

Capacitance Properties of Electrodeposited Polyaniline Films on Stainless Steel Substrate

A.A. Al-Owais¹, I.S. El-Hallag², M.A. Ghanem¹ and E.H. El-Mossalamy³

¹Chemistry Department, Faculty of Science, King Saud University, Riyadh, SA

²Chemistry Department, Faculty of Science, Tanta University, Tanta, 31527, Egypt

³Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

Received: July 25, 2014, Accepted: December 15, 2014, Available online: February 13, 2015

Abstract: Polyaniline (PANI) thin films were successfully synthesized from a mixed solution of 1M aniline and two different concentration solutions of H_2SO_4 on a stainless steel substrate. The capacitance properties of polyaniline (PANI) films, have been determined and examined in the selected media of two different concentrations of H_2SO_4 acid using cyclic voltammetry technique. Cyclic voltammetric measurements have shown that PANI films grown by cycling the potential between $-0.2V$ and $1V$ in $1M H_2SO_4$ and $2M H_2SO_4$ on SS electrode. The electrochemical characterization of the electrode was carried out by means of cyclic voltammetry. The results show that polyaniline has a high specific capacitance of $702.1 F.g^{-1}$ and $810.5 F.g^{-1}$ at $10 mV s^{-1}$ in $1M H_2SO_4$ and $2M H_2SO_4$ respectively. This indicates that the promising feasibility of the polyaniline used as an electrochemical capacitor material in the sulphuric acid solutions.

Keywords: Polyaniline; Electrodeposition; cyclic voltammetry; Capacitance properties.

1. INTRODUCTION

The electrochemical capacitors (ECs) are attracting growing attention as electrical energy storage systems because of higher specific power than batteries and higher specific energy than conventional capacitors, owing to the high capacitance of the electrode materials[1-4]. They can be classified into two types based on their charge storage mechanisms: (I) electrical double-layer capacitors (EDLCs) and (II) redox supercapacitors[5]. Compared to the EDLC-based capacitors, -redox capacitors based on transition-metal oxides or conducting polymers such as RuO_2 [6], MnO_2 [7], NiO [8], and polyaniline[9,10] may provide much higher specific capacitances up to $1000 F.g^{-1}$ of the active material. Metal oxides and electrochemical conducting polymers are widely studied materials and are used as pseudocapacitive electrode materials with remarkable performance. However, the use of metal oxides is limited due to the high cost of the materials. Thus, a key issue is to develop cost-effective polymers for use in the fabrication of electrochemical supercapacitors.

Among the wide variety of conducting polymers, polyaniline

(PANI) has received considerable attention due to its good redox reversibility and chemical stability[11-16]. Various methods can be used to grow PANI films, and PANI films prepared by different methods show dissimilar supercapacitive properties with respective advantages and disadvantages. Polyaniline nanofibers were synthesized by using interfacial polymerization, and an electrochemical capacitance of $554 F.g^{-1}$ was reported. However, in this case, the capacitance values decreased rapidly during electrochemical cycling. In addition, efforts have been made to improve the stability of PANI films by preparing composite PANI/CNT films[17]. Girija and Sangaranarayanan studied the electrochemical polymerization of PANI by means of potential cycling between -0.2 and $1.2 V$ at a scan rate of $300 mVs^{-1}$ for 50 cycles and reported capacitance values in the range of 346 to $404 F.g^{-1}$ at different current densities[18]. In addition, PANI films coated and uncoated with Naflon were studied, and their enhanced cycle life was reported; however, the presented capacitance values were too low[19].

Electrochemical deposition (ED) is of particular interest due to its low cost, environmental friendliness, and the feasibility of low temperature growth. The aim of this work was to test the applica-

*To whom correspondence should be addressed: Email:
Phone:

bility of the ED technique for supercapacitor applications. We propose the synthesis of PANI films using cyclic voltammetry technique, and also for examining the supercapacitive properties of the films. SEM were used for characterization of the electrodeposited films of PANI.

2. EXPERIMENTAL

In this study, analar grade aniline was distilled under reduced pressure and stored in dark before use. Electrochemical measurements were carried out in a one-compartment cell with a three-electrode configuration. Ag/AgCl was used as reference electrode, 304 stainless steel rods as the working electrode and a platinum sheet as a counter-electrode. Before each experiment, the working electrode was polished with wet emery papers of different grit sizes (180, 400, 800, 1000 and 1500). After polishing, the working electrode was washed with doubly distilled water and acetone before immersion in test solution.

