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PSEUDOCAPACITANCE PROPERTIES OF ELECTRODEPOSITED HYBRID FILMS OF POLYANILINE AND MANGANESE DIOXIDE ON STAINLESS STEELS

Ngo Duc Tung[1], Le Thi Thu Hang[2]

[1]*Hung Yen University of Technology and Education*

[2]*Hanoi University of Science and Technology*

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Abstract

Hybrid films of polyaniline and manganese dioxide (PANi/MnO_2) were synthesized on stainless steels in different solutions containing aniline and $MnSO_4$ through potential cycling technique. The obtained films showed pseudocapacitive properties from 0 to 0.65 vs Ag/AgCl in aqueous solution of 0.5 M Na_2SO_4. While in 0.5 M H_2SO_4, the films displayed characteristic redox peaks of polyaniline (PANi) on cyclic voltammograms. The codeposition of MnO_2 with PANi had dramatic effect on capacitive behavior of the obtained hybrid films. In comparison with the sample pure PANi only achieving the specific capacitance of 420 F/g, after co-deposition with MnO_2, capacitive behavior was improved significantly. A specific capacitance maximum of 508F/g was obtained responding to sample M50 prepared in the solution containing 50 mM Mn^{2+} at a scan rate of 5mV/s. The sample also displayed a coulombic efficiency 98% over 800 cycles with 67% specific capacitance maintained.

1. INTRODUCTION

Electrochemical capacitors (ECs), also called supercapacitors, have attracted great interest as an important energy-storage/ conversion device. According to their charge storage principle, the ECs are classified into two types [1]: (i) electrical double-layer capacitor which store energy by utilizing the double-layer capacitance arising from the charge separation at the electrode–electrolyte interface, mainly focusing on carbon materials; (ii) pseudocapacitors, which store energy by utilizing the pseudo-capacitance arising from the fast and reversible Faradic reactions in the electrode surface formed with electro-active materials, mainly focusing on transition metal oxides and conducting polymers.

The pseudocapacitance of a pseudo-capacitor is the result of a capacitive relationship between the level of charge acceptance and the change in potential from a Faradaic redox reaction between the electrode material and electrolyte [2]. Among the various transition metal oxide materials used in pseudocapacitors, amorphous and hydrated ruthenium oxide has been reported to show a remarkably high specific capacitance (720 F/g) compared with other oxides [3]. However, its commercial use is limited by its expense. Therefore, considerable effort has been devoted to identify alternative and inexpensive metal oxide electrode materials with acceptable electrochemical properties.

PANi has been known well as one of the most promising materials of the conducting polymers for a number of applications, including rechargeable batteries, electro-chemical sensors [4 - 6], electrochemical capacitors [7 - 9], because of its electrochemical reversibility, stability and easily synthesis. Manganese dioxide is one of the candidates on account of its electrochemical behavior, low cost and environmental compatibility [10, 11]. So nowadays, composite materials consisting of PANi and manganese dioxide have attracted considerable attention as they can combine the advantages of both components and have potential applications in electrochemical capacitors. The combination of these two components was achieved by chemical and electrochemical method [4, 12]. Both of the above composites displayed good capacitive behaviors in neutral aqueous solution.

This paper reports the electrochemical properties of PANi-MnO_2 nano-composite in 0.5 M Na_2SO_4 at pH ~ 6 for pseudocapacitor applications.

2. EXPERIMENTAL

Aniline was purchased from Merck. The other chemicals (Shanghai Medical and Chemical Works, China) were used without further purification. All the solutions were prepared using doubly distilled water.

Thin hybrid films of PANi-MnO_2 were electrodeposited on the samples of stainless steel foil through cyclic voltammetries in potential range from -0.1 to 0.85 V versus Ag/AgCl at 20 mV/s in 25 cycles from 0.5 M H_2SO_4 solutions of 0.2 M aniline and 25, 50, 100 or 200 mM Mn^{2+}. All the experiments were carried out at room temperature. Platinum mesh was used as the counter electrode. Potentials were measured and reported versus Ag/AgCl electrode. The films (an area of 1 cm^2) obtained after electrodeposition were washed thoroughly with doubly distilled water and then vacuum dried at room temperature in 6 hours. The films were labeled as M25, M50, M100 and M200, respectively. PANi film was deposited similarly in 0.5 M H_2SO_4 solutions containing 0.2 M aniline and denoted as M0. Before and after electrodeposition, the electrodes were weighed using microbalance with an accuracy of 10^{-5} g.

