



## Electrosynthesis and Electrochemical Properties of Metal Oxide Nano Wire/ P-type Conductive Polymer Composite Film

S.O. Ranaei Siadat\*

University of Shahid Beheshti, Tehran, Iran

### Abstract

This study introduces a facile strategy to prepare metal oxide/conducting polymer nanocomposites that may have promising applications in energy storage devices. Poly aniline/nano wire manganese dioxide (PANI/NwMnO<sub>2</sub>) was synthesized by cyclic voltammetry on glassy carbon electrode. Morphology and structure of the composite, pure PANI, MnO<sub>2</sub> nanowires were fully characterized using XRD and SEM analysis. Electrochemical studies shows excellent synergistic effect between PANI and MnO<sub>2</sub> nanowires which results in its capacitance increase and cycle stability against PANI electrode. Specific capacitances of PANI/NwMnO<sub>2</sub> and PANI were 456 and 190 F/g respectively. The electrochemical performance of electrodes studied using cyclic voltammetry, Galvanostatic charge/discharge and impedance spectroscopy.

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### 1. Introduction

Electrochemical capacitors (ECs) represent an emerging class of energy storage devices that have attracted increasing attention because of a number of important features including high power density, fast charge/discharge rate, and excellent cycle stability [1,2]. In ECs, the electrode material is one of the extremely important factors affecting the performance of ECs (energy, power density, safety, cycle life, etc) [3,4]. Carbon-based materials [5], metal oxides [6], conductive polymers [7] and their composites [8,9] have been used for producing ECs. High specific capacitance, flexibility and low cost are some advantages of conducting polymers, while they have disadvantages like shrinking nature during charge/discharge process. Based on its Mott-Schottky

diagram, Polyaniline (PANI) is a p-type conductive polymer [10]. Because of excellent organic conductivity, biocompatibility and good environmental stability, PANI has been widely used in ECs and biosensors [11,12].

Many reports have been published on PANI and nano materials composites [13-17]. Increasing capacitance and stability is the goal of using PANI nano composite materials. There are two methods for PANI composite synthesis: chemical polymerization, and electropolymerization. In chemical method, the reaction product is always a powder. So, it has to be dried which leads to change the polymer structure [18,19]. Furthermore, in order to making electrode using the composite, binder is needed which in turn decreases its electrical and electrochemical performance.

\*Corresponding author. Tel.:

E-mail address: Ranaeisiadat@hotmail.com

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Electropolymerisation of PANI has many advantages: not needing oxidants, film uniformity on the electrode, saving the use of binder, decreasing contact resistance between polymer and current collector [20-22]. Because of synergistic effect between two composite components, Dramatic improvements have been achieved in electrochemical properties of composites.

MnO<sub>2</sub> has been used as an active material in energy storage field. It has low cost, environmentally friendly nature, and various forms with different properties. So, It has been the subject of many researches as an electrode material for electrochemical capacitors [23-25]. In this paper we synthesized  $\alpha$ -MnO<sub>2</sub> nano-wire which then was used to make PANI/NwMnO<sub>2</sub> in order to investigate the supercapacitive behavior and synergistic effect of these active materials together.

## 2. Experimental

### 2.1. Chemicals

All the chemical materials used in this work were Merck products by analytical grade and were used without further purification. Double distilled water was used throughout. Aniline (ANI) was doubly distilled and the resulting colorless liquid was kept in the dark at 5°C. MnO<sub>2</sub> nanowires were synthesized via a simple hydrothermal method. In a typical synthesis, 16.85 mmol KMnO<sub>4</sub> and 22.60 mmol MnSO<sub>4</sub>.H<sub>2</sub>O were dissolved in 120 mL deionized water under vigorous stirring. After 20 min, the prepared mixture was transferred into a 125 mL Teflon-lined stainless steel autoclave followed by heating at 140°C for 12 h [26].

