

Poly(*o*-toluidine) for carbon fabric electrode modification to enhance the electrochemical capacitance and conductivity

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Abstract

Capacitance and conductivity enhancements of activated carbon fabric employed as electrodes of electrochemical capacitors (ECs) were achieved by electrochemical deposition of conducting poly(*o*-toluidine) (POT). Potentiodynamic polymerization of *o*-toluidine onto the carbon in H₂SO₄ was employed for this carbon modification. The capacitance of the activated carbon was enhanced by superimposing the pseudocapacitance of poly(*o*-toluidine) onto the double-layer capacitance of the carbon. Deposition of polyaniline was also conducted for the purpose of comparison. With the presence of the electron-donating methyl group in the phenyl ring, poly(*o*-toluidine) is more effective than polyaniline in enhancing the capacitance of the carbon fabric. The specific capacitance of the electrodes increased with the amount of poly(*o*-toluidine) deposited and more than twice of that of the bare carbon can be achieved. However, the capacitance per unit weight of the deposited polymer decreased with the extent of deposition, probably due to an increase of the ion migration resistance that increasingly obstructs some polymer from the access of ions. The resistance of the carbon electrode was found to decrease upon polymer deposition, and this was found to be more significant with poly(*o*-toluidine) than with polyaniline. The low resistance resulting from poly(*o*-toluidine) deposition enabled the assembly of capacitors of relatively high power densities, more than three times of that of a capacitor with the bare carbon.

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1. Introduction

Electrochemical capacitors (ECs), which are also called as supercapacitors or ultracapacitors, are expected to become promising energy storage devices, due to their high energy and power densities [1–4]. Many researchers are currently investigating two types of energy storage mechanisms in ECs, namely the electric double layer and the redox reaction pair [5]. The capacitance in double-layer capacitors is purely electrostatic origin due to the separation of electron and ionic charges at the interface between the electrode and electrolyte [6,7]. In redox capacitors, fast faradaic charge transfer reactions takes place at the electrode surface

and this produces the so-called redox- or pseudocapacitance [4,8–14].

Activated carbon is attractive as an electrode material for electrochemical capacitors due to their high accessibility, good processability, chemical inertness, low cost, and high surface area up to 2000 m² g⁻¹ in the forms of powder, fiber, or fabric [15–24]. Chemical treatment of carbon enriches the surface functionality, and this can as well be employed to improve the capacitance [25–27]. The improvement of capacitance for carbon materials has been achieved by deposition of conducting polymer [28] and impregnation of electroactive transition metal oxides such as RuO₂ and MoO₃ [29–31].

Electrically conducting polymers are gifted materials for high performance ECs because of their high specific capacitance resulting from the doping process, high conductivity in the charged states, and fast charge–discharge mechanism

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[5,32]. Polymers of aniline ($C_6H_5NH_2$) and its derivatives have attracted much attention for applications in ECs because of their high environmental stability and easy processability in comparison with other conducting polymers [33,34]. Polyaniline (PANI) synthesized by an electrochemical method has been investigated on its performance as an electrode material for redox capacitors [35,36]. Nevertheless, carbon materials are still favored for ECs because of the physical nature of double layer formation that makes the electrodes more durable.

Modification of activated carbon by conducting polymers supplies an interesting feature of pseudocapacitance in combination with electric double-layer capacitance. Conducting polymers have ability for charge storage and this storage process depends on the conditions of preparation, the state of oxidation, and the type of electrolyte [37]. The specific capacitance of activated carbon fabrics modified by PANI has been shown to have a significant increase [28].

Energy storage in conducting polymers is mainly due to p- and n-doping processes. *o*-Toluidine ($C_6H_4CH_3NH_2$), OT, containing a methyl group on its benzene ring may exhibit a more promising charge storage capability than polyaniline, e.g. [38]. The present work aims to modify activated carbon fiber by electropolymerization of OT using slow-scan cyclic voltammetric method. Electrochemical behaviors of the modified carbons are tested to assess the applicability of poly(*o*-toluidine) in ECs, in comparison with that of extensively explored PANI.

2. Experimental

Polyacrylonitrile-based activated carbon fabric with a BET surface area of $1200\text{ m}^2\text{ g}^{-1}$ and a thickness of 0.4–0.6 mm was chosen as the base electrode material for the ECs. Prior to each experiment, the carbon fabric was heat treated at 900°C for 20 min under helium purge to remove any oxygen functional groups and volatile impurities on the surface of the carbon. The treated carbon (ca. 2 cm^2 and 0.02 g) was fixed on a stainless-steel current collector to serve as electrodes for all experiments.

