Short communication

# Electropolymerization of high stable poly(3,4-ethylenedioxythiophene) in ionic liquids and its potential applications in electrochemical capacitor

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## Abstract

Poly(3,4-ethylenedioxythiophene) (PEDOT) has been successfully electropolymerized using a purified 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) as both the growth medium and the supporting electrolyte. The electrochemical performance of the PEDOT thin film was investigated in 1 mol L$^{-1}$ H$_2$SO$_4$ solution. It possesses nearly ideal capacitive property, and its specific capacitance is about 130 F g$^{-1}$. Compared with other conducting polymers, enhanced cycling lifetime (up to 70,000 cycles), which is close to that of active carbon materials, was observed on repetitive redox cycling.
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## 1. Introduction

Electrochemical capacitors, also known as supercapacitors, are now widely used in hybrid electric vehicle along with the improvement in transportation field [1–4]. It is clear that ideal electrochemical capacitors should have high power density, high energy density as well as a long cycle-life and the performances of capacitors mainly depend on the properties of the electrode materials [5]. The most successful and frequently used capacitive materials so far are carbon materials [6–9]. However, the main disadvantage of these materials is their relatively poor energy density [10–12]. Though it can be improved through oxidating modification, the cycle-life would descend largely [13–15]. As a capacitive material, amorphous hydrous RuO$_2$·$x$H$_2$O has excellent comprehensive performances but its price is too high to be commercially available [5]. Conducting polymers, such as polyaniline, polypyrrole, polythiophene and their derivatives, would be the most promising electrode materials owing to the combination of high energy density, high specific power density, lower cost, easy to be prepared and

fabricated on needs [16–20]. Amongst conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has received a significant amount of attention in commercial applications [21]. Nevertheless, the relatively poor stability of conducting polymers, whose cycle-life is only several thousand, is still a major obstacle to their applications [22–24].

The nature of dopant and electrolyte would strongly influence the electrochemical and physical properties of polymers during the polymeric process [25,26]. Based on this viewpoint, different methodologies have been applied to increase their stability [27–29]. Recent researches have reported that using ionic liquids as electrolytes can increase the stability of conducting polymers [30–32]. Ionic liquids comprised entirely of ions are liquid at ambient temperature. Being distinct from traditional solvents, ionic liquids possess unique physical–chemical properties, such as non-volatility, non-flammability, high ionic conductivity, wide potential windows (>5 V) and high thermal/electrochemical stability. They are green solvents and favor doping for the composition of inorganic anions [33,34], forming uniform films due to the high viscosity as well [35]. Considering the above merits, they are extremely beneficial for polymerization-conducting polymers [36–38]. Additionally, some ionic liquids are air and moisture stable, making them especially suitable for applications in electrochemical systems from

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which moisture must exclude over long periods of operation [39]. Therefore, the electrochemical performance of PEDOT as an electrode material for supercapacitor, has been studied in ionic liquids electrolyte [40,41].

In this paper, we present results on the synthesis, performances of highly stable PEDOT obtained by potentiostatic method in a purified environmentally stable ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]). It is found that the stability of PEDOT is greatly improved by using ionic liquid as electrolyte.

## 2. Experimental

### 2.1. Reagents

3,4-Ethylenedioxythiophene (EDOT) was purchased from Bayer AG (more than 97%) and used as received. Acetonitrile was of HPLC grade and distilled prior to use. All the other reagents were of analytical grade.

### 2.2. Synthesis and purification of [bmim][BF$_4$]

N-methylimidazole was synthesized according to an open patent [42]; just the aqueous solution of reagents was refluxed for 5 h at 65 °C. Excess reagents and water were removed in vacuum. The preparation of [bmim]Br was carried out in a microwave (MW) oven (Panasonic NN-S740WA-1200). N-bromibutane (~0.4 mol) was reacted with methylimidazole (~0.45 mol) at the power P2 corresponding to 280 W (22 s irradiation with 12 s mixing) for 4 h. Firstly, the mixture was extracted by diethyl ether. Subsequently, the solvent was removed in vacuum. The synthesis of the [bmim][BF$_4$] was based on a metathesis reaction of [Bmim]Br and Ag[BF$_4$] in methanol [43,44]. The insoluble AgBr was filtered off from this mixture, and the filtrate was treated with activated charcoal, which should be filtered after 2 h. The product was then dried under vacuum at 80 °C.

The residual impurities, Br$^-$ and Ag$^+$, in the resultant were got rid of by constant potential electrolysis. The counter electrode was platinum sheet with an Ag wire pseudo-reference electrode. The electrolysis Br$^-$ was performed at 85 °C with a working potential of 1.0 V, the working electrode was a Pt-disc electrode ($D$ = 1.0 mm) and the NaOH solution was used to absorb bromine vapor. The electrolysis of Ag$^+$ was performed at room temperature with an applied potential of −0.30 V, and the working electrode was a carbon rod. The Bromide ion-selective electrode and the atomic absorption spectroscopy (GBC-932 plus, Australian) were respectively used to detect the content of Br$^-$ and Ag$^+$ in [bmim][BF$_4$]. The purified ionic liquid was stored in a desiccator prior to use.

### 2.3. Preparation of PEDOT

The electropolymerization of EDOT was carried out in a one-compartment cell with a Pt-disc ($D$ = 1.0 mm) working electrode, and a Pt sheet counter electrode. The reference electrode was an Ag wire pseudo-reference electrode. The working electrode was polished prior to use. The electrolyte was deaerated by dry nitro-gen stream before polymerization, and a slight nitrogen over-pressure was maintained during the polymerization. The polymer film was grown over 500 s at 1.0 V in purified [bmim][BF$_4$] solution containing 0.1 mol L$^{-1}$ EDOT, and the consumed charge was 0.051 C. The gained polymer film was rinsed thoroughly with acetonitrile and dried with nitrogen gas stream.