### 2.2. Synthesis of PANI and PANI/NwMnO<sub>2</sub> composite electrodes

PANI/NwMnO<sub>2</sub> composite was synthesized electrochemically by cyclic voltammetry in solution of 0.03M ANI in H<sub>2</sub>SO<sub>4</sub> 1M, 0.2% wt. MnO<sub>2</sub> nano wire and 0.005M of sodium dodecyl sulfate (SDS) that was dispersed in solution by sonication. PANI electrode was synthesized in same solution without MnO<sub>2</sub> nano wire and SDS. Polymerizations were conducted by 10 cycles at the sweep rate of 50mV/s. The mass of PANI films was approximated assuming a current efficiency for the electro polymerization process of 100%, using Faraday's law of electrolysis[27].

### 2.3. Materials characterization and electrochemical evaluation

All electrochemical experiments were carried out by an Autolab General Purpose System PGSTAT 30 (Eco-chime, Netherlands). A conventional three electrode cell with an Ag/AgCl reference electrode (Argental, 3 M KCl) was used in order to electro polymerization of the PANI, the Platinum wire with a diameter of 0.5 mm and an exposed area of 0.65 cm<sup>2</sup> was used as the counter electrode. A glassy carbon electrode with the area of 0.03 cm<sup>2</sup> was used as the working electrode. A wide frequency range of 15 mHz to 100 kHz was used for EIS studies. Morphological investigations of the polymeric and composite films were carried out by using SEM (Philips XL 30). X-ray diffraction patterns were obtained from an X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu-K $\alpha$  monochromatized radiation source and a Ni filter.

## 3. Results and Discussion

Fig. 1(a, b, c) presents the SEM graphs of PANI/NwMnO<sub>2</sub> composite electrode. As can be seen, MnO<sub>2</sub> nanowires have been coated on the surface of PANI filaments uniformly. The shape and structure of  $\alpha$ -MnO<sub>2</sub> nanowire is shown in Fig. 1(d) It can be clearly seen that MnO<sub>2</sub> nanowires is actually composed with uniform shape.

X-ray diffraction was used to investigate the crystal structure of prepared materials. shows the XRD patterns of MnO<sub>2</sub> nanowires, PANI and PANI/NwMnO<sub>2</sub> electrodes. For MnO<sub>2</sub> nanowires, it can be seen clearly that all diffraction peaks can be exclusively indexed as the tetragonal  $\alpha$ -MnO<sub>2</sub> (JCPDS 44-0141) and no other impurities were observed. XRD diagram of PANI/NwMnO<sub>2</sub> shows that by adding MnO<sub>2</sub> nanowires to the PANI matrix, its crystal structure was changed and some peaks in XRD pattern of PANI/NwMnO<sub>2</sub> were appeared.

Cyclic voltammetry technique was used to evaluate the electrochemical performance of electrodes. Fig. 3(a) present's cyclic voltammograms of electropolymerised PANI and PANI/NwMnO<sub>2</sub> electrodes at 10<sup>th</sup> cycle of electro polymerization process. It can be clearly seen that the electropolymerization charge of PANI/NwMnO<sub>2</sub> electrode is higher than that of PANI electrode and this has been considered as the contribution of faradic pseudo capacitance of

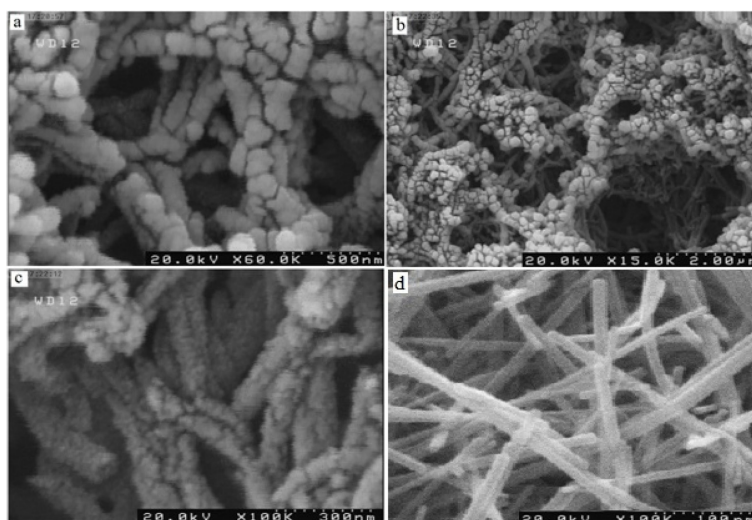


Fig. 1. SEM graphs of PANI /NwMnO<sub>2</sub> (a, b, c) composite electrodes and MnO<sub>2</sub> nano wire (d).