Electrochemical deposition of poly(*o*-toluidine), POT, on activated carbon fabric was carried out in 1 M H_2SO_4 . Potentiodynamic method was selected for the deposition. All the deposition experiments were carried out in a three-electrode system consisting of the activated carbon as the working electrode and Pt wire and Ag/AgCl as the counter and reference electrodes, respectively. N_2 gas was purged through the system during the whole process. Electropolymerization was carried out by cycling the potential between -0.2 and 0.9 V (versus Ag/AgCl) in a solution containing 5–50 mM of OT. With a slow-scan rate of 1 mV s^{-1} , each deposition was conducted for 10 cycles, with initiation and completion both at -0.2 V (versus Ag/AgCl). After deposition, the electrode was soaked in 1 M H_2SO_4 to remove any unreacted monomer under nitrogen atmosphere for 24 h. The POT-

modified carbon fiber was dried under vacuum for 48 h. The amount of polymer deposited onto the carbon fiber was determined by weighing. Cyclic voltammetric measurements of the polymer-modified carbon electrodes were conducted in 1 M H_2SO_4 to explore the capacitive behavior.

Two-electrode capacitor cells were fabricated to examine the electrochemical performance of the resulting capacitors. The cells were assembled with two facing carbon electrodes, sandwiching a piece of filter paper as separator. Cyclic voltammetric measurements were conducted within a bias range of -0.8 and 0.8 V at different scan rates in 1 M H_2SO_4 . Galvanostatic charge–discharge test of the capacitors was also performed to determine the overall resistance of the capacitors. Surface morphologies of the carbons were examined by a scanning electron microscope (SEM).

For the purpose of comparison, the carbon electrodes modified with PANI were prepared and tested using the same electrochemical techniques and conditions described above. According to the deposition voltammograms, the major polymerization reactions for both POT and PANI occur within the potential range employed, i.e. -0.2 to 0.9 V (versus Ag/AgCl).

3. Results and discussion

3.1. Electropolymerization of POT onto carbon fabric

Surface modification of activated carbons by electroactive polymer has been proved to result in an effective enhancement of carbon capacitance [28]. Slow-scan potentiodynamic method was selected here in an attempt to allow the conducting polymer interpenetrate into the micropores of the activated carbon. Before starting the polymerization, a soaking period of 30 min was given, allowing the equilibrium between pore wall and monomer to be reached. Fig. 1 shows the typical cyclic voltammogram recorded during the electropolymerization of OT at a scan rate of 1 mV s^{-1} . In the first cycle starting from -0.2 V (versus Ag/AgCl) a sharp increase in anodic current shows up after 0.6 V (versus Ag/AgCl). The sharp current increase up to 0.9 V (versus Ag/AgCl) represents that OT molecules are oxidized to give oligomers, which would subsequently be oxidized [38–40]. The oxidized oligomers formed in the first cycle get reduced at ca. 0.36 V (versus Ag/AgCl) in the reverse scan, as reflected by the cathodic peak current in Fig. 1. The presence of the cathodic peak current verifies the incorporation of polymer onto the carbon.

In the second and further cycles two broad peaks were observed at 0.35 and 0.55 V (versus Ag/AgCl) in the anodic sweep. These peaks are assigned for the formation of polaronic and bipolaronic oxidation states of incorporated polymers, respectively [41]. The 0.35 V (versus Ag/AgCl) peak is relatively vague. The ion diffusion in carbon pores and the double layer formation must have affected the sharpness of this peak. The polymer film growth was suggested to occur

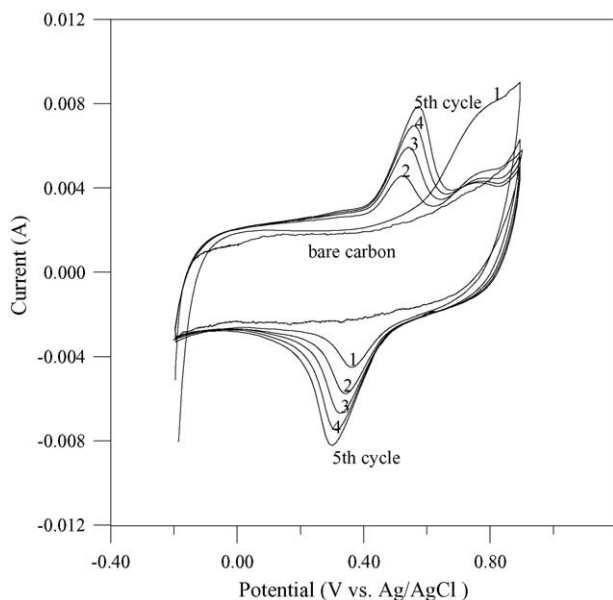


Fig. 1. Cyclic voltammograms recorded against Ag/AgCl during the electropolymerization of OT onto the activated carbon fabric (2 cm^2) in $1\text{ M H}_2\text{SO}_4$ and 5 mM OT at a potential sweep rate of 1 mV s^{-1} .

near 0.55 V (versus Ag/AgCl) [42], less positive than that for the formation of oligomers ($>0.6\text{ V}$). An increase in the polymer-oxidation peak current at 0.35 and 0.55 V (versus Ag/AgCl) with cycle number is an evidence for the increasing amount of polymer incorporation.

