

Short communication

# Electrochemical deposition of polypyrrole for symmetric supercapacitors

B. Muthulakshmi, D. Kalpana\*, S. Pitchumani, N.G. Renganathan

*Central Electrochemical Research Institute, Karaikudi, Tamilnadu 630 006, India*

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## Abstract

Composite electrodes for supercapacitors were prepared via electrochemical polymerization onto activated carbon. The capacitance properties were investigated using cyclic voltammetry (CV), AC impedance spectroscopy and charge–discharge tests. These electrodes show a specific capacitance of about  $354 \text{ F g}^{-1}$ . This indicates that the in situ electro-polymerization of pyrrole onto carbon could improve the performance of carbon electrodes for use in supercapacitors.

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## 1. Introduction

Conducting polymers have been used as alternatives to metals or inorganic semiconductors in the fabrication of micro-electronic, optoelectronic and microelectro-mechanical devices [1–3]. The conjugated double bonds in the backbone of the conducting polymers allow free movement of electrons within the conjugating length, which makes them electrically conductive [4]. Among the conducting polymers, polypyrrole is an intrinsically conducting polymer most studied because of its high conductivity, high storage ability, good thermal and environmental stability, high redox and capacitive current and biocompatibility [5–9].

Polypyrrole can be synthesized by chemical polymerization [10], chemical vapor deposition [11] and electrochemical polymerization [12]. However, the disadvantages of conducting polymers include a lower cycle life in charge–discharge than carbon based electrodes because the redox sites in the polymer backbone are not sufficiently stable for repeated redox processes. While activated carbon (AC) has a higher cycle life, its electrical conductivity and capacitance values are lower than those of conducting polymers [13].

In order to enhance the capacitance and the conductivity of carbon-based supercapacitors, utilization of carbon as a composite especially with electronically conducting polymers is consid-

ered to be a better option. Hence we have attempted to fabricate a AC/polypyrrole composite by in situ electro-polymerization of pyrrole onto activated carbon which has indeed shown high capacitance and conductivity. This methodology also permits incorporation of polypyrrole onto larger size electrodes similar to the electrodeposition of metals. The additional advantage of using polypyrrole in the carbon composite is an increase in the permissible voltage for charge/discharge of the capacitor, which has an important practical application. For this purpose, we have chosen dopant-induced morphology modulation in polypyrrole preparation and customized it onto carbon to produce a new type of carbon–polypyrrole composite and evaluated this as an electrode in a p/p symmetrical supercapacitor cell configuration.

In the present study, polypyrrole/activated carbon composite electrodes are electrochemically fabricated and the application of composites as active electrode materials in electrochemical supercapacitors have been evaluated using cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge behaviour. The microstructures of carbon/polypyrrole composites as seen through SEM photomicrographs have determined the choice of the electrode.

## 2. Experimental

### 2.1. Preparation of carbon electrode

Activated carbon (Aldrich) was made into a paste by using *N*-methyl pyrrolidine along with a binder, polyvinylidene fluoride,

\* Corresponding author. Tel.: +91 4565 227 551; fax: +91 4565 227 651.  
E-mail address: [kalpss@yahoo.com](mailto:kalpss@yahoo.com) (D. Kalpana).

in the ratio of 70:30 using a pestle and mortar. This paste was then applied with a brush to a pre-weighed stainless steel current collector and dried at room temperature.

## 2.2. Incorporation of polypyrrole onto carbon

Pyrrole (SRL, 98%) was distilled prior to use.  $\beta$ -Naphthalene sulphonic acid ( $\beta$ -NSA) (99% Himedia, India) was used in as-received condition as a dopant cum electrolyte. The growth of polypyrrole was carried out at room temperature in a one-compartment cell by galvanostatic polymerization using an electrochemical analyzer (BAS Electrochemical Analyzer 100B). The working electrode was activated carbon coated stainless steel ( $1\text{ cm}^2$ ) and a Pt plate ( $5\text{ cm}^2$ ) was used as the counter electrode. All potentials were referred to a saturated calomel electrode (SCE). The typical electrolyte was an aqueous solution of 0.5 M Pyrrole and 0.5 M  $\beta$ -NSA. Polypyrrole was electrochemically deposited onto the carbon material with a constant current density of  $0.36\text{ mA cm}^{-2}$  for 300 s. Electrochemical half-cell measurements were conducted in a three-electrode cell equipped with a reference electrode (SCE), Pt as counter electrode and carbon/polypyrrole composite electrode as the working electrode.

