Performance evaluation of poly(*N*-methylaniline) and polyisothianaphthene in charge-storage devices

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Abstract

The charge–discharge characteristics of Li/poly(*N*-methylaniline) (PNMA) coin cells with an ethylenecarbonate–dimethylcarbonate mixture containing 1 M LiClO$_4$ as electrolyte are studied. The PNMA is modified from a p-doped polymer to a self-doped polymer by a simple sulfonation procedure and its performance in a rechargeable cell is evaluated. Parallel experiments on polyaniline and sulfonated polyaniline are also performed. The application of the low band-gap polymer polyisothianaphthene (PITN) in a non-aqueous rechargeable cell and also in a capacitor is studied.
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1. Introduction

Conducting polymers are expected to be potential cathode active-materials in rechargeable batteries due to certain specific advantages such as light weight, rapid synthesis by electrodeposition, and absence of electrode dissolution. The literature on the application of various conducting polymers in rechargeable batteries has been reviewed in detail [1–3]. Polyaniline is the most studied electroactive polymer for both aqueous and lithium battery applications and specific capacity values that range from 44 to 270 Ah kg^{-1} have been reported. Apart from the use of conducting polymer electrodes in rechargeable cells, there have been several innovative approaches in the design of polymeric supercapacitors [4–6]. Conducting polymers such as polypyrrole, polyaniline, poly(3-arylthiophene), poly(3-methylthiophene), poly(3,4-fluorothiophene) and poly(1,5-diaminoanthraquinone) have been suggested by several authors as electrodes for electrochemical capacitors [7–21]. Recently, some composite polymer electrodes with carbon and carbon nanotubes have been tested as positive and negative electrodes in supercapacitors for electric-vehicle applications [15,22,23].

Recently, we reported the characterization of poly(*N*-methylaniline) (PNMA) and its sulfonated analogue in aqueous rechargeable batteries [24]. In this study, for the first of time, the application of PNMA and polyisothianaphthene (PITN) as cathode active-materials in non-aqueous coin cells with lithium as anode has been attempted. For comparative purposes, a few related experiments on polyaniline (PANI) have also been conducted. The performance of a capacitor based on PITN is also evaluated.

PNMA is expected to be different from polyaniline because of the blockage of the proton-exchange sites by methyl substituents [25–27]. Our recent study has shown that PNMA is more redox active with a lower risk of degradation compared to PANI [28]. PITN is a low-band gap polymer and can be both p- and n-doped [29,30]. There have been some studies on its synthesis, electrochemical properties and applications in antistatic coatings and electronic memory devices [31–36].

2. Experimental

Analar grade aniline (s.d.fine) and *N*-methylaniline (SRL) were used after vacuum distillation. Propylene carbonate (PC), ethylene carbonate (EC) and dimethylcarbonate (DMC) (Merck) were vacuum distilled, treated with molecular sieves to remove any residual water, and then used. AR grades of α,α′-dibromo-*o*-xylene (Acros), sodium sulfide,

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sodium periodate (s.d.fine), alumina (SRL), tetrabutylammoniumtetrafluoborate (Merck), lithium perchlorate (Acros), phenylhydrazine, diethylether, dichloromethane (Merck), sulfuric acid and 20% fuming sulfuric acid (s.d.fine) were used as received.

Electrochemical experiments were performed with an EG&G, PAR potentiostat/galvanostat (model 263 A). Impedance studies were conducted with an EG&G PAR (model 6310) electrochemical impedance analyzer. Surface images of thin films of PITN coated on indium tin oxide were obtained by means of a Shimadzu (model SPM 9500) atomic force microscope (AFM).

Details of the preparation of PANI, PNMA sulfonated polyaniline (SPANI) and sulfonated poly(*N*-methylaniline) (SPNMA) have been reported previously [24]. The PANI was electrodeposited on a Pt substrate from an aqueous electrolyte of 0.5 M aniline and 0.5 M HClO$_4$ by potentiostatic control at 0.65 V versus SCE. A galvanostatic (2 mA cm^{-2}) method was employed to obtain bulk quantities of PNMA. The p-doped polymers were dried completely in a vacuum desiccator for 1 week. The PANI sample gave a conductivity of 14 S cm^{-1} while PNMA showed a value of 1.1 × 10^{-2} S cm^{-1}.