In the first cycle of deposition, the oligomers, which initially are not precipitated on the surface, would eventually saturate and form polymer-growing nuclei on the surface. This causes time delay and has been given as the reason for the appearance of the anodic peak current at potentials more positive than 0.6 V (versus Ag/AgCl) [43,44]. The delayed peak current for the second and further cycles is much smaller than that in the first cycle and it decreases with cycle number. This indicates that carbon surface is gradually saturated with polymers and oligomer precipitation is replaced by polymer film growth.

It can be seen from Fig. 1 that the anodic and cathodic peak potentials show positive and negative shifts, respectively, with the cycle number. Similar potential shifts with OT concentration were also observed. Fig. 2 shows the variation of anodic peak potential with cycle number and concentration. The amount of POT deposition on activated carbon is found to increase with the cycle number and OT concentration. It is likely that the increased amount of deposited polymer causes the increase in the resistance for ion diffusion in pores and polymer films and thus the delayed appearance of the peak current.

3.2. Cyclic voltammetric behavior of POT-modified carbon electrodes

Fig. 3 shows the three-electrode voltammograms of the POT-modified carbon fiber (prepared with deposition in

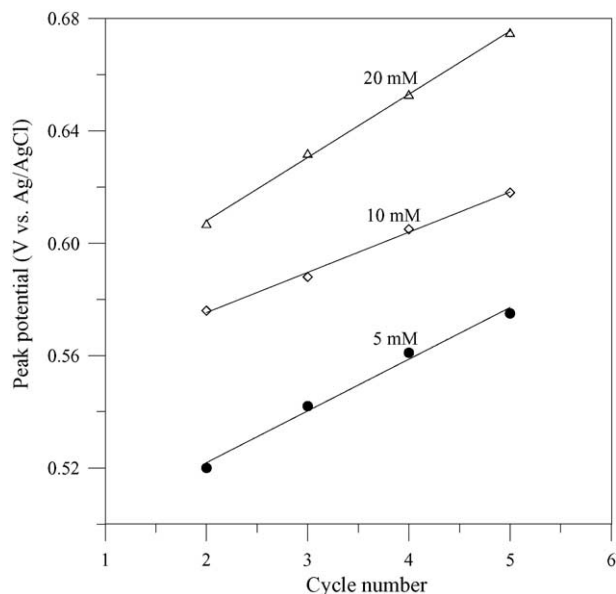


Fig. 2. Variation of the anodic peak potential during POT growth with cycle number at different OT concentrations.

20 mM OT) in $1\text{ M H}_2\text{SO}_4$ swept between -0.2 and 0.8 V (versus Ag/AgCl) at 1 mV s^{-1} . Very similar voltammogram patterns are observed for more than 50 cycles in this test, reflecting the applicability of the electrode in ECs. The voltammogram of the bare carbon is provided for comparison, showing a significant current increase in both directions of potential sweep due to the POT deposition. It can be deduced from Fig. 3 that the voltammogram of the POT-modified carbon is given by superimposing the voltammogram of POT on that of the bare carbon. This indicates that the carbon and poly-

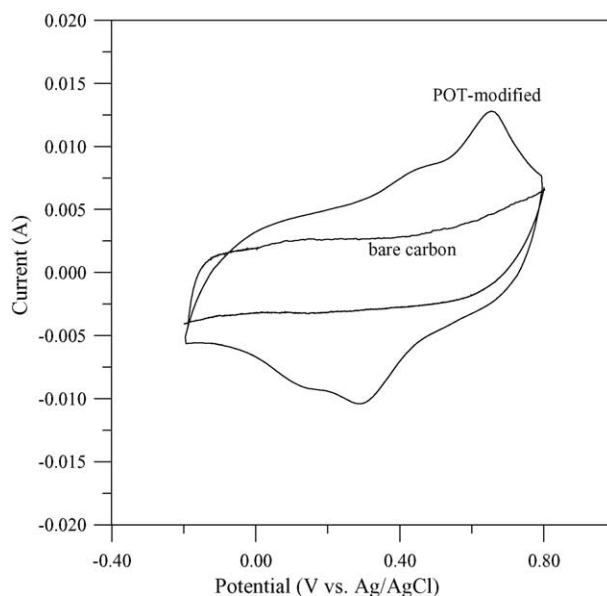


Fig. 3. Cyclic voltammograms (the 10th cycle) recorded against Ag/AgCl for the POT-modified and bare carbons (2 cm^2) swept at 1 mV s^{-1} in $1\text{ M H}_2\text{SO}_4$. The POT-modified carbon was prepared by the electrochemical deposition in 20 mM OT for 10 cycles.