Deposition of PANI was carried out potentiodynamically by subjecting the working electrode to potential cycling between -0.2 V and 1 V at a scan rate of 10 mV s^{-1} in an electrolyte solution consisting of 1 M aniline, 1M H_2SO_4 and 2M H_2SO_4 for 40 cycles under nitrogen atmosphere. After deposition, the samples were rinsed with distilled water and dried for 12 h under nitrogen atmosphere.

Electropolymerisation and electrochemical characterizations were carried out using the computerised Autolab PGSTAT 30 electrochemical instrument with GPES software. The underlying steel surfaces were investigated after peeling off the polymer layer with a tape paste, washed with redistilled water, and finally rinsed with acetone in ultrasonic bath. Scanning electron microscope (SEM) images were obtained by using Joel JSM-6360LVSEM.

3. RESULTS AND DISCUSSION

The electrochemical and supercapacitor properties of PANI electrodes were determined using cyclic voltammetry technique. The cyclic voltammetry measurements, were performed at room temperature. Figure 1 shows measured cyclic voltammograms (CVs) of PANI films recorded in 1M H_2SO_4 and 2M H_2SO_4 electrolyte at various scan numbers. The CVs were cycled between -0.2 V (versus Ag/AgCl) to 1 V. The CVs started at -0.2 V, reversed at 1 V, and terminated at -0.2 V (versus Ag/AgCl). CVs provide valuable information on oxidation-reduction (charge-discharge) behavior. Here, the capacitance was mainly based on the redox reaction because the shape of the CVs is distinguished from the shape of electric double-layer capacitance, which is normally close to an ideal rectangle. During the CV scans, two well defined oxidation and two well defined reduction peaks were observed, thus presenting an exchange between the leucoemeraldine/emeraldine and emeraldine /pernigraniline states of the PANI film[20]. As the scan number was increased, the current response, which is a measure of the capacitance, increased. The relatively higher current density for the PANI films indicate good rate capability for supercapacitor applications. The similar shape of the CVs recorded at different scan number indicates excellent electro-chemical reversibility of the PANI films. The specific capacitance of the PANI electrode can be calculated from the CV curves according to the following equation:

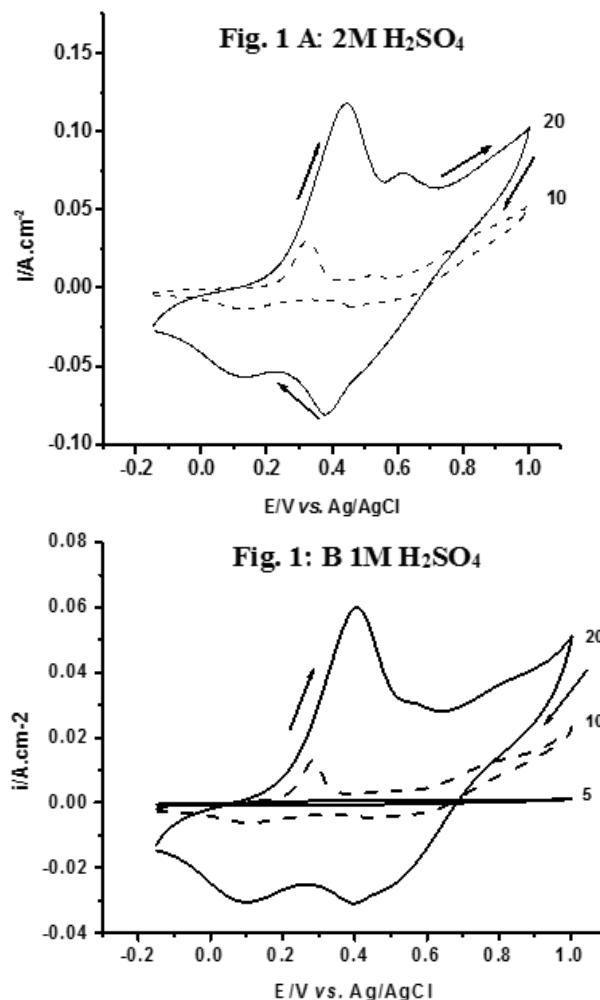


Figure 1. Cyclic voltammograms of PANI at various scan numbers in 1 M H_2SO_4 (A) and 2M H_2SO_4 (B).

$$C_{sp} = i / r \times m \quad (1)$$

where i is the average anodic current, r is the scan rate, and m is the mass of the active electrode. The specific capacitance values were found to be 301.2 Fg^{-1} and 294.4 Fg^{-1} for the PANI films in 2M & 1M H_2SO_4 respectively at a scan number of 20. Capacitors depends on many factors, such as the mass of the active electrode, the conductivity of the active electrode, the concentration of the electrolyte, and the morphology of the electrode. Electrochemical stability is one of the important indicators of device quality.