## 2.3. Fabrication of symmetrical p/p supercapacitor cell

The capacitor cells were constructed with an electrolyte-impregnated separator sandwiched between two symmetrical AC/polypyrrole composite electrodes (p/p). The electrodes were pre-wetted with electrolyte before use. The capacitor performance was characterized by means of cyclic voltammetry

(CV) (BAS Electrochemical Analyzer 100B), AC impedance measurements in the frequency range 100 KHz–10 Hz (EG&G Princeton Applied Research, system model 6310) and galvanostatic charge/discharge cycling at different current densities (Won-A-Tech Automatic Battery Cycler).

## 3. Results and discussions

### 3.1. SEM analysis

Fig. 1(a)–(d) shows the scanning electron microscopic images of polypyrrole microstructures deposited onto stainless steel panel and on activated carbon obtained by in situ electro-polymerization. These indicate that the different microstructures can be evolved through the use of  $\beta$ -naphthalene sulfonic acid as a dopant in the form of rods (Fig. 1(a)) porous (Fig. 1(b)) dense film like form (Fig. 1(c)) and globular particulate (Fig. 1(d)). Of these the porous structure as seen in Fig. 1(b) is chosen for the electrode fabrication as it is expected to yield a high capacitance. In this manner, the required electrode morphology has been chosen for subsequent supercapacitor cell assembly and evaluation.

### 3.2. Cyclic voltammetry responses

Cyclic voltammogram for the AC/polypyrrole single electrode and p/p supercapacitor cell assembled at various sweep rates are shown in Fig. 2(a) and (b). The single electrode response clearly shows the capacitive characteristic as well as the corresponding redox features of polypyrrole under doping and dedoping. On the other hand the cell assembled has shown the typical

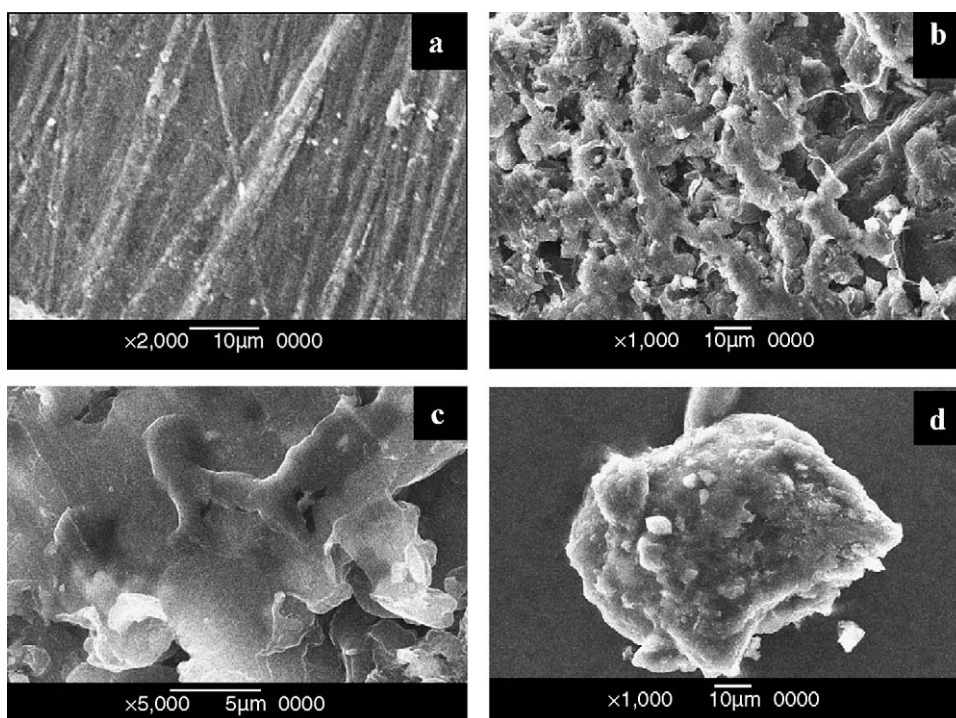


Fig. 1. SEM of polypyrrole microstructure (a) on stainless steel panel (b) on activated carbon. Polypyrrole/activated carbon composite with (c) 5000 magnification and (d) 1000 magnification.