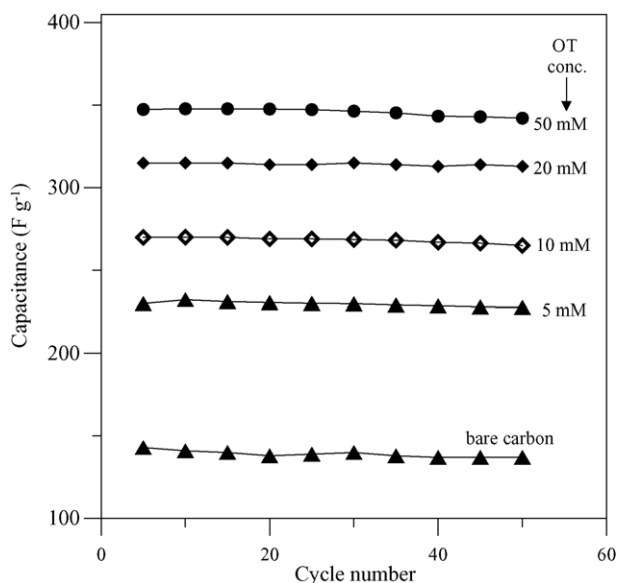


Fig. 4. Variation of the capacitance with cycle number in 1 M H_2SO_4 for the POT-modified carbon ($2\ cm^2$) prepared at different OT concentrations with 10 cycles of deposition. The capacitance, based on per unit mass of the POT/carbon composite, was calculated using integration of the cyclic voltammograms swept between -0.2 and $0.8\ V$ (vs. $Ag/AgCl$) at $1\ mV\ s^{-1}$.

mer contribute to the total capacitance in a parallel way. The first oxidation peak at $0.45\ V$ (versus $Ag/AgCl$) represents the removal of electrons from the N-atom of amine units of the polymer, i.e. conversion of amine units to semiquinone radical cation (polaronic state). The second oxidation peak at $0.66\ V$ (versus $Ag/AgCl$) can be assigned to the oxidation of semiquinone radical cation to quinone imine (bipolaronic state), i.e. the transformation of polaronic emeraldine to bipolaronic pernigraniline [45]. The reduction process (i.e. the cathodic sweep) is simply the reverse of the oxidation. The voltammogram reveals that the charge–discharge of the POT-modified carbon electrode is a typical two-electron redox process.

Fig. 4 shows the capacitance of POT-modified carbon fibers at different cycles of potential sweep. The capacitance, based on per unit mass of the POT/carbon composite, was calculated using integration of the voltammogram within the potential range applied. It is seen that the capacitance is stable for 50 cycles and its value increases with the OT concentration during deposition. The increase in capacitance can be attributed to the increasing amount of POT. The capacitance per unit area of the electrode was plotted against the deposited POT weight in Fig. 5. Both the capacitance and deposited POT weight are presented on the basis of the geometric (planar) area of the electrode. The plot does not show a linear relationship. The slope (i.e. the derivative) of the curves can be used to estimate the capacitance per unit weight of the deposited POT. It is seen that the POT capacitance, i.e. the slope, decreases with the increasing deposited POT weight. The decrease in the POT capacitance can be attributed to an increase of the ion migration resistance, which would in-

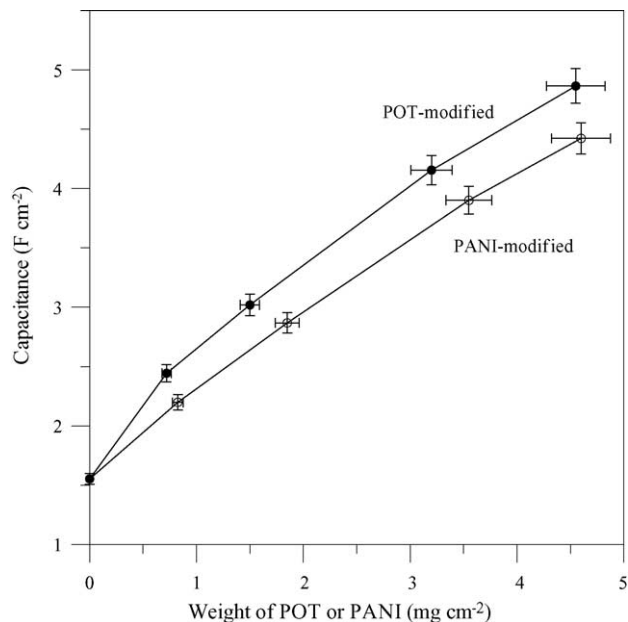


Fig. 5. Variation of the capacitance per unit geometric (planar) area of the polymer-modified electrodes in 1 M H_2SO_4 with the weight of the deposited polymer per unit geometric electrode area. The capacitance data were obtained from Fig. 4.

creasingly obstruct some polymer from the access of ions. As a matter of fact, the increase in resistance has been demonstrated in Fig. 1, which shows the peak potential shift with the deposition cycle number.