The morphologies of PANi-MnO_2 hybrid films were observed by scanning electron microscope (SEM). Compositions of the films were estimated by Energy-dispersive X-ray spectroscopy (EDS). Electro-activities and electrochemical capacities of films were studied through cyclic voltammetry and constant current charge-discharge experiments by chronopotentiometry in 0.5 M Na_2SO_4 (pH ~ 6).

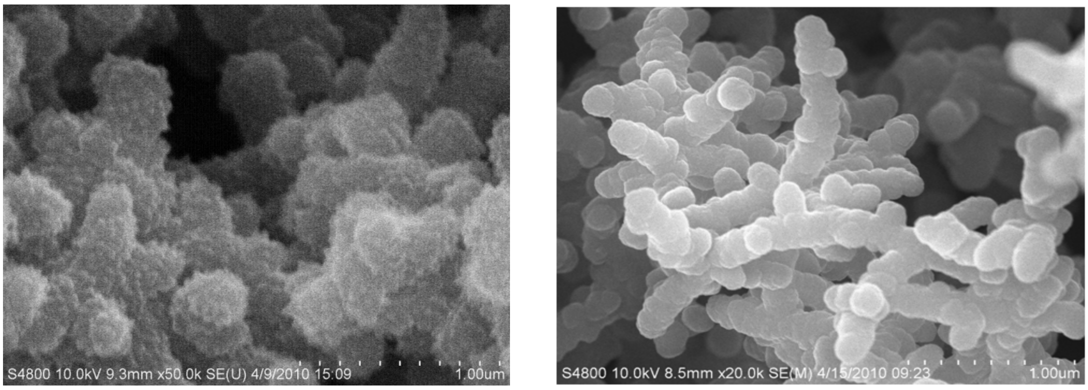
3. RESULTS AND DISCUSSION

Surface morphologies of PANi-MnO_2 and PANi were investigated by SEM and typical results are showed in Fig. 1. The SEM image of PANi (Fig. 1a) displays a compact granular morphology while the hybrid film M50 displays fibrous structure (Fig. 1b). The notable difference is due to dramatic effect of MnO_2 deposition on aniline electropolymerization.

During MnO_2 deposition, H^+ is released according to the following equation [5]:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad (1)$$

So the concentration of H^+ is especially high near the electrode surface during hybrid film depositions. As high concentration of dopant acid may prevent agglomerates of PANi, PANi is codeposited with MnO_2 in the fibrous structure. As a result, the effective areas of PANi-MnO_2 hybrid films are larger than that of PANi without MnO_2. This will be helpful to enhance capacitances for pseudocapacitors due to the facilitation of better charge transfer at the interface of electrode material and supporting electrolyte.



(a) (b)

Fig. 1: SEM images of PANi (a) and the hybrid film M50 (b)

All the hybrid films obtained reveal characteristic redox behaviors of PANi in 0.5 M H_2SO_4. Typical results of the hybrid films are in Fig. 2a, together with the cyclic voltammogram of PANi made similarly. All the curves display two characteristic redox peaks of PANi in the potential range investigated (-0.2 to 0.65V), similar to those of reported PANi [5, 13]. Redox peaks A_2/A_1 should correspond to the exchange between leucoemeraldine and emeraldine states of PANi while B_2/B_1 should be associated with degradation products of PANi. However, peak B_2/B_1 is hardly sharp. A maximum of current density is obtained for M50 sample. This demonstrates that the highest electrochemical activity is also obtained in the sample. To study the capacitive properties of PANi-MnO_2 hybrid films, the hybrid films were investigated in 0.5 M Na_2SO_4 at pH ~ 6 by cyclic voltammetry method in the potential range from 0 ÷ 0.65 V at a sweep rate of 5 mV/s. Recorded cyclic voltammograms are shown in Fig. 2b. At the first glance, all voltammograms are nearly rectangular in shape. The rectangular shape of the voltammogram is a fingerprint for capacitive behavior [1,5]. Thus, the hybrid films display a capacitive behavior in the potential range investigated.