The self-doped sulfonated polymers were prepared as follows. PANI and PNMA were first obtained by chemical polymerization of the monomer (0.5 M) in the presence of 0.5 M H$_2$SO$_4$ using ammonium persulfate (0.6 M) at 0–5 °C. The product, emeraldine salt, was washed well in double-distilled water and dried in vacuum. It was then stirred with 1 M NH$_4$OH for 2 h to give the emeraldine base form. The emeraldine base was then sulfonated by treatment of 0.5 g of the material with 2.5 ml of phenylhydrazine for 1 h followed by washing with ether and drying. The product was then treated with 10 ml of 20% fuming sulfuric acid that was pre-cooled to 5 °C for 1 h. The resulting mixture was then poured into 100 ml of ice-cold methanol, filtered, washed repeatedly with fresh methanol, and dried. The yield of both of the sulfonated polymers was about 60%. The conductivity of the pellets of sulfonated polyaniline and sulfonated poly(*N*-methylaniline) was found to be 2 × 10^{-2} and 4 × 10^{-4} S cm^{-1}, respectively.

The monomer isothianaphthene was synthesized from α,α′-dibromo-*o*-xylene following the methods of King et al. [37,38] and Cava et al. [39]. The procedure involved three steps: (i) refluxing α,α′-dibromo-*o*-xylene with Na$_2$S for 1 h to obtain 1,3-dihydroisothianaphthene; (ii) oxidation of the above product using NaIO$_4$ to produce 1,3-dihydroisothianaphthene-2-oxide; (iii) conversion of the oxide to isothianaphthene by sublimation in the presence of neutral Al$_2$O$_3$. The electrochemical deposition of PITN on Pt and ITO substrates was carried out by applying a constant potential of 1 V versus Ag in propylene carbonate that contained 0.2 M Bu$_4$NBF$_4$ and 10 mM of the monomer. The conductivity of PITN was 0.1 S cm^{-1}.

3. Results and discussion

3.1. Application of PNMA in rechargeable batteries

Coin cells (model CR 2032) were constructed with PNMA as the positive electrode and lithium as the negative electrode. The electrolyte was a 1:1 mixture of ethylene carbonate and dimethyl carbonate (DMC) containing 1 M LiClO$_4$. The polymer is found to be redox active and also shows good stability in the chosen electrolyte. Representative results of the charge–discharge cycling of the assembled Li/PNMA coin cell under a constant current density of 100 μA cm^{-2} are given in Fig. 1(a). The specific capacity of a cell is plotted against cycle number in Fig. 1(b). From the cycle numbers 1 to 8, the cut-off potentials for charging and discharging are fixed at 3.6 and 2.5 V, respectively. Except for the first cycle, the cell gives a nearly constant specific capacity of about 52 mAh g^{-1}. The coulombic efficiency of the cell is practically 100%. The open-circuit voltage (OCV) of
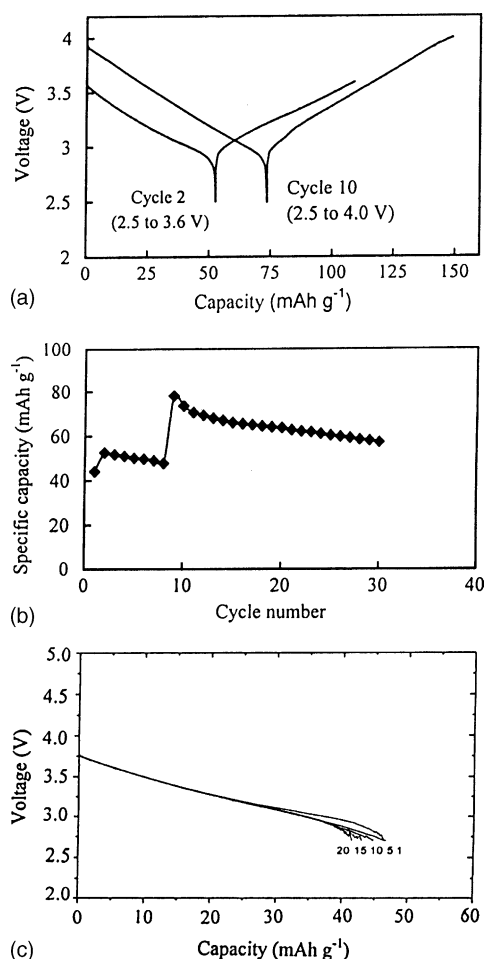