A similar electrochemical method was applied for PANI deposition to modify the carbon fabric and the variation of electrode capacitance with PANI weight is shown in Fig. 5 as well. The figure shows that PANI is less effective than POT in capacitance enhancement. Here, for both POT and PANI, the electrochemical p-doping takes place on the polymer backbone during charge process by extraction of electrons to the external circuit, accompanied by HSO_4^- anion binding [46]. The association of counter ions with polymer chain charges leads to development of a Helmholtz double layer. The presence of electron-donating methyl groups in the phenyl ring of OT molecules may lead to a higher tendency of p-doping onto the polymer backbone of POT than PANI [47]. This is considered as one of the major reason for the higher capacitance of POT in comparison with that of PANI.

3.3. Performance of the assembled capacitors

Cyclic voltammetry was employed to study the assembled two-electrode capacitor cells. Fig. 6 shows the cyclic voltammograms recorded at different potential sweep rates for the resulting capacitor equipped with the POT-modified carbons (from deposition in 20 mM OT). The capacitor consists of two facing identical carbon electrodes sandwiching a separator. It exhibits a typical mirror image type of cyclic voltammogram within a potential range of -0.8 to $0.8\ V$. The voltammogram for the capacitor equipped with the bare

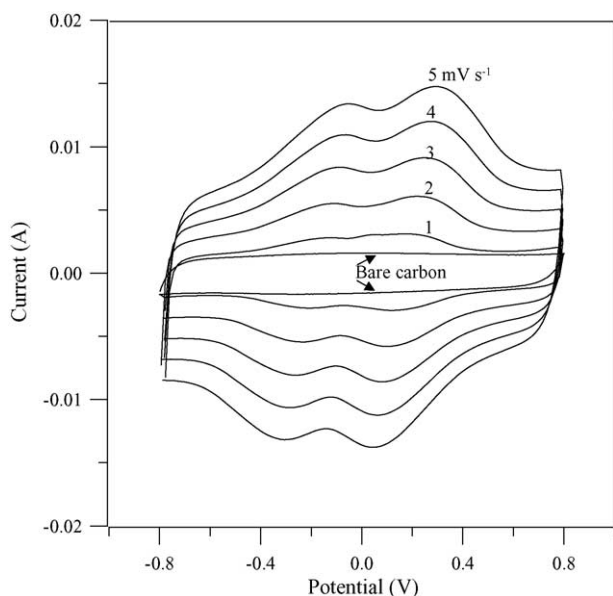


Fig. 6. Cyclic voltammograms of the resulting two-electrode capacitors in 1 M H_2SO_4 at different potential scan rates. The capacitors are assembled with the bare carbon or the POT-modified carbon ($0.32 \text{ g POT g}^{-1} \text{ C}$) prepared with 10 cycles of deposition in 20 mM OT.

carbon swept at 1 mV s^{-1} is also provided in the figure for comparison. A rectangular voltammogram is observed for the bare-carbon capacitor, indicating the dominance of the double-layer mechanism in this energy storage process. It has to be noted here that the voltammogram shape of a two-electrode capacitor is associated with the open circuit potential (OCP) and voltammogram of its constituting electrodes in a three-electrode system (see Fig. 3). At 0 V of a symmetric capacitor, both the constituting electrodes are situated at their OCP, which has a value of ca. 0.25 V versus Ag/AgCl for all the electrodes in the present work. As the capacitor is charged from 0 V to other potentials, the potential of the constituting electrodes shift from the OCP toward opposite directions and the potential difference between the two opposing electrodes should be the observed potential of the capacitor system as shown in Fig. 6 [48]. The positive charge stored in one electrode has to be identical to the negative charge in the other. Based on this principle, the cyclic voltammetric behavior of symmetric two-electrode capacitors can be estimated from the three-electrode voltammogram of their constituting electrodes around the OCP.

For the capacitor with POT deposition, obvious redox peaks can be observed above the double-layer background current. These peaks should correspond to the p-doping and p-dedoping of POT that have been described in Fig. 3. The anodic peak current near 0.3 V is plotted against the potential-sweep rate in Fig. 7. A fairly linear relationship between the peak current and the potential-sweep rate is observed within the potential-sweep rate employed, reflecting a pseudocapacitive behavior of the deposited POT. However, the linear relationship seems to disappear with scan rate higher than

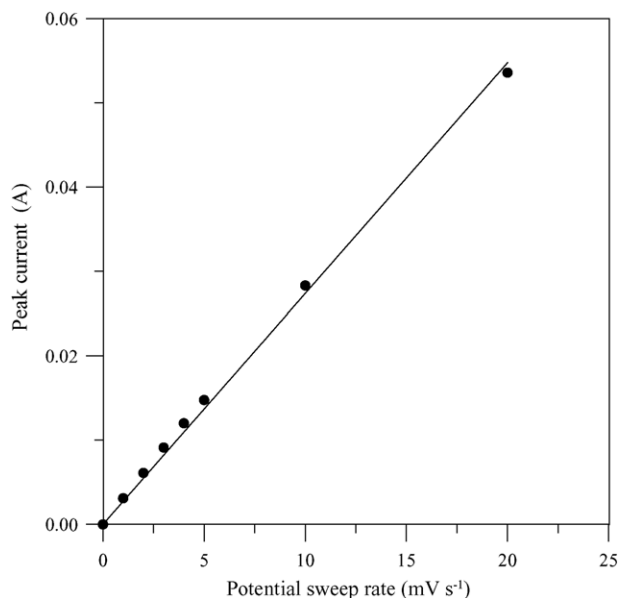


Fig. 7. Effect of potential sweep rate on the anodic peak current near 0.3 V of the voltammograms in Fig. 6 for the capacitor assembled with the POT-modified carbon.