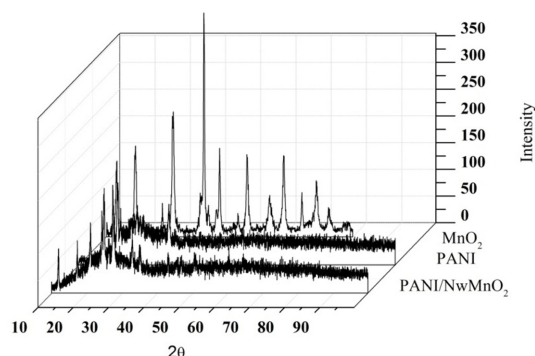


Fig. 2. XRD diagrams of MnO<sub>2</sub> nanowire, PANI and PANI/NwMnO<sub>2</sub>.

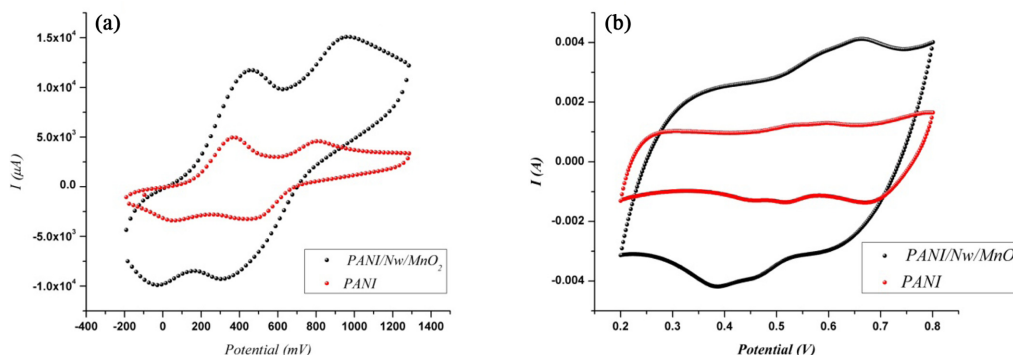
MnO<sub>2</sub> nanowires and double layer behavior of PANI. In both cyclic voltammograms there are two redox peaks. The first one which is in negative potentials is related to the formation of free radicals in the polymerization of PANI and PANI/NwMnO<sub>2</sub> nano wire electrodes. The second one is due to oxidation of Polymer in both electrodes. Fig. 3(b) presents cyclic voltammograms of PANI and PANI/NwMnO<sub>2</sub> electrodes at the scan rate of 25 mV/s in 1 M H<sub>2</sub>SO<sub>4</sub> solution. PANI/NwMnO<sub>2</sub> electrode, a remarkable difference can be seen in the cyclic voltammogram loop areas. This shows that the electrochemical behavior of the composite electrode is distinctly improved after adding MnO<sub>2</sub> nanowires to PANI matrix. The charge storage in faradic process is achieved by electron transfer that leads to chemical

changes in the electro active materials according to Faraday's law related to the potential [28,29]. Furthermore, symmetrical and rectangular shape of composite cyclic voltammogram curve shows an ideal capacitive behavior for this electrode involving two types of capacitive performances: contributing the electric double-layer capacitance produced by PANI and pseudo capacitive behavior of MnO<sub>2</sub> nanowires. As shown in Fig. 3(b), a redox peak in potentials between 0.5 - 0.6 V were appeared that is attributed to PANI transition from emeraldine to pernigraniline form [30]. Specific capacitance (SC) of electrodes calculated from cyclic voltammogram curves according to following equation:

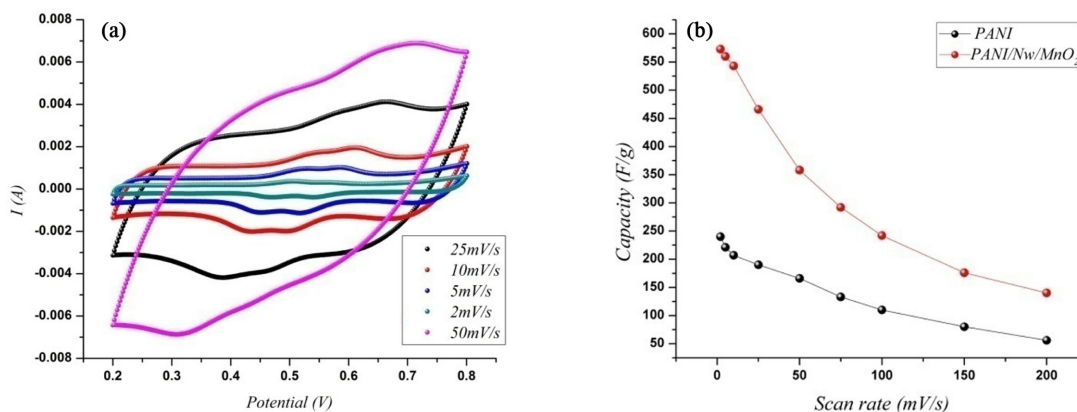
$$C = \frac{I}{mv} \quad (1)$$

Where  $I$  is the current,  $m$  is the mass of reactive material and  $v$  is the potential scan rate. The SC of PANI and PANI/MnO<sub>2</sub> electrodes at the scan rate of 25 mV/s were calculated 190 and 456 F/g respectively.

Cyclic voltammograms of composite electrodes in 1M H<sub>2</sub>SO<sub>4</sub> media in different scan rates is shown in a. As can be seen the excellent capacitive performance of dPANI/NwMnO<sub>2</sub> electrode was also verified based on these curves. With an increase of scan rate the current response increases that indicate an ideally capacitive behavior of PANI/NwMnO<sub>2</sub> electrode [30]. Furthermore the good rectangular shape



**Fig. 3.** (a) Comparative cyclic voltammograms for electropolymerization of PANI electrode and PANI/NwMnO<sub>2</sub> composite electrode at the 10th cyclic voltammogram, (b) cyclic voltammogram curves of PANI and PANI/NwMnO<sub>2</sub> electrode at the scan rate of 25 mV/s in 1M H<sub>2</sub>SO<sub>4</sub> solution.



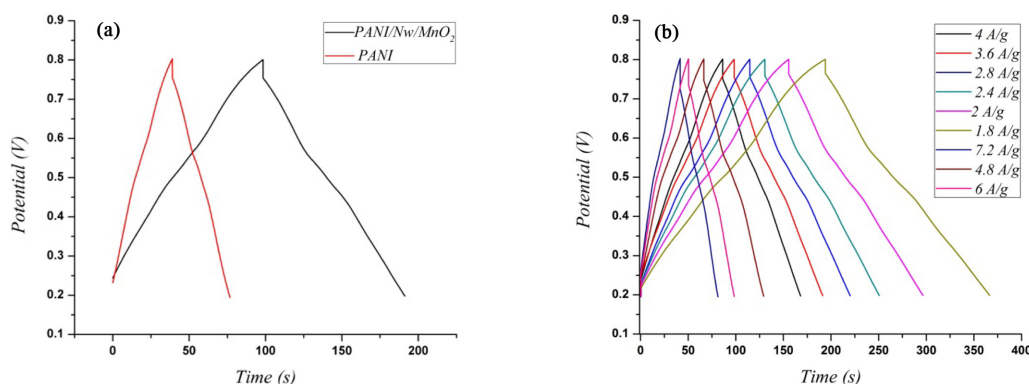
**Fig. 4.** (a) cyclic voltammograms of PANI/NwMnO<sub>2</sub> nanowires electrode at different scan rates in 1 M H<sub>2</sub>SO<sub>4</sub> in the potential window of 0.2 - 0.8 V, (b) variations of the specific capacitance for PANI/NwMnO<sub>2</sub> electrode as a function of the scan rate in 1M H<sub>2</sub>SO<sub>4</sub> solution.

of PANI/NwMnO<sub>2</sub> voltammograms is remained up to the scan rate of 100 mV/s. The deviation from rectangularity in cyclic voltammograms becomes obvious as scan rate increases. This phenomenon can be attributed to the electrolyte and film resistance, and this distortion is depending on scan rate. By increasing the sweep rate, active sites in electrode don't have enough time to react with ions.