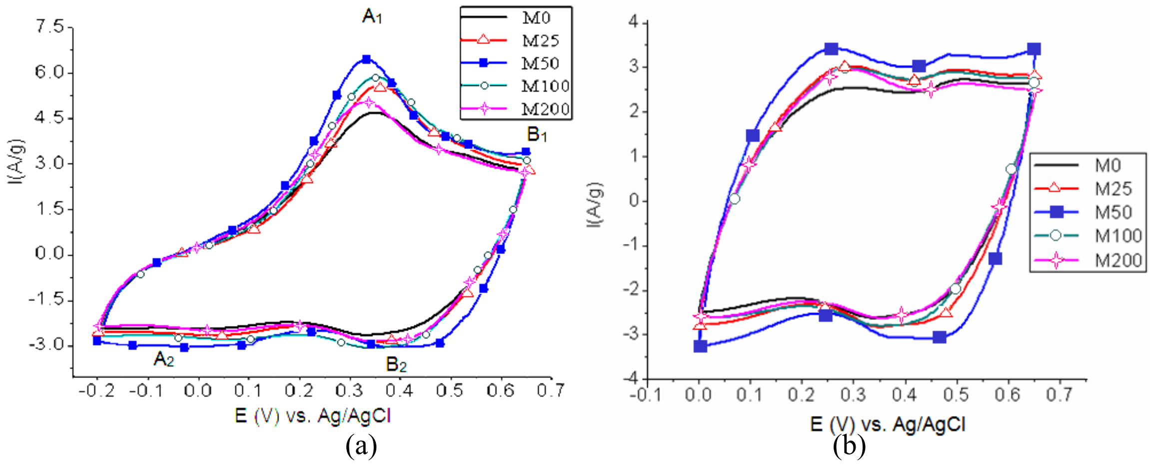


Fig. 2: Cyclic voltammetries of various samples at scan rate = 5 mV/s in: (a) 0.5 M H_2SO_4, (b) 0.5 M Na_2SO_4 at pH ~ 6

To estimate the specific capacitance of the films the following equation is used from the cyclic voltammetries [13]:

$$C = \frac{It}{V} \quad (2)$$

where: C (F/g) is the specific capacitance of the electrode; t (s) is the discharge time; V (V) is the potential range from the end of charge to the end of discharge; I (A/g) is the applied current density based on the electrode material. Based on equation (2), obtained results are showed in Fig. 3 displaying dependence of the specific capacitance of hybrid films on Mn^{2+} concentration in deposition bath. As observed the specific capacitances of films increase with increasing Mn^{2+} concentration. A maximum of 508 F/g is obtained for the hybrid film M50 corresponding to sample obtained from solution containing 50 mM Mn^{2+}. This can be attributed to higher porosity and greater surface area in relation to the rest of the samples. Moreover, as showed in Fig. 2a, it is the film M50 to possess highest electrochemical activity. However, with Mn^{2+} concentration over 50 mM the capacitances decrease with increasing Mn^{2+} concentration. This can be reasoned that the presence of MnO_2 induces surface areas of films to be larger than that of pure PANi with respect to low Mn^{2+} concentration in deposition bath. This results in their specific capacitance growing higher. Meanwhile, the high MnO_2 content increases the total mass of the film if Mn^{2+} concentration keeps increasing. So the specific capacitance decreases as more MnO_2 codeposited with PANi.

In order to get more information about the ability of the synthesized hybrid films as electrode materials in a supercapacitor, constant current charge/discharge measurement was carried out in 0.5 M Na_2SO_4 at pH ~ 6. Fig. 4 presented charge/discharge curves for hybrid films in the potential range from 0 ÷ 0.65 V at a current density of 0.85 mA/cm^2. It could be found from the curves that the voltage varies nearly linear with time, which indicates good capacitive behavior. It is notable that drop potentials IR appear in the discharge curves because of film resistance and solution resistance. The inset in Fig. 4 shows drop potentials for hybrid films. Obviously, a drop potential value of 52 mV is obtained for the hybrid film M50 indicating this film possesses smallest resistance while the values of 79, 80 , 82 , 92 mV correspond with M25, M100, M200, and M0 sample, respectively. The results indicate that the materials have good rate capacitance.