Fig. 1. (a) Charge–discharge curves of Li/EC + DMC (1:1)–1 M LiClO$_4$/PNMA cell at constant current density of 100 μA cm^{-2}. (b) Variation of specific capacity with charge–discharge cycling of cell in (a). (c) Discharge curves of cell Li/EC + DMC (1:1)–1 M LiClO$_4$/PANI at a constant current density of 100 μA cm^{-2}.

the cell is 3.4 V. The discharge reaction in this non-aqueous medium is due to the elimination of perchlorate dopant ion from the PNMA cathode with the simultaneous dissolution of the lithium anode. The results show that the charging of the polymer can take place even beyond 3.6 V. Therefore, the cut-off potential for charging was further extended from 3.6 to 4.0 V during the ninth cycle and the specific capacity was measured for a further 21 cycles. An increase of about 62% in the specific capacity is observed by extending the charging potential to 4 V. Further cycle tests show, however, a gradual decrease in the specific capacity. On the other hand, the average specific capacity of the Li/PNMA coin cell is twice that of a Zn/PNMA aqueous cell [24]. There have been several studies of the performance of Li/PANI cells and specific capacity values between 40 and 270 mAh g^{-1} have been reported [3]. For the sake of comparison, in the present work a coin cell was made with a dry PANI sample; the discharge profiles obtained during cycling at 100 μA cm^{-2} in the potential window between 2.7 and 3.8 V against Li are given in Fig. 1(c). The Li/PANI cell gives an OCV of 3.2 V and the specific capacity values are 46.7 and 41.5 mAh g^{-1} for the first and 20th cycles, respectively.

3.2. Sulfonated PANI and PNMA for battery applications

In order to examine the possibility of improving the specific capacity of PNMA, it was modified from an anion-exchange polymer to a cation-exchange electrode material by the incorporation of sulfonate groups in the backbone. Other researchers have shown that such self-doped PANI derivatives are endowed with several unique properties such as improved solubility and redox thermal stability, and are of special interest for redox-based applications [40–43]. The possible application of SPANI as cation insertion electrode in rechargeable cells has been reported by Barbero et al. [44,45]. They obtained a specific charge of 37 Ah kg^{-1} in aqueous solution and 68 Ah kg^{-1} in non-aqueous media from a calculation that involved cyclic voltammetric redox charge and polymer mass. As there have been no detailed studies on the application of SPANI in rechargeable batteries, a few systematic experiments have been carried out in the present study with SPANI as well for comparison with SPNMA.

Data from the testing of an assembled Li/SPANI cell are presented in Fig. 2. Twenty charge–discharge cycles were recorded at a current loading of 100 μA cm^{-2} in the potential window between 2.7 and 3.8 V. The cell has a high coulombic efficiency with an OCV of 3.3 V. The specific capacity, however, is only about 5 mAh g^{-1} on the first cycle. Continuous charging and discharging results in a gradual increase in the specific capacity to 13 mAh g^{-1} on the 20th cycle. The results obtained on the charge–discharge cycling of a Li/SPNMA coin cell are shown in Fig. 3. This cell was also charged and discharged at a constant current density of 100 μA cm^{-2}, and was subjected to about 100 cycles. The cell performance is improved by extending the charg-

(a)

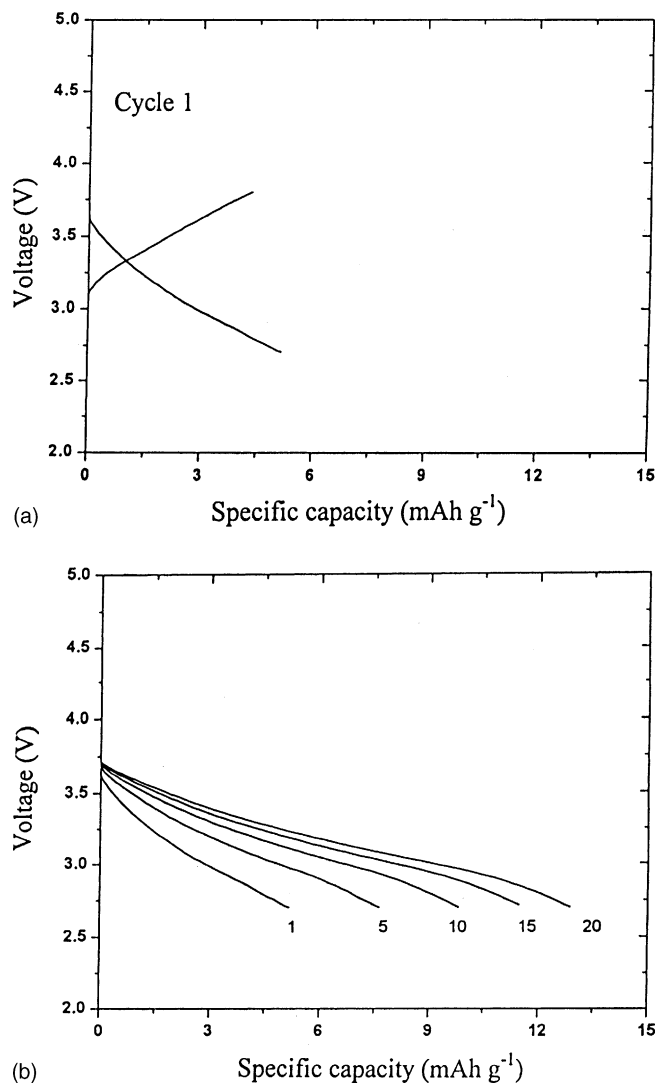
(b)