Fig. 4(b) presents the calculated SCs of both electrodes at different scan rates. PANI/NwMnO<sub>2</sub> composite electrode shows SCs of 575 and 150 F/g at the scan rates of 2 and 200 mV/s, respectively, whereas at the same range these magnitudes for PANI electrode were calculated from 240 and 60 F/g. As can be seen, the capacitance of both electrodes decayed over the entire range of scan rate, but for PANI/NwMnO<sub>2</sub>

electrode the slope of SC vs. scan rate was not only more than that of PANI electrode, but also less than it. This phenomenon can be resulted from the fact that both electrodes are porous and the presence of MnO<sub>2</sub> nano wires do not cause to block the porosities of PANI film. Therefore, different electrochemical behaviors of the electrodes could come from the synergistic effect between MnO<sub>2</sub> nanowires and PANI. Chemical methods of composite fabrication could motivate to block some porosities of polymer film which cause to decay PANI super capacitive behavior. Therefore using electrochemical method, the whole pseudocapacitive behavior of PANI electrode could be saved.

Galvanostatic charge-discharge (CD) is one of the methods that have been used to study the capacitive



**Fig. 5.** (a) CD diagrams of PANI and PANI/NwMnO<sub>2</sub> nano wires electrodes at the current density of 3.6 A/g, (b) CD diagrams of PANI/MnO<sub>2</sub> electrode at 1.8, 2, 2.4, 2.8, 3.6, 3.6, 4, 4.8, 6 and 7.2 A/g in 1 M H<sub>2</sub>SO<sub>4</sub> solution.

properties of active materials[31]. Fig. 5(a) shows the CD behavior of PANI and PANI/NwMnO<sub>2</sub> electrodes in the potential range from 0.2 to 0.8 V at the current density of 3.6 A/g. In this range, a triangular shape can be seen indicating that PANI/NwMnO<sub>2</sub> composite electrode have a good Columbic efficiency and ideal capacitive behavior in order to use for supercapacitors. The charge and discharge phase of PANI/NwMnO<sub>2</sub> lasts longer than that of PANI electrode which shows it has more capacitance than PANI. In addition, Because of increasing conductivity, using MnO<sub>2</sub> nanowires cause to decrease the voltage drop ( $iR$ ) which appears in the curves during the change of current sign [31,32].

Fig. 5(b) presents the CD curves of PANI/NwMnO<sub>2</sub> electrode at various specific currents of 1.8, 2, 2.4, 2.8, 3.6, 3.6, 4, 4.8, 6 and 7.2 A/g. As can be seen, the shapes of all curves are approximate isosceles triangles which are the characteristic of super capacitors. Here, SC was measured according to the charge/discharge curves, using Eq. (2).

$$SC = I / [-(\Delta E/\Delta t) m] \quad (2)$$

With  $I$  being the applied current;  $-\Delta E/\Delta t$ , the slope of discharge curve after voltage drop at the beginning of each discharge process (ESR); and  $m$  is the mass of composite electrodes. The highest SC for composite electrode was obtained when the current density for CD process was 1.8 A/g. The SC of PANI/NwMnO<sub>2</sub> changes in the range of 677 to 340 F/g. It can be seen that enhancing the specific current due to the intercalation of ions at the surface of active materials in the electrode/electrolyte interface, the specific