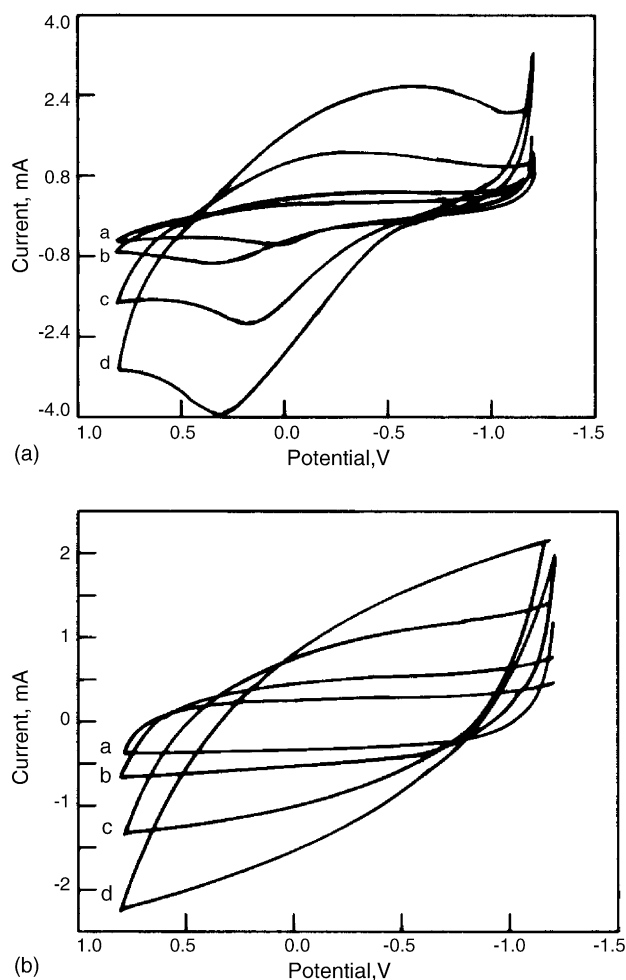


Fig. 2. (a) CV response for the AC/polypyrrole single electrode at scan rates: (a)  $1 \text{ mV s}^{-1}$ , (b)  $2 \text{ mV s}^{-1}$ , (c)  $10 \text{ mV s}^{-1}$ , and (d)  $20 \text{ mV s}^{-1}$ . (b) Symmetric capacitor at scan rates: (a)  $1 \text{ mV s}^{-1}$ , (b)  $2 \text{ mV s}^{-1}$ , (c)  $10 \text{ mV s}^{-1}$ , and (d)  $20 \text{ mV s}^{-1}$ .

features of capacitive behaviour synchronizing both double layer and redox capacitive features.

The capacitance values for the symmetric capacitor have been calculated from the cyclic voltammograms using the equation:

$$C_L = \frac{i}{s}$$

where  $s$  is the potential sweep rate and  $i$  is the average current.

Specific capacitance of  $354 \text{ F g}^{-1}$  was obtained for the single electrode at the sweep rate of  $1 \text{ mV s}^{-1}$ . The output currents

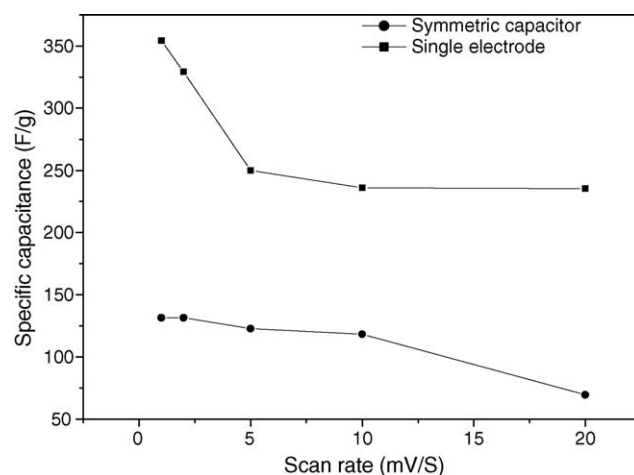


Fig. 3. Specific capacitance of the single electrode and the symmetric capacitor at various scan rates.