Fig. 2. (a) Charge–discharge curve of cell Li/EC + DMC (1:1)–1 M LiClO$_4$/SPANI at current density of 100 μA cm^{-2}. (b) Variation of specific capacity with successive cycles. Numbers inside figure represent cycle number.

ing potential from 3.6 to 4.5 V against Li. The discharging potential is fixed at 2.5 V versus Li. The representative charge–discharge cycles obtained at each potential window with variable charging potential are shown in Fig. 3(a). The specific capacity of the cell was calculated after each cycle and the values are plotted against cycle number in Fig. 3(b). The results demonstrate the importance of the charging potential limit. A maximum specific capacity of 30 Ah kg^{-1} can be obtained for the Li/SPNMA cell. This value is about 40% lower than that of the Li/PNMA cell but higher than the value obtained for the Li/SPANI cell.

3.3. Application of PITN in rechargeable batteries

The redox properties of the PITN film have been studied in a background electrolyte solution of 0.2 M Bu$_4$NBF$_4$ in propylene carbonate. The cyclic voltammogram shows
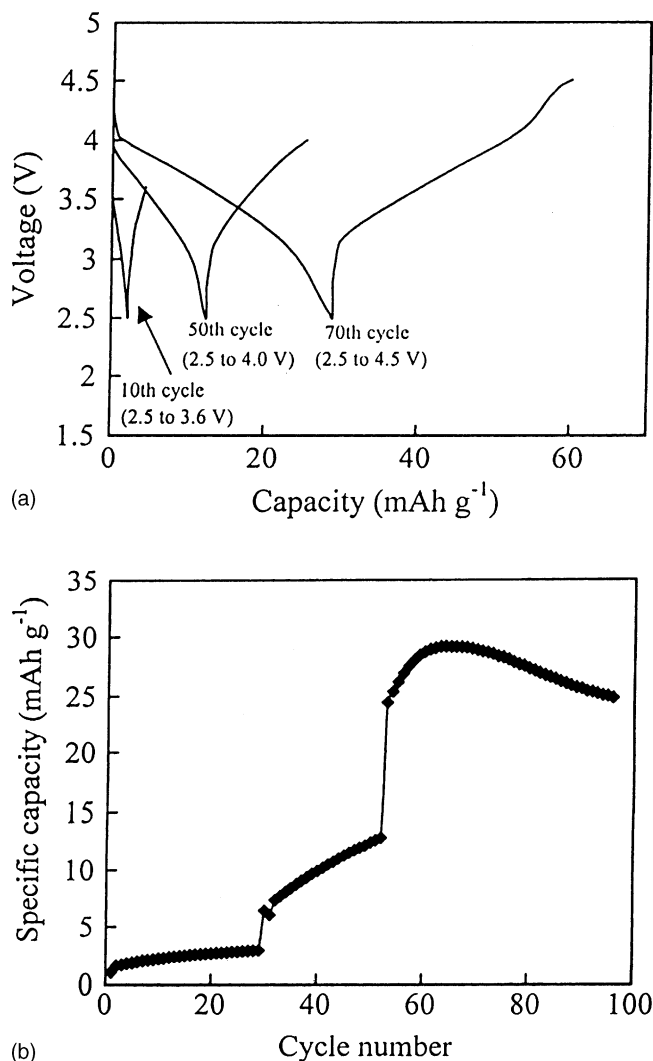
(a)

(b)

Fig. 3. (a) Charge–discharge curves of Li/EC + DMC (1:1)–1 M LiClO$_4$/SPNMA cell at constant current density of 100 μA cm^{-2}. (b) Variation of specific capacity with charge–discharge cycling of cell in (a).