20 mV s^{-1} , indicating that the reaction tends to be diffusion-controlled.

The IR drop, a sudden potential drop at the very beginning of galvanostatic discharge, was measured by charging the capacitors to 0.8 V followed by discharge. The IR drop is plotted against the discharge current in Fig. 8. This potential drop results mainly from the bulk solution resistance, electrode resistance, and ion migration resistance in the elec-

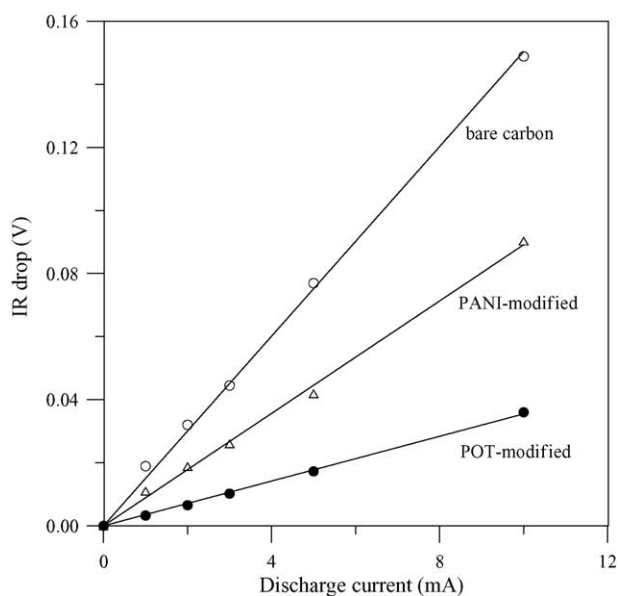


Fig. 8. Variation of IR drop with discharge current for the capacitors assembled with the POT-modified ($0.32 \text{ g POT g}^{-1} \text{ C}$), PANI-modified ($0.35 \text{ g PANI g}^{-1} \text{ C}$), and bare carbons. The modified carbons were prepared with 10 cycles of deposition in 20 mM monomer solutions. The capacitors have been charged to 0.8 V in 1 M H_2SO_4 prior to discharge.

trode [19,22]. The slope of the linear relationship between the IR drop and discharge current can be used to estimate the overall resistance of the capacitors. The results in Fig. 8 are used to calculate the overall resistances of the capacitors assembled with the bare, PANI-modified, and POT-modified carbons and values of 14, 8.9, and 3.5 Ω , respectively, are obtained. It has been shown in our previous study [22] that the electrode resistance is the major contribution to the overall resistance of the carbon fabric electrode. The lower resistance of the polymer-modified electrodes can be attributed to the fact that the conducting polymers serve as the media to improve the electrical conduction among the fibers of the fabric.

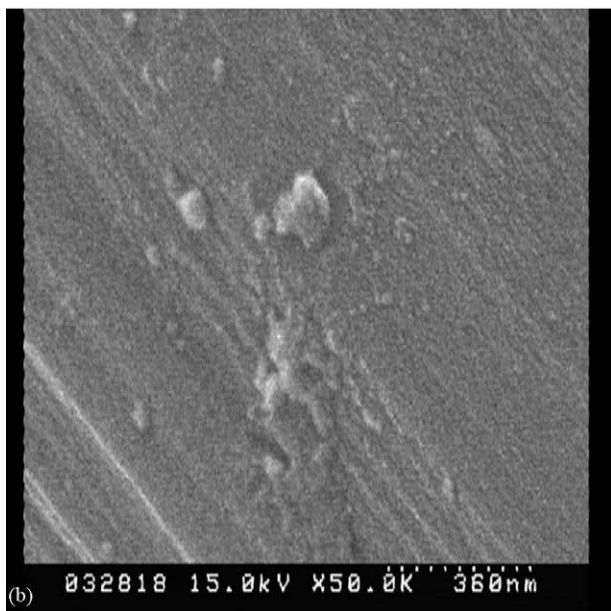
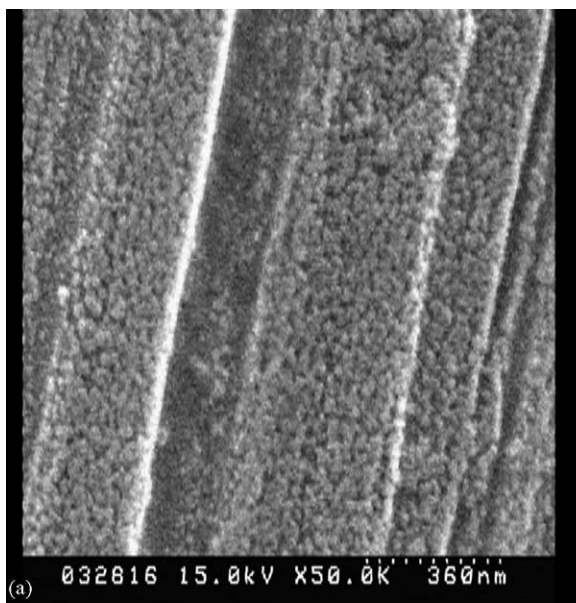