indicate that the capacitance of the polypyrrole single electrode was about twice that of the AC/polypyrrole composite. This is quite justifiable, as two carbon/polypyrrole electrodes constitute the electrochemical configuration of a parallel plate condenser connected in series. The capacitance of the individual carbon and polypyrrole composite electrode is given in Table 1. Specific capacitance of AC/polypyrrole composite electrode is higher at all sweep rates compared to specific capacitance values of AC electrode. The value of capacitance is one order higher than for single polypyrrole electrode which is attributed to the combined effect of double layer and redox supercapacitor capacitive behaviour as seen in their cyclic voltammogram compared to redox capacitance in simple polypyrrole electrode. Fig. 3 shows the specific capacitance for the single electrode and symmetric capacitor at various scan rates. The slightly decreased slope of the specific capacitance indicates good power characteristics of the symmetric configuration.

### 3.3. Electrical properties of electrochemical capacitor

The AC impedance response of single electrode is shown in Fig. 4. Electrodes were subjected to various potentials and the impedance characteristics were recorded is given in Fig. 5. For the single electrode and the capacitor, a semicircle is obtained at high frequency in the range 100 KHZ–10 Hz and a straight line in

Table 1  
Capacitance of the individual AC/polypyrrole and symmetric capacitor

Specific capacitance from CV (single electrode) ( $\text{F g}^{-1}$ )		Specific capacitance from CV (symmetric capacitor) ( $\text{F g}^{-1}$ )		Specific capacitance from charge–discharge at various current densities		
Scan rate ( $\text{mV s}^{-1}$ )		Scan rate ( $\text{mV s}^{-1}$ )		$1 \text{ mA cm}^{-2}$	$2 \text{ mA cm}^{-2}$	$5 \text{ mA cm}^{-2}$
1	354.25	1	131.57	$40.4 \text{ F g}^{-1}$	$36 \text{ F g}^{-1}$	$8.33 \text{ F g}^{-1}$
2	329.28	2	131.52			
5	250.0	5	122.77			
10	236.07	10	118.41			
20	235.35	20	69.44			

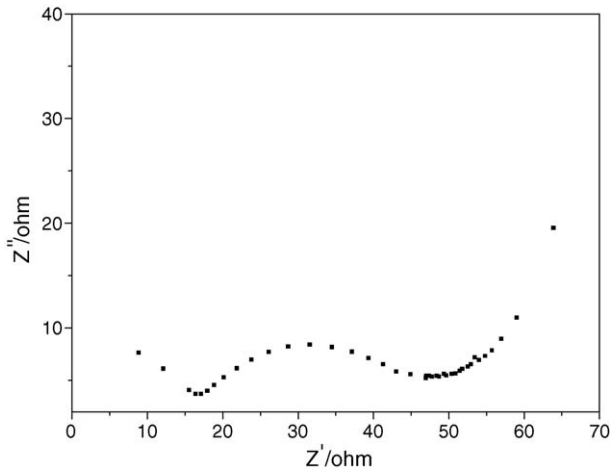


Fig. 4. The AC impedance response of the AC/polypyrrole single electrode.

the low-frequency region. The capacitance values increase at low frequencies due to a larger number of ions moving which cause a decrease in the bulk resistance of the capacitor. The semicircle results from the parallel combination of resistance and capacitance and the linear region is due to Warburg impedance. In the low frequency region, the linear region leans more towards imaginary axis and this indicates good capacitive behavior (as the angle  $\phi$  approaches  $\sim 90^\circ$  it exhibits a good capacitive behavior). Hybrid capacitor and carbon capacitor electrodes behave almost similarly in the high frequency region but AC/polypyrrole hybrid is more capacitive compared to simple carbon capacitors as is evident in the low frequency region. From Fig. 5, it is evident that at 0 V the AC/polypyrrole hybrid capacitor is more capacitive than at 1 V.