The variation of capacitance and peak current of PANI with scan rate are collected in table 1. Figure 2 shows the specific capacitance values calculated from the CV measurements as a function of scan rate. The decrease in the capacitance values is described according to the Randle-Sevcik relationship (Eq. 2), in which the current (which is a measure of the supercapacitive properties) of the electrochemical redox reaction is linearly proportional to the concentration of the electroactive species and the square root of the scan rate.

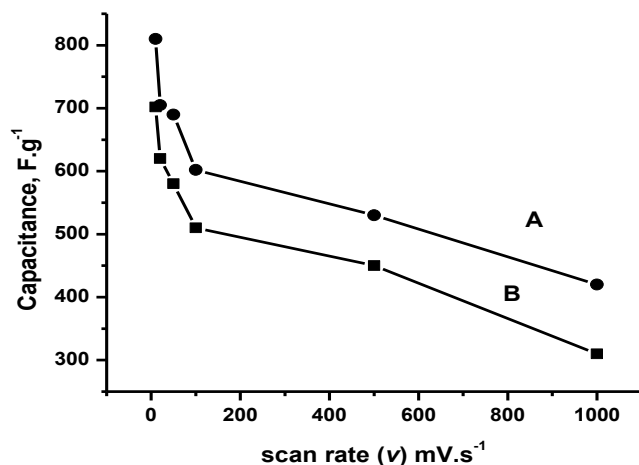


Figure 2. Specific capacitance versus scan rate, curve (A) in 2M H₂SO₄ and curve (B) in 1M H₂SO₄.

$$i_p = Kn^{3/2}AD^{1/2}Cv^{1/2} \quad (2)$$

where the constant $K = 2.72 \times 10^5$, n is the number of moles of electrons transferred per mole of electroactive species, A is the area of the electrode in cm^2 , D is the diffusion coefficient in cm^2s^{-1} , C is the solution concentration in mole/L, and v is the scan rate of the potential in V.s^{-1} . Here, the concentration of the electroactive species is the same at different scan rates. If the peak current increases linearly with the scan rate, then it is reasonable to say that it is a diffusion-controlled (reversible) reaction. According to Fig. 2, the reaction is an irreversible redox reaction at the electrode electrolyte interface at low sweep rate. This irreversible nature of the electrode reduces the charge-transfer processes at the interface. We believe that this is a possible reason for the decrease in the supercapacitive properties with the scan rate.

To test the stability of the devices, the films were charged-discharged repeatedly for 40 cycles in H₂SO₄ electrolyte at a constant current density of 1 mAcm^{-2} . Figure 3 shows the measured specific capacitances of the PANI with scan number in 1M and 2M H₂SO₄ respectively for 40 cycles. The capacitance values were initially found to increase with increasing the scan cycle and then

Table 1. Variation of Capacitance and peak current of PANI with scan rate

mVs ⁻¹	Peak current (i_p) uA		Capacitance Fg ⁻¹	
	1M H ₂ SO ₄	2M H ₂ SO ₄	1M H ₂ SO ₄	2M H ₂ SO ₄
10	3	5	702.1	810.5
20	5	9	620.1	705.3
50	12	17	580.5	690.2
100	23	35	510.4	602.1
500	115	160	450.8	530.3
1000	220	315	310.6	420.7