Fig. 9. External features of the POT-modified and PANI-modified carbons (a and b, respectively) from SEM. The modified carbons were prepared with 10 cycles of deposition in 20 mM monomer solutions.

In addition, the resistance of ion migration to store pseudo-capacitance in the polymers may be much smaller than that to store double-layer capacitance in carbon micropores. This can result in a smaller overall resistance for the energy storage process with the presence of the polymers. As for the lower resistance of the POT-modified electrode in comparison with the PANI-modified one, it is attributable to the loose framework of the deposited POT due to the presence of the methyl group that hinders the formation of impenetrable tangles of polymer chains. The loose framework may facilitate the penetration of ions into the film, thus leading to the low resistance of the POT-modified electrode. In addition, the POT film forms a void structure. Fig. 9 shows the external features of the POT- and PANI-modified carbons from SEM. The POT film is fully of voids and this would provide a larger surface area exposed to the electrolyte, thus lowering the resistance for ion migration.

On the basis of the above data and by applying a regular bias potential of 1 V for aqueous electrolytes, the energy densities were calculated to be ca. 18, 35, and 39 J g^{-1} and the power densities to be ca. 0.89, 1.0, and 2.7 W g^{-1} for the capacitors (in Fig. 8) assembled with the bare, PANI-modified, and POT-modified carbons, respectively. The energy density of the carbon capacitor was significantly improved by deposition with both PANI and POT. However, because of the lower resistance of the POT-modified carbon, the resulting capacitor of the POT-modified carbon has shown its superiority in power density over the capacitor assembled with the PANI-modified carbon.

4. Conclusions

The present work has shown that POT is more effective than widely recognized PANI in enhancing the electrochemical capacitance of activated carbon fabric through electrochemical deposition. Because of the presence of the electron-donating methyl group in the phenyl ring of POT, the p-doping of the polymer during charge can be enhanced, thus improving the energy storage capability of POT. The capacitance of the POT-modified carbon can be more than twice higher than that of the bare carbon. The capacitance per unit weight of the deposited POT was found to decrease with the amount of POT deposition, indicating an increase of the ion migration resistance that increasingly obstructs some polymer from the access of ions.

In addition to the capacitance enhancement, POT shows its superiority over PANI in reducing the resistance of the carbon electrode in H_2SO_4 . The low resistance resulting from POT deposition can be attributed to the loose tangle of polymer chains due to the presence of methyl group and the void feature of the polymer film, both of which facilitate ion migration into the polymer film and carbon micropores. The low resistance of the POT-modified carbon resulted in an assembled capacitor exhibiting a relatively high power density.