### 3.4. Charge–discharge characteristics

Fig. 6a shows the charge–discharge curves at a constant current density of  $1 \text{ mA cm}^{-2}$  at  $25^\circ\text{C}$ . It is realized that this type

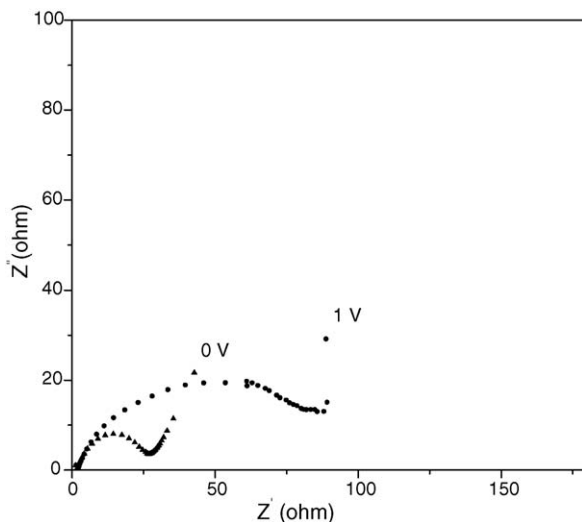


Fig. 5. The AC impedance response of the capacitor at 0 and 1 V.

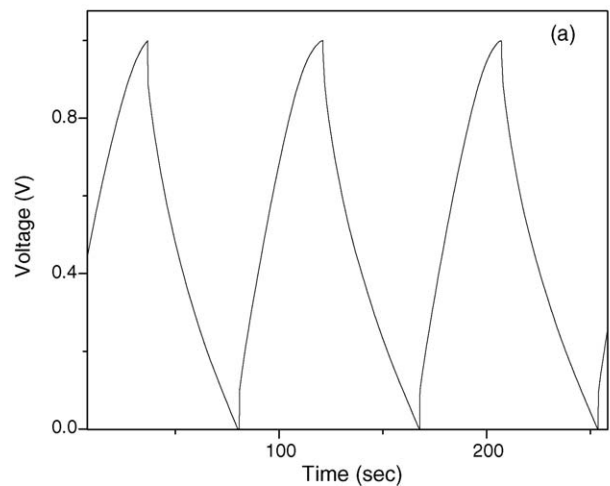
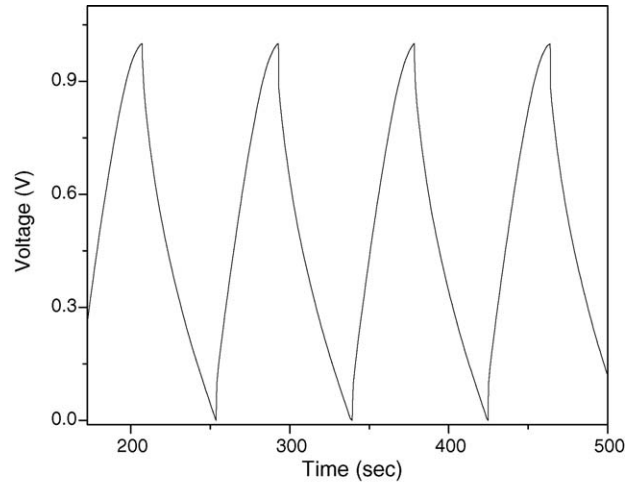


Fig. 6. (a) Charge–discharge curves at a constant current density of  $1 \text{ mA cm}^{-2}$  at  $25^\circ\text{C}$  and (b) after 4000th cycle.

of p/p supercapacitor configuration based on polypyrrole has a lower IR drop after 4000 cycles clearly indicating that the composite features of carbon and polypyrrole are noteworthy and an optimized composition may lead to higher capacitance with the required electrical connectivity between carbon and polypyrrole. However after 4000 cycles (Fig. 6(b)), the IR drop was observed during both charge and discharging processes and is attributed to the beginning of the degradation of polypyrrole redox activity. Though the charging and discharging process was found to be possible up to 20,000 cycles, the supercapacitor cell in this particular configuration was best up to 4000 cycles. Further, the increase of current density in the charging–discharging cycles has been found to decrease the time required to obtain the cut-off voltage, which ultimately leads to a decrease in capacitance. This may be overcome by choosing appropriate packing conditions for the cell assembly. Based on this study, a preliminary evaluation of the cell capacitance has been made and is indicated in Table 1. The symmetric type EC capacitor based on electrochemically prepared polypyrrole and activated carbon composites possesses a cycle life of about 20,000 cycles and a coulombic efficiency of about 98% (Fig. 7).