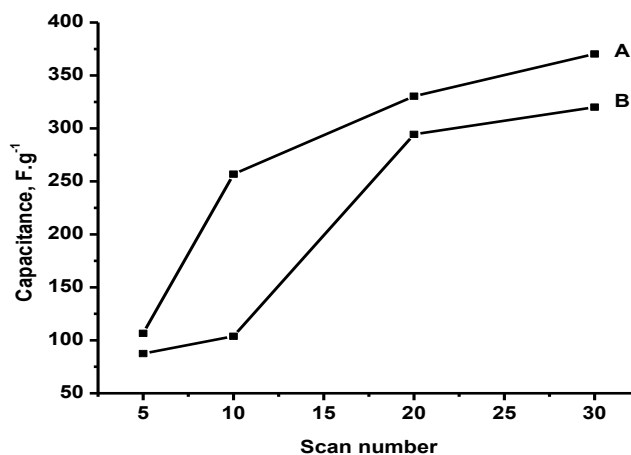


Figure 3. Specific capacitance versus scan number, curve (A) in 2M H₂SO₄ and curve (B) in 1M H₂SO₄.

become stable starting from 30 cycle. Even after 40 cycles, the charge-discharge curve appears similar, with only a negligible change in capacitance values. These results suggest that PANI films synthesized using the ED technique are suitable for supercapacitor applications. Table 2 summarizes the calculated values of capacitance with scan number in 1M H₂SO₄ and 2M H₂SO₄ respectively. Figure 4(A) and (B) shows the 20th scan of CVs of PANI electrodes after oxidation-reduction cycles in 1M H₂SO₄ and 2M H₂SO₄ electrolyte, respectively. It was found that as the number of cycles increase, the capacitance current increased for both the PANI films in 1M H₂SO₄ and in 2M H₂SO₄. This increase is attributed to the growing of polyaniline films due to mechanical doping by the acid[20]. The shape of the CV is one of the important factors used to judge the electrochemical stability of the electrode during charge-discharge cycling. The shape of the measured CVs for the PANI film remained relatively unchanged. This indicates that the PANI film is electrochemically more stable.

3.1. SEM measurements

To confirm the formation of polyaniline films the electrodeposited samples were pictured by scanning electron microscopy, SEM, (Fig. 5.). As shown the net-like pure PANI film is exhibited by the figure which is favorable to strengthen the adhesion of PANI to the electrode surface. The SEM image indicates that the compact na-

Table 2. Values of capacitance PANI in 1M H₂SO₄ and 2M H₂SO₄ at different scan number

Scan number	Capacitance	
	1M H ₂ SO ₄	2M H ₂ SO ₄
30	320.1	370.3
20	294.4	301.2
10	103.8	256.8
5	87.5	106.6

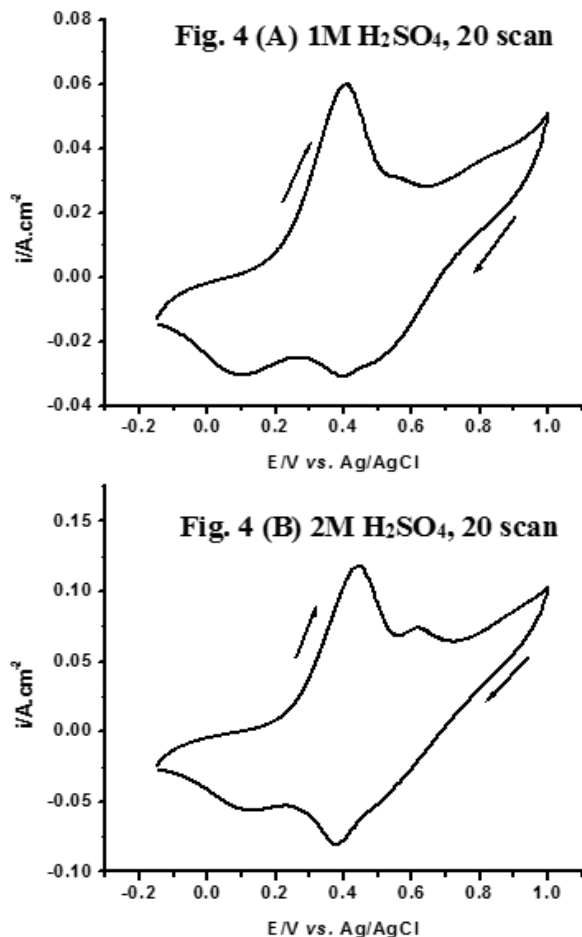


Figure 4. shows the 20th scan of CVs of (a) PANI electrodes after oxidation-reduction cycles in 1M H₂SO₄ and (b) in 2M H₂SO₄ electrolyte.

ture of the PANI films. Also the image confirm that the PANI film is amorphous.