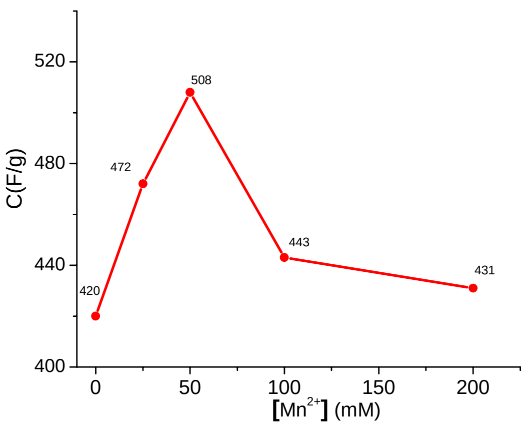


Fig. 3: Specific capacitance of hybrid films synthesized in different concentrations of Mn^{2+}

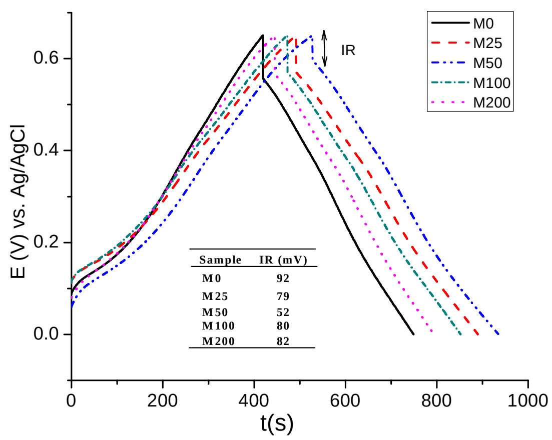


Fig. 4: Charge - discharge curves for the hybrid films obtained at a constant current density of 0.85 mA/cm^2 in 0.5 M Na_2SO_4 at pH ~ 6

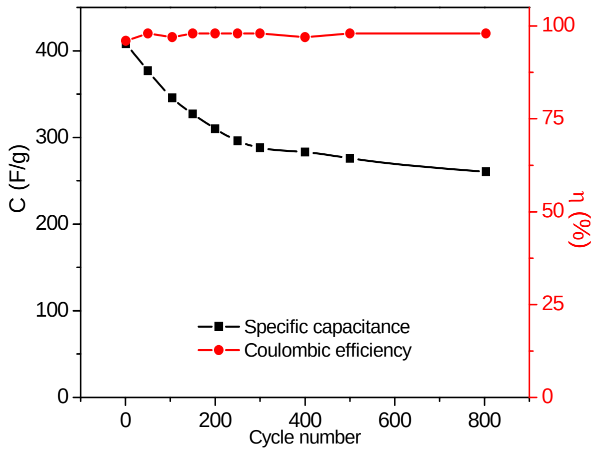


Fig. 5: Variation of specific capacitance and coulombic efficiency with charging-discharging cycle number for M50 at 0.85 mA/cm^2 in 0.5 M Na_2SO_4 at pH ~ 6

The long-term cycling stability of a composite electrode made of the hybrid film M50 was investigated, and the variation of specific capacitance over 800 cycles is depicted in Fig. 5. The specific capacitance decreases slightly in the first 300 cycles and then nearly remains unchanged. After 800 cycles the capacitance is still 67 % of the first cycle demonstrating the sturdy nature of PANi-MnO_2 hybrid films in energy storage applications.

The coulombic efficiency (η) of the hybrid film M50 is calculated according to equation (3):

$$\eta = \frac{t_D}{t_C}100,\% \qquad (3)$$

Where t_D is the discharging times, t_C is the charging times, respectively. The result shows that the coulombic efficiency is very table about 98% over 800 cycles.

4. CONCLUSION

In this study, hybrid films of PANi-MnO_2 were electro-codeposited on SS substrate. The codeposition of MnO_2 with PANi had significant effect on the morphologies of the hybrid films. The surface area of the hybrid film with fibrous structure gets larger than that of PANi with compact granular structure. The electrochemical properties of hybrid films were investigated in 0.5 M Na_2SO_4 at pH ~ 6. At scan rate of 5mV/s the highest specific capacitance of 508 F/g was obtained in sample M50 from electrolyte containing 50 mM Mn^{2+} compared with 420 F/g of pure PANi and also exhibited a good cycle performance under a current density of 0.85 mA/cm^2. After 800 charge-discharge cycles, the film sustained 67% of its capacitance with 98% of coulombic efficiency.

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