CF/PANI/MnHCF nanoparticle electrode, which clearly showed that the PANI/MnHCF nanoparticles are uniformly deposited on the electrode surface.

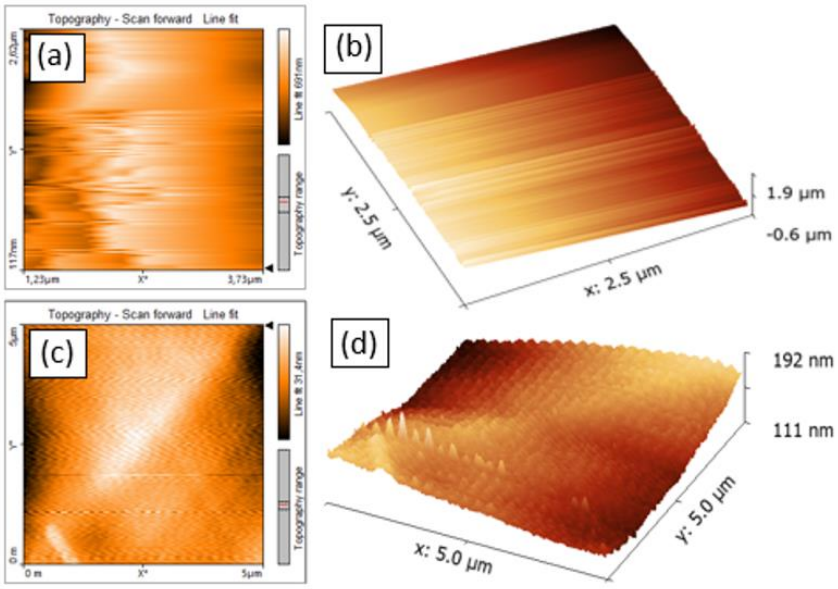

Figure 3. (a) AFM 2-D image (bare CF), (b) AFM 3-D image (bare CF), (c) AFM 2-D image (CF/PANI/MnHCF) and (d) AFM 3-D image (CF/PANI/MnHCF).

The surface morphology of the fabricated CF/PANI/MnHCF nanoparticles electrode was studied using FESEM. From the FESEM images (Fig. 4a and b), it can be observed that the nanostructures are composed of spherical shaped MnHCF nanoparticles electrodeposited around the surface of CF electrode and the size distribution ranges from 150-200 nm. It can be seen that the average size of the MnHCF nanoparticles is less than 200 nm.

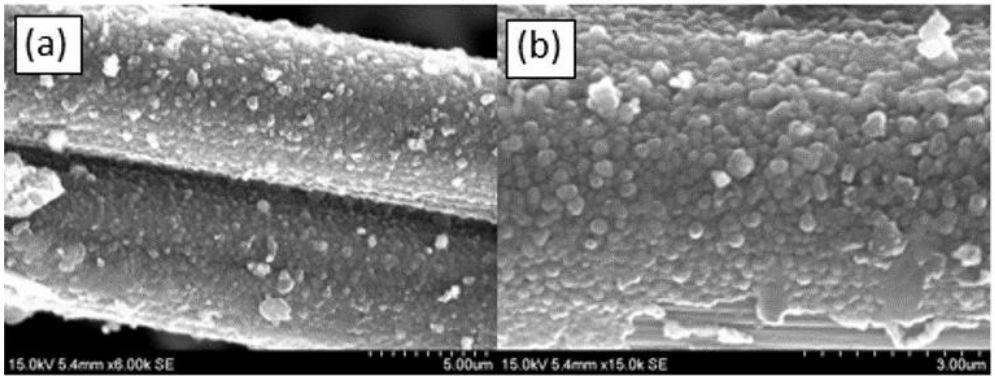

Figure 4. (a) FESEM image (6,000x magnification) and (b) FESEM image (15,000x magnification).

The last technique used in the electrode physical characterization was the FTIR, which measures the capacity of the substance absorbing, transmitting and reflecting the infrared radiation, revealing the bonds in the sample. The spectrum showed in Fig. 5 reveals the presence of the bridged binuclear (Fe, Mn) on the Mn^{2+}–CN–Fe^{3+} a band triple bound at

2061 cm^{-1}, and two peaks at 1713 cm^{-1} and 1495 cm^{-1} corresponding to stretching vibration mode of ν(C═C) and ν(N═C), respectively.