(a)

(b)

Fig. 4. (a) Cyclic voltammogram of PITN film electrodeposited on Pt electrode in electrolyte solution of propylene carbonate containing 0.2 M Bu$_4$NBF$_4$. Scan rate: 20 mV s^{-1}. (b) Representative cyclic voltammograms showing effect of repeated potential cycling of PITN film coated on Pt electrode in 1 M LiClO$_4$/propylene carbonate. Scan rate: 20 mV s^{-1}. Numbers in figure represent cycle number.

the close proximity of two redox couples (Fig. 4(a)). This observation agrees well with the data of other workers for PITN in acetonitrile containing Bu$_4$NBF$_4$ [30–32]. The more positive redox couple ($E_p^a = 0.98$ V, $E_p^c = 0.74$ V) was attributed to a doping–de-doping process. The other redox couple ($E_p^a = 0.71$ V, $E_p^c = 0.47$ V) was assigned to the effects of residual charge in the polymer after de-doping. It has not been possible to prepare PITN doped with other anions such as perchlorate. Application of a constant potential of 1 V to a cell that contained 10 mM of monomer and 0.2 M of LiClO$_4$ resulted in the formation of a milky white precipitate around the anode with no film deposition. By contrast, a PITN film prepared in the presence of Bu$_4$NBF$_4$ electrolyte displays stable redox properties when transferred to the solution containing 1 M LiClO$_4$ (Fig. 4(b)). In this case, the cyclic voltammogram reveals only one redox couple ($E_p^a = 0.53$ V, $E_p^c = 0.11$ V). Repeated cycling of the film causes a marginal increase in the peak currents together
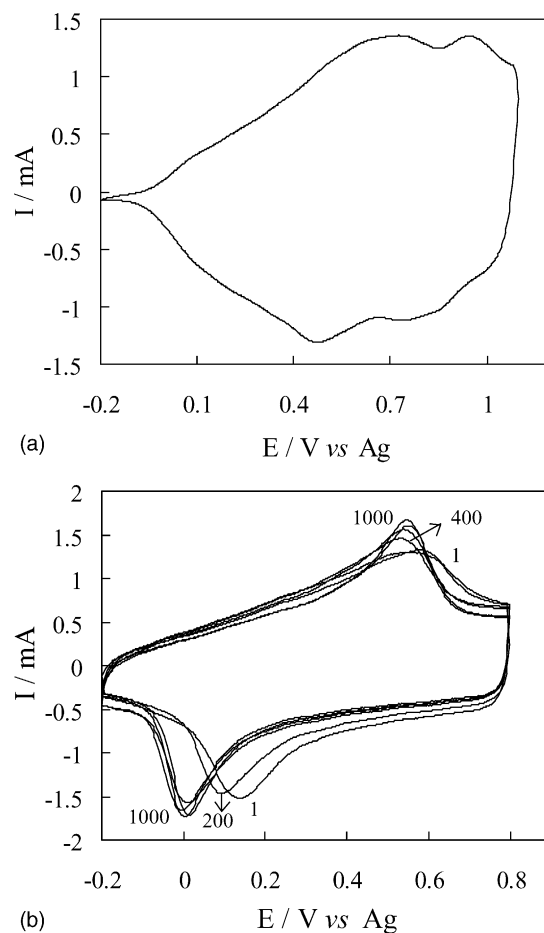
with a shift in potential. The dopant anion can influence the kinetics of the reaction [46]. The cyclic voltammogram in 1 M LiClO$_4$ represents faster kinetics (lower redox potential) with combined faradaic and capacitive currents. AFM data also supports this observation. The as-grown PITN film doped with BF$_4^-$ on ITO has a smooth and compact morphology, whereas, the same film after cycling in 1 M LiClO$_4$ has a porous structure (Fig. 5). The porous nature of the PITN-perchlorate film will be an advantage for its use as a cathode in rechargeable cells.