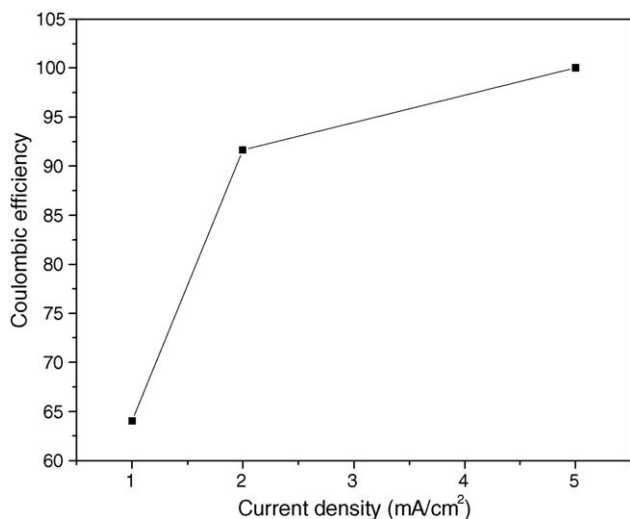


Fig. 7. Coulombic efficiency of the symmetric AC/polypyrrole supercapacitor.

#### 4. Conclusion

Using dopant-induced polypyrrole microstructures, a new composite of AC/polypyrrole has been evolved using in situ electro-polymerization and evaluated as a supercapacitor electrode. SEM photomicrographs have been used as a diagnostic tool to identify the best electrode morphology. The electrode so formed has been found to be a suitable electrode for capacitive applications and the cyclic voltammetric data has indicated

an electrode specific capacitance of  $345 \text{ F g}^{-1}$ , which, configured as p/p supercapacitor, shows a specific capacitance of  $131 \text{ F g}^{-1}$ . The AC impedance studies show that the capacitance value increases at low frequencies. The charge–discharge curves obtained at a constant current density of  $1 \text{ mA cm}^{-2}$  at  $25^\circ\text{C}$  have shown that there is a minimal IR drop up to 4000 cycles in the new configuration of p/p supercapacitor cells based on polypyrrole.

#### References

- [1] B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic Publishing/Plenum Press, New York, 1999.
- [2] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483.
- [3] A. Burke, *J. Power Sources* 91 (2000) 37.
- [4] Y. Shen, M. Wan, *Synth. Met.* 96 (1998) 127.
- [5] Q.-Wu Zhang, X. Zhou, H.-S. Yang, *J. Power Sources* 125 (2004) 141.
- [6] H.C. Kang, K.E. Geckeler, *J. Polym.* 41 (2000) 6931.
- [7] A. Laforgue, P. Simon, C. Sarrazin, J.F. Fauvarque, *J. Power Sources* 142 (1999) 80.
- [8] J.Y. Lee, D.Y. Kim, C.V. Kim, *Synth. Met.* 74 (1995) 103.
- [9] K. Hycok, A.K. Ku, J. Jeong, K. He, H. Lee, *J. Electrochem. Soc.* 149 (2002) A1058.
- [10] Q. Xiao, X. Zhou, *J. Electrochem. Acta* 48 (2003) 575.
- [11] Y.K. Zhou, B.L. He, W.J. Zhou, J. Hiuang, X. Li, B. Wu, H. Li, *J. Electrochem. Acta* 49 (2004) 257.
- [12] C. Arbizzani, M. Mastragostino, L. Meneghello, *Electrochim. Acta* 41 (1996) 21.
- [13] K. Jurewicz, S. Delpeux, V. Bertagna, F. Béguin, E. Frackowiak, *J. Chem. Phys. Lett.* 347 (2001) 36.