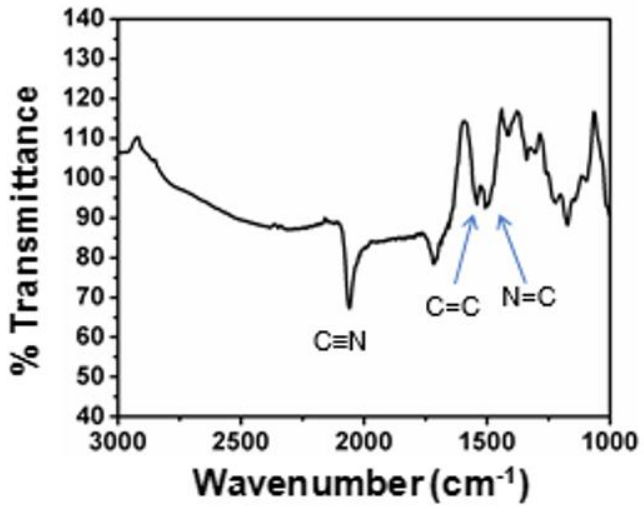

Figure 5. FTIR spectrum of CF/PANI/MnHCF electrode.

The first electrochemical characterization of the electrode was obtained through the cyclic voltammetry method to measure the electrical current generated by the redox reactions when it was applied the different scan rates of the potential from -0.2 to 1 V. The typical cyclic voltammetry of CF/PANI/MnHCF nanoparticles electrode was performed in 0.5 M H_2SO_4 + 0.5 M Na_2SO_4 electrolyte solution, and was obtained at a scan rate of 2 mVs^{-1}, showed in Fig. 6.

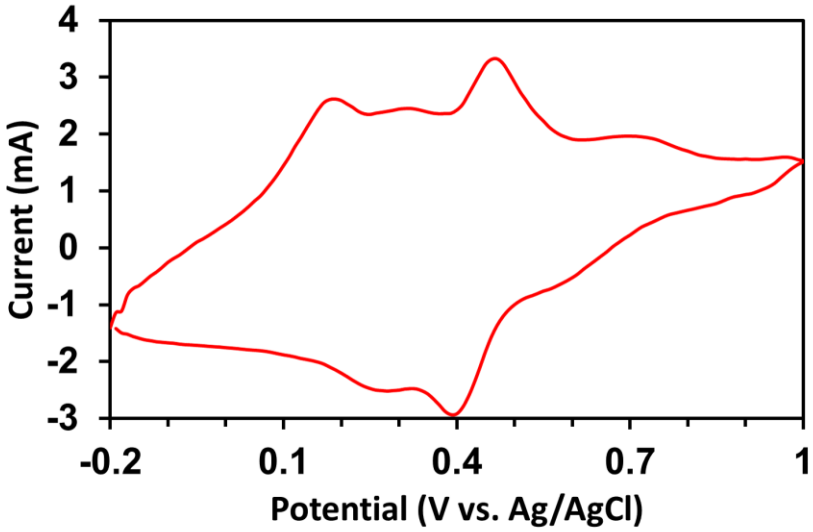

Figure 6. Cyclic voltammogram of CF/PANI/MnHCF nanoparticle electrode at the scan rate of 2mVs^{-1}.

From the cyclic voltammogram, it was observed three pairs of redox peaks over the entire range of scan rates from the CF/PANI/MnHCF nanoparticles electrode. The first redox couple (around +0.18 V and -0.11 V) is ascribed to the conversion of leucoemeraldine to emeraldine form, which characterizes one of the redox stages of polyaniline. The second redox couple (around +0.46 V and +0.39 V) corresponds to redox reactions of Fe^{2+} to Fe^{3+} of MnHCF, and the third redox peak couple (around +0.7 V and +0.58 V) is assigned to the conversion of emeraldine to pernigraniline.