Rechargeable coin cells (model CR 2032) were constructed with PITN as the positive electrode and lithium as the negative electrode. The electrolyte was ethylene carbonate–dimethyl carbonate (EC–DMC) (1:1) containing 1 M LiClO$_4$. The charge–discharge curve of the cell for the second cycle is given in Fig. 6(a). The cut-off potentials are 3 and 4 V for discharging and charging at 50 μA cm^{-2}, respectively. The curves are almost symmetrical with respect to the switching line. The coulombic efficiency is virtually
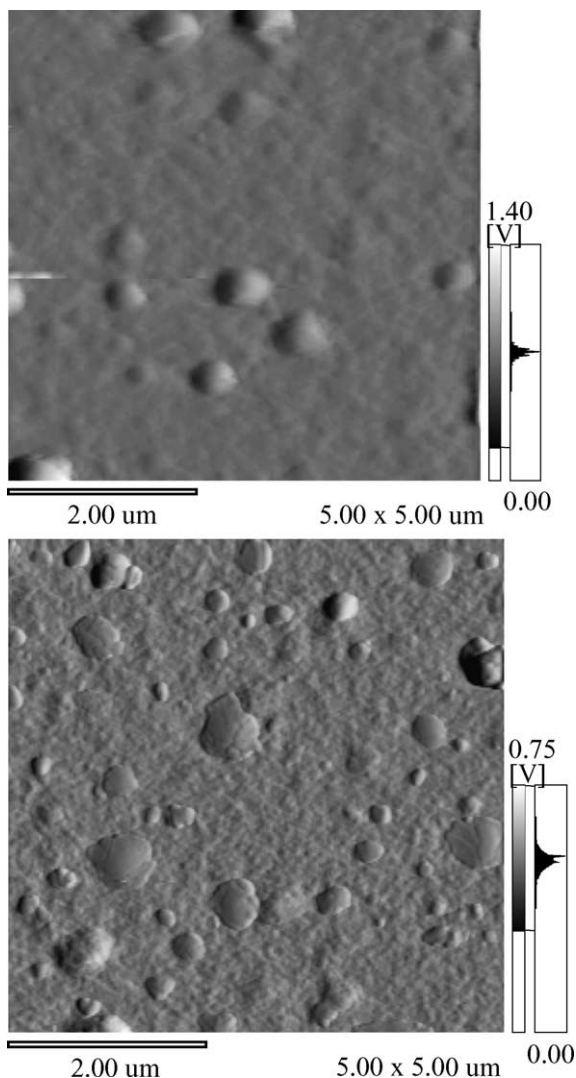
Fig. 5. AFM images of PITN film electrodeposited on ITO substrate doped with BF_4^- ion (top) and for same film after repeated cycling in solution containing ClO_4^- ion.

Fig. 6. (a) Charge–discharge curve of Li/EC + DMC (1:1)–LiClO$_4$/PITN cell at constant current density of $50\,\mu A\,cm^{-2}$. (b) Variation of specific capacity with repeated charge–discharge cycling of cell in (a).

100%. As with other conducting polymers, the charge and the discharge of PITN are due to the doping and undoping of the polymer. The specific capacity values have been calculated for 10 cycles (Fig. 6(b)). After the first cycle, the cell attains a stable specific capacity with an average of $33.5\,mAh\,g^{-1}$. The cell OCV is 3.1 V.

3.4. Performance of PITN in supercapacitors

Various types of supercapacitors can be envisioned according to the polymer or set of polymers under consideration [4]. Type I supercapacitors use the same p-dopable conducting polymer at both electrodes. In Type II devices, two different p-dopable conducting polymers are used as the active materials, while in Type III, the conducting polymer electrode can be both p- and n-doped. The cell voltage can be about 1, 1.5 and more than 3 V in Types I, II and III capacitors, respectively. Type III has two further advantages
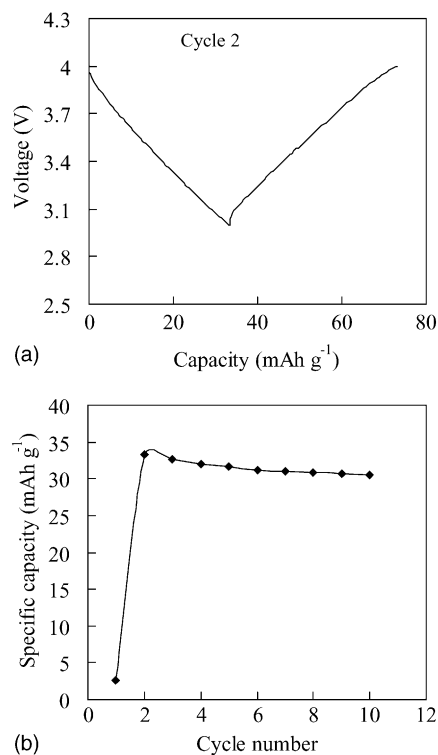
over Types I and II. First, the instantaneous power density on discharge is greater, because both electrodes are in a doped, conducting state when the capacitor is fully charged. In Types I and II, however, one of the polymer films is in the undoped, semi-insulating state when the capacitor is charged and this could introduce a higher resistance into the fully-charged device. Second, Type III capacitors are advantageous because all the charge is released at relatively high cell voltages, and hence, there will be no redundant charge stored at voltages that are too low to be useful.