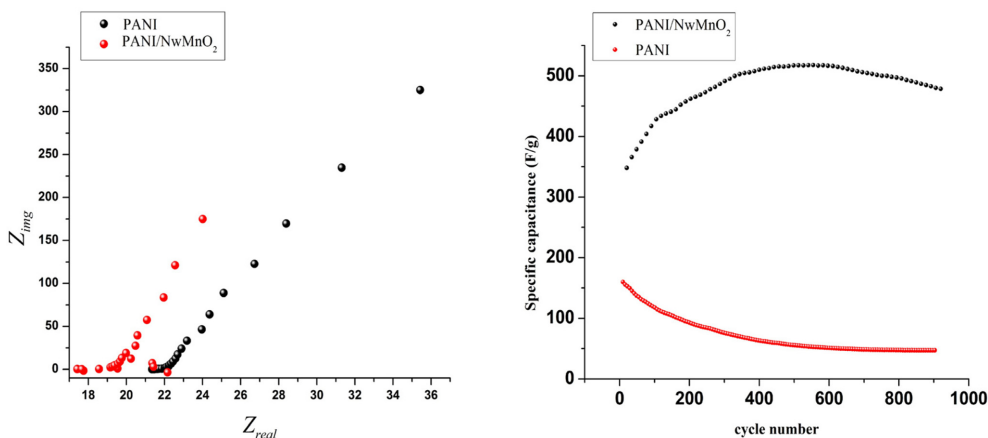
capacitance values decrease. On the other hand, at low specific currents, the specific capacitance increases because there would be enough time for insertion and deinsertion of ions at deeper porosities of the active materials in the electrode/electrolyte interface.

EIS technique was used for further studying the supercapacitive behavior of polymeric film and composite electrodes. The Nyquist plots of PANI and PANI/NwMnO<sub>2</sub> electrodes is shown in a. As illustrated, there is a semicircle in high frequencies related to the charge transfer resistance ( $R_{ct}$ ) caused by the Faradic Reactions and the double-layer capacitance ( $C_{dl}$ ) at the contact interface between electrode and electrolyte solution. The magnitude of  $R_{ct}$  in PANI/NwMnO<sub>2</sub> electrode was smaller than that of PANI electrode, because the addition of MnO<sub>2</sub> nanowires enhances the conductivity and improves charge transfer performance of PANI/NwMnO<sub>2</sub> electrode. Both electrodes exhibit a nearly linear branch in the low-frequency region. A transition to linearity at low frequencies exhibit an ideal capacitive behavior which was observed for PANI/NwMnO<sub>2</sub> electrode clearer than PANI one. The low frequency capacitance ( $C_{lf}$ ) of each film was determined using Eq. (3):

$$C_{lf} = (2\pi f Z'' )^{-1} \quad (3)$$

where  $f$  and  $Z''$  are the frequency and imaginary component of impedance respectively.

It can be seen that PANI/NwMnO<sub>2</sub> electrode has more capacitance than PANI one. These results also confirmed the data obtained by cyclic voltammetry and galvanostatic charge-discharge techniques. One



**Fig. 6.** Nyquist plots recorded from 10 kHz to 0.01 Hz with an ac amplitude of 5 mV for PANI and PANI/NwMnO<sub>2</sub> electrode, cycle ability of electrodes as a function of time during 20000 seconds at the scan rate of 50 mV/s.

of the important features of supercapacitor electrodes is the stability of electrodes against consecutive or life cycles. Life cycles of both electrodes were investigated by cyclic voltametry at the scan rate of 50 mV/s for 900 cycles in 1M H<sub>2</sub>SO<sub>4</sub> solution ( b). Synergistic effect of PANI and MnO<sub>2</sub> nanowires is illustrated in the figure. As can be seen after 900 cycles, PANI electrode losses its capacitance down to 70% while for PANI/NwMnO<sub>2</sub> electrode, the capacitance increases up to about 450<sup>th</sup> cycle and then decreases with a gentle slope. Increasing the capacitance of composite electrode can be attributed to surface modification of MnO<sub>2</sub> nano wires in consecutive cycles. During the polymerization of PANI/MnO<sub>2</sub> composite, some parts of MnO<sub>2</sub> is covered by polymer chains which in turn are refreshed during next cycles resulted in increasing the electrode capacitance.

#### 4. Conclusion

In summary, an electrochemical method to produce a polymer/metal oxide composite has been proposed. The morphology and the structure of the composite as well as pure PANI and MnO<sub>2</sub> nanowires were fully characterized using XRD and SEM analysis. Electrochemical studies showed excellent synergistic effect between PANI and MnO<sub>2</sub> nanowires resulted in increasing the capacitance and cycle stability of composite electrode against PANI one. Specific capacitance of 456 F/g was obtained at the scan rate of 25 mV/s for composite electrode against 190 F/g for PANI. Increasing the cycle ability of electrode is

another advantage of using MnO<sub>2</sub> nanowires polymer matrix.

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