4. CONCLUSION

PANI thin films with different thicknesses were successfully synthesized onto 304 stainless steel rods as the working electrode by using an electrodeposition technique for electrochemical supercapacitor applications. SEM measurements showed that the PANI films were compact and amorphous. The electrochemical supercapacitor measurements were performed in a 1M H₂SO₄ and 2M H₂SO₄ electrolyte by using cyclic voltammometry technique. The highest supercapacitance values were found to be 810.5 Fg⁻¹ for 250 nm thick PANI film and 702.1 Fg⁻¹ for 220 nm thick PANI film. According to electrochemical stability measurements, the thicker PANI film was electrochemically more stable than the thinner film.

5. ACKNOWLEDGEMENT

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

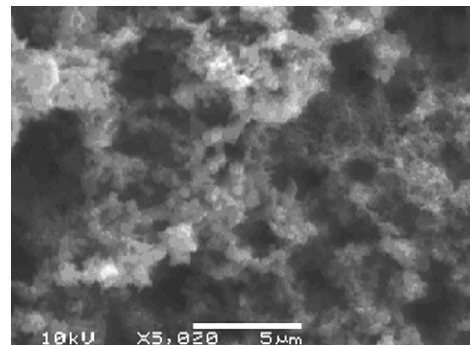


Figure 5. Scanning electron image of electrodeposited PANI.

REFERENCES

- [1] B.E. Conway, J. Electrochem. Soc., 138, 1539 (1991).
- [2] W.C. Chen, T.C. Wen, J. Power Sources, 117, 273 (2003).
- [3] R. Kotz, M. Carlen, Electrochim. Acta, 45, 2483 (2000).
- [4] E. Frackowiak, F. Beguin, Carbon, 40, 1775 (2002).
- [5] A.I. Inamdar, Y.S. Kim, S.M. Pawar, J.H. Kim, H. Im, H. Kim, J. Power Sources, 196, 2393 (2011).
- [6] C.C. Wang, C.C. Hu, Electrochim. Acta, 50, 2573 (2005).
- [7] M. Nakayama, T. Kanaya, R. Inoue, Electrochem. Commun., 9, 1154 (2007).
- [8] J.W. Lang, L.B. Kong, W.J. Wu, Y.C. Luo, L. Kang, Chem. Commun., 35, 4213 (2008).
- [9] Y.G. Wang, H.Q. Li, Y.Y. Xia, Adv. Mater., 18, 2619 (2006).
- [10] S.R. Sivakumar, W.J. Kim, J.A. Choi, D.R. MacFarlane, M. Forsyth, D.W. Kim, J. Power Sources 171, 1062 (2007).
- [11] P. Sivaraman, R.K. Kushwaha, K. Shashidhara, V.R. Hande, A.P. Thakur, A.B. Samui, M.M. Khandpekar, Electrochim. Acta, 55, 2451 (2010).
- [12] S.R. Sivakumar, R. Saraswathi, J. Power Sources, 137, 322 (2004).
- [13] K.S. Ryu, K.M. Kim, N.G. Park, Y.J. Park, S.H. Chang, J. Power Sources, 103, 305 (2002).
- [14] P. J. Kulesza, M. Skunik, B. Baranowska, K. Miecznikowski, M. Chojak, K. Karnicka, E. Frackowiak, F. Beguin, A. Kuhn, M.H. Delville, B. Starobrzynska, A. Ernst, Electrochim. Acta, 51, 2373 (2006).
- [15] A.M.P. Hussain, A. Kumar, F. Singh, D.K. Avasthi, J. Phys. D: Appl. Phys., 39, 750 (2006).
- [16] A.M.P. Hussain, A. Kumar, Eur. Phys. J. Appl. Phys., 36, 105 (2006).
- [17] S.R. Sivakumar, W.J. Kim, J.A. Choi, D.R. MacFarlane, M. Forsyth, D.W. Kim, J. Power Sources, 171, 1062 (2007).
- [18] T.C. Girija, M.V. Sangaranarayanan, J. Power Sources, 156, 705 (2006).
- [19] B.C. Kim, J.S. Kwon, J.M. Ko, J.H. Park, C.O. Too, G.G. Wallace, Synth. Met., 160, 94 (2010).
- [20] J. Liu, M. Zhou, L.Z. Fan, P. Li, X. Qu, Electrochim. Acta, 55, 5819 (2010).