PITN is considered to be a suitable active electrode material for the construction of a supercapacitor due to the following two reasons.

(i) Observations in literature [30,32] that PITN can be both p- and n-doped electrochemically make it a viable candidate material for assembling a Type III supercapacitor which can give a higher output voltage and energy density compared with Types I and II.
(ii) In the present work, the cyclic voltammogram of PITN doped with either BF_4^- ions or ClO_4^- ions approximates the behavior of a quasi-reversible couple with the distinguishing characteristics of large capacitive currents [47] once oxidation is complete.

In this study, it has been possible to construct only a Type I capacitor and not a Type III capacitor, as stable films of n-doped PITN could not be obtained electrochemically under the conditions employed. Two identical p-doped
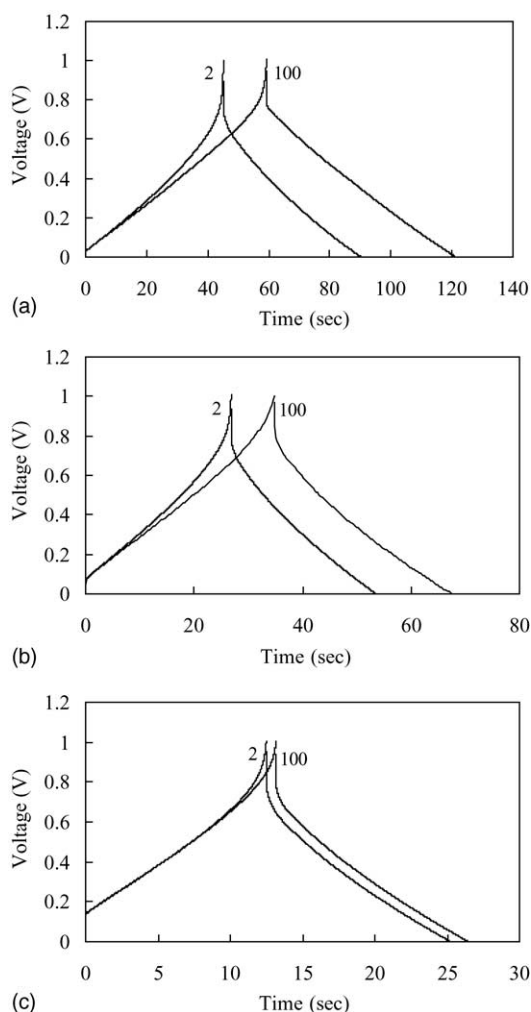
Fig. 7. Galvanostatic charge–discharge cycling of PITN–PITN supercapacitor in 1 M Et$_4$NBF$_4$/propylene carbonate at current density of (a) 0.25, (b) 0.5 and (c) 1 mA cm^{-2}. Numbers in figure denote cycle number.

Fig. 8. Impedance spectrum of PITN–PITN supercapacitor in 1 M Et$_4$NBF$_4$/propylene carbonate in frequency range 10 mHz to 100 kHz. Polarization potential is 0 V.

Fig. 9. Variation of open-circuit voltage of PITN–PITN supercapacitor against time.

PITN films were prepared and assembled at a separation distance of 0.5 cm. The electrolyte was 1 M Et$_4$NBF$_4$ in propylene carbonate. The cell was charged up to 1 V and discharged to 0 V at 0.25, 0.5 and 1 mA cm^{-2}. In order to characterize the polymer under conditions that simulate those used in practical applications of supercapacitors, about 100 cycles of charge and discharge were recorded at each of the chosen three current densities. The typical charge–discharge curves obtained for the 2nd and 100th cycle are presented in Fig. 7. The curves are symmetrical with respect to the switching line and the coulombic efficiency is nearly 100%. There is, however, a gradual increase in the charge–discharge time on continuous cycling of the cell as has been found for poly(3-methylthiophene) and poly(cyano-substituted-diheteroareneethylene) [14,16].