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References

- [1] L. Bonnefoi, P. Simon, J.F. Fauvarque, C. Sarrazin, J.F. Sarrau, A. Dugast, *J. Power Sources* 80 (1999) 149.
- [2] R. Kötz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483.
- [3] H. Shi, *Electrochim. Acta* 41 (1996) 1633.
- [4] J.P. Zheng, T.R. Jow, *J. Power Sources* 62 (1996) 155.
- [5] B.E. Conway, *Electrochemical Supercapacitors*, Kluwer-Plenum, New York, 1999.
- [6] I. Tanahashi, A. Yoshida, A. Nishino, *J. Electrochem. Soc.* 137 (1990) 3052.
- [7] M. Ishikawa, M. Ihara, M. Morita, Y. Matsuda, *Electrochim. Acta* 40 (1995) 2217.
- [8] A. Rudge, I. Raistrick, S. Gottesfeld, J.P. Ferraris, *Electrochim. Acta* 39 (1994) 273.
- [9] V. Barsukov, S. Chivikov, *Electrochim. Acta* 41 (1996) 1773.
- [10] K. Roßberg, G. Paasch, L. Dunsh, S. Ludwig, *J. Electroanal. Chem.* 443 (1998) 49.
- [11] H.Y. Lee, J.B. Goodenough, *J. Solid State Chem.* 144 (1999) 220.
- [12] C.C. Hu, K.H. Chang, *Electrochim. Acta* 45 (2000) 2685.
- [13] V. Srinivasan, J.W. Weidner, *J. Electrochem. Soc.* 147 (2000) 880.
- [14] J.H. Park, O.O. Park, *J. Power Sources* 111 (2002) 185.
- [15] K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, John Wiley and Sons, New York, 1988.
- [16] I. Tanahashi, A. Yoshida, A. Nishino, *Carbon* 28 (1990) 477.
- [17] S. Biniak, B. Dzielonczyk, J. Siedlewski, *Carbon* 33 (1995) 1255.
- [18] X. Liu, T. Osaka, *J. Electrochem. Soc.* 144 (1997) 3066.
- [19] M. Endo, T. Maeda, T. Takeda, Y.J. Kim, K. Koshihara, H. Hara, M.S. Dresselhaus, *J. Electrochem. Soc.* 148 (2001) 910.
- [20] E. Frackowiak, F. Béguin, *Carbon* 39 (2001) 937.
- [21] C.T. Hsieh, H. Teng, *Carbon* 40 (2002) 667.
- [22] Y.R. Nian, H. Teng, *J. Electrochem. Soc.* 149 (2002) 1008.
- [23] D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, S. Shiraishi, H. Kurihara, A. Oya, *Carbon* 41 (2003) 1765.
- [24] Y. Soneda, M. Toyoda, K. Hashiya, J. Yamashita, M. Kodama, H. Hatori, M. Inagaki, *Carbon* 41 (2003) 2680.
- [25] T. Momma, X. Liu, T. Osaka, Y. Ushio, Y. Swada, *J. Power Sources* 60 (1996) 249.
- [26] K. Jurewicz, E. Frackowiak, *Mol. Phys. Rep.* 27 (2000) 36.
- [27] M. Ishikawa, A. Sakamoto, M. Morita, Y. Matsuda, K. Ishida, *J. Power Sources* 60 (1996) 233.
- [28] W.C. Chen, T.C. Wen, H. Teng, *Electrochim. Acta* 48 (2003) 641.
- [29] J.M. Miller, B. Dunn, T.D. Tran, R.W. Pekala, *J. Electrochem. Soc.* 144 (1997) 309.
- [30] Y. Sato, K. Yomogida, T. Nanaumi, K. Kobayakawa, Y. Ohsawa, M. Kawai, *Electrochem. Solid-State Lett.* 3 (2000) 113.
- [31] W. Sugimoto, T. Ohnuma, Y. Murakami, Y. Takasu, *Electrochem. Solid-State Lett.* 4 (2001) 145.
- [32] K. Naoi, K.I. Kawase, M. Mori, M. Komiyama, *J. Electrochem. Soc.* 144 (2001) 173.
- [33] B. Carcia, D. Belanger, *Synth. Met.* 98 (1998) 135.
- [34] J.P. Ferraris, M.M. Eissa, I.D. Brotherson, D.C. Loveday, *Chem. Mater.* 10 (1998) 3528.
- [35] F. Fusalba, P. Guerec, D. Villers, D. Belanger, *J. Electrochem. Soc.* 148 (2001) 1.
- [36] D. Belanger, X. Ren, J. Davey, F. Uribe, S. Gottesfeld, *J. Electrochem. Soc.* 147 (2000) 2923.
- [37] A. DiFabio, A. Giorgi, M. Mastragostino, F. Soavi, *J. Electrochem. Soc.* 148 (2001) 3167.
- [38] D.E. Stillwell, S.M. Park, *J. Electrochem. Soc.* 135 (1988) 2254.
- [39] K. Rajendraprasad, N. Munichandraiah, *J. Electrochem. Soc.* 149 (2002) 1393.
- [40] S. Cattarin, L. Doubova, G. Mengoli, G. Zotti, *Electrochim. Acta* 33 (1988) 1077.
- [41] Y.B. Shim, M.S. Won, S.M. Park, *J. Electrochem. Soc.* 137 (1990) 538.
- [42] T.C. Wen, C. Sivakumar, A. Gopalan, *Spectrochim. Acta, Part A* 58 (2002) 167.
- [43] R. Schrebler, H. Gómez, R. Córdova, L.M. Gassa, J.R. Vilche, *Synth. Met.* 93 (1998) 187.
- [44] S.Y. Cui, S.M. Park, *Synth. Met.* 105 (1999) 91.
- [45] W.W. Focke, G.E. Wneck, G.E. Wei, *J. Phys. Chem.* 91 (1987) 5813.
- [46] C. Gabrielli, M. Keddad, N. Nadi, H. Perrot, *J. Electroanal. Chem.* 485 (2000) 101.
- [47] Y. Gofer, J.G. Killian, H. Sarker, T.O. Poehler, P.C. Searson, *J. Electroanal. Chem.* 443 (1998) 103.
- [48] Y.R. Lin, H. Teng, *Carbon* 41 (2003) 2865.