In order to further evaluate the electrochemical performance of the CF/PANI/MnHCF nanoparticles electrode, the galvanostatic charge/discharge curves were measured with a current density from 1 Ag^{-1} to 20 Ag^{-1}, as shown in the Fig. 7. There is symmetry between charging and discharging time due to the supercapacitor property of high power density, which assurances a large current flow on the electrode. The high surface area from PANI/MnHCF nanoparticles electrode facilitates the electrons transport and the ionic transfer on the electrolyte. When the current density increases from 1Ag^{-1} to 20 Ag^{-1}, the charge/discharge process is faster. The specific capacitance slowly decreases from 731.25 to 350 Fg^{-1}.

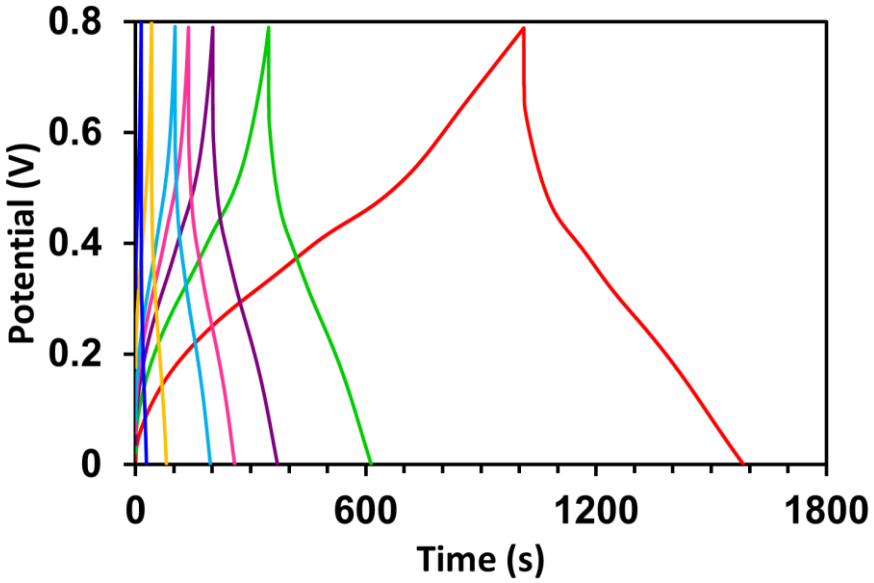

Figure 7. Galvanostatic charge/discharge curves of CF/PANI/MnHCF nanoparticles electrode with different current densities.

From the data obtained from the charge/discharge test it was calculated the specific capacitance *C* using the relation showed on Eq. (1), where *i* is the density current, *t* is the discharge time, *V* is the discharge potential window and *m* is the mass of the material electrodeposited. The relation between the specific capacitance and the current density is illustrated in the Tab. 1. The specific capacitance of the CF/PANI/MnHCF nanoparticles electrode achieved a maximum of 731.25 Fg^{-1} at a low current density of 1 Ag^{-1}.

$$C = \frac{i * t}{V * m} \qquad (1)$$

Table 1. Specific capacitances at different current densities.

Current Density (Ag^{-1})	Specific Capacitance (Fg^{-1})
1	731.25
2	682.5
3	645
4	615
5	593.75
10	500
20	350

4. CONCLUSIONS

In this work, a simple approach for preparation of binder free CF/PANI/MnHCF nanocomposites as a supercapacitor material was presented. The MnHCF nanoparticles can be alternatively interconnected to PANI through electrostatic interaction. Their maximum specific capacitance was about 740 Fg^{-1} at a discharge density of 1 Ag^{-1}. Electrochemical tests are also indicated for notably high specific capacitance of PANI/MnHCF nanocomposites with high discharge densities, which makes the material a viable candidate for energy applications. The electrode has very good stability, being able to maintain 85% of its initial specific capacitance after 1000 charge/discharge cycles. Thus, reveals that the CF electrode surface with high porosity facilitates the access of the electrolyte ions during the transfer of charges with the electrode, and that the junction of the PANI with MnHCF promotes the high performance of the device due to its redox properties. Therefore, these superior properties of CF/PANI/MnHCF nanocomposites will prompt their extensive use as the promising electrode materials for supercapacitors.

5. ACKNOWLEDGEMENT

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