The impedance spectrum of the capacitor when one of the PITN electrodes is polarized at 0 V is given in Fig. 8. The plot shows the charge saturation region in the frequency range between 10 and 60 mHz. The low-frequency capacitance is calculated to be 40 F g^{-1}, based on the weight of
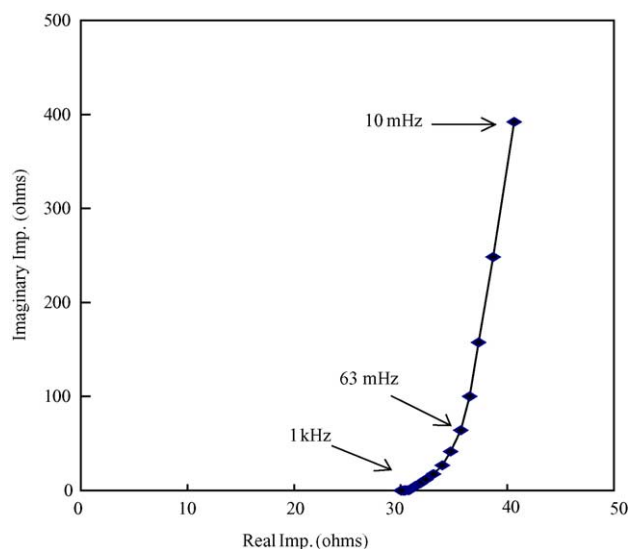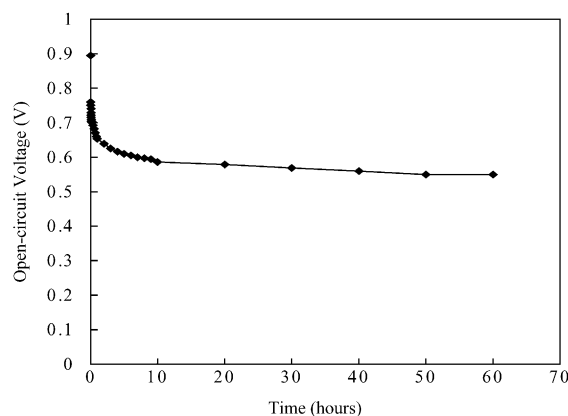
the polymer deposited on both of the electrodes (1 mg). To measure the OCV, capacitor is charged to 1 V for 1 min and the change in cell potential is monitored as a function of time (Fig. 9). The capacitor shows a stable output voltage of about 0.55 V after a time of 10 h of standing.

4. Conclusions

Coin cells are constructed using PANI, PNMA, SPANI, SPNMA and PITN cathodes with lithium as anode in a mixture of ethylene carbonate + propylenecarbonate containing 1 M LiClO$_4$ as electrolyte. The cell characteristics are summarized in Table 1. Of the five cells, the Li/PNMA cell offers the best performance with an OCV of 3.4 V and a specific capacity of 52 Ah kg^{-1}. Both Li/SPANI and Li/SPNMA give low values of specific capacity. PITN is considered to perform better in a supercapacitor device. A

Table 1
Comparison of cell performance for five polymers

No.	Cathode	Anode	Electrolyte	OCV (V)	Specific capacity (Ah kg^{-1}) (current rating)
1	PANI	Li	EC + DMC (1:1), 1 M LiClO$_4$	3.2	41.5 (100 μA cm^{-2})
2	PNMA	Li	EC + DMC (1:1), 1 M LiClO$_4$	3.4	52 (100 μA cm^{-2})
3	SPANI	Li	EC + DMC (1:1), 1 M LiClO$_4$	3.3	13 (100 μA cm^{-2})
4	SPNMA	Li	EC + DMC (1:1), 1 M LiClO$_4$	3.4	30 (100 μA cm^{-2})
5	PITN	Li	EC + DMC (1:1), 1 M LiClO$_4$	3.1	33.5 (50 μA cm^{-2})
6	PITN[a]	PITN	PC, 1 M Bu$_4$NBF$_4$	0.55	Capacitance is 40 F g^{-1}

[a] Supercapacitor.

Type I supercapacitor shows a stable output voltage of 0.55 V with a low-frequency capacitance of 40 F g^{-1}.

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