### 2.4. Characterizations of PEDOT

All the electrochemical results were recorded at room temperature with a CHI 660b electrochemical workstation, and all potentials were given with respect to Ag reference electrode besides specially labeled. The electrochemical impedance experiment was performed by using an AUTO LAB instrument (AUT 72782, The Netherlands). The FT-IR Instrument (VECTOR-22, Bruker, German) was used to study the structure of PEDOT. The surface morphology of the polymer was characterized by ESEM (XL-30, FEI, USA).

## 3. Results and discussion

### 3.1. Purifying results of [bmim][BF$_4$]

The impurities in ionic liquid can influence the monomer oxidation potential, polymer growth rate and electrochemical responses of the polymer film [45]. So it is necessary to get a relatively pure ionic liquid as electrolyte. Constant potential electrolysis was used to get rid of the residual Br$^-$ and Ag$^+$. Fig. 1d displays the cyclic voltammogram of [bmim][BF$_4$] after disposal of Br$^-$, and no oxidation peak of Br$^-$ is observed, which indicates that the residual Br$^-$ has not produced electrochemical interference. Similar result is obtained after disposal of Ag$^+$ in [bmim][BF$_4$] as shown in Fig. 2. After the purification, the content of Br$^-$ in ionic liquid is reduced from 5.9 to 0.0032 wt.%, and the content of Ag$^+$ is reduced from 0.804 to 0.012 wt.%.
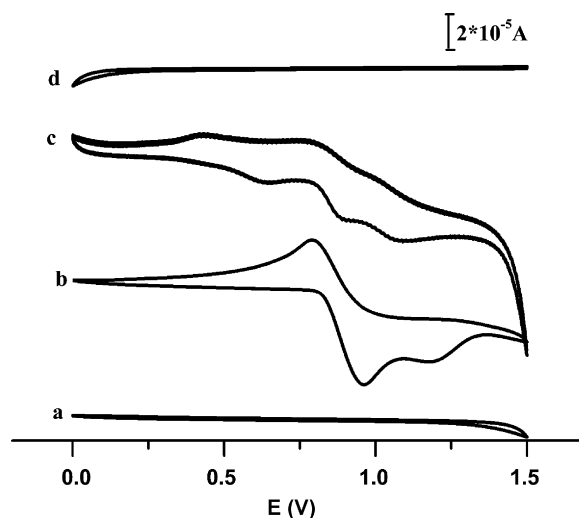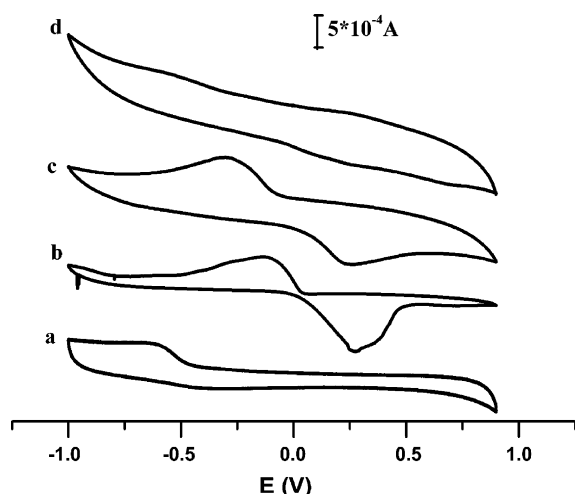


Fig. 1. Cyclic voltammograms of Br$^-$ on Pt-disc electrode in different electrolytes: (a) 1 mol L$^{-1}$ NaNO$_3$ aqueous solution; (b) 1 mol L$^{-1}$ NaNO$_3$ +0.6 mol L$^{-1}$ NaBr aqueous solution; (c) unpurified [bmim][BF$_4$]; (d) [bmim][BF$_4$] after disposal of Br$^-$.

Fig. 2. Cyclic voltammograms of $Ag^+$ on carbon rod electrode in different electrolytes: (a) $1 \, mol \, L^{-1}$ $NaNO_3$ aqueous solution; (b) $1 \, mol \, L^{-1}$ $NaNO_3$ $+0.05 \, mol \, L^{-1}$ $AgNO_3$ aqueous solution; (c) [bmim][BF$_4$] after disposal of $Br^-$; (d) purified [bmim][BF$_4$] with no electrochemical interference of $Ag^+$ and $Br^-$.

## 3.2. Characterization and properties of PEDOT

The structure of PEDOT film grown onto indium tin oxide (ITO) glass substrate in [bmim][BF$_4$] was identified by FT-IR spectroscopy. Fig. 3 shows the spectrum of PEDOT, and it can be observed that this polymer has the same absorption bands as the PEDOT synthesized by chemical method [46].

Fig. 4 shows the ESEM image of the PEDOT film. It shows a nodular accumulating structure. The size of the nodules ranged from a few hundred nanometers to $2 \, \mu m$ in diameter and they aggregate to form gobbets. Between the gobbets, large spaces are observed. This open structure permits good access for the electrolyte molecules in the polymer matrix to form ionic conducting road.

The current–voltage characteristic of PEDOT film among the potential range of $-0.2$ to $0.8 \, V$ in $1 \, mol \, L^{-1}$ $H_2SO_4$ solution is shown in Fig. 5. For comparison, the current–voltage wave of PEDOT polymerized in $0.1 \, mol \, L^{-1}$ $LiClO_4$/MeCN electrolyte is also displayed in Fig. 5. As can be seen, the curves of these two samples have nearly ideal rectangular shape, which is typical of the pure capacitive behavior of the tested object [5]. However, the current of film obtained in [bmim][BF$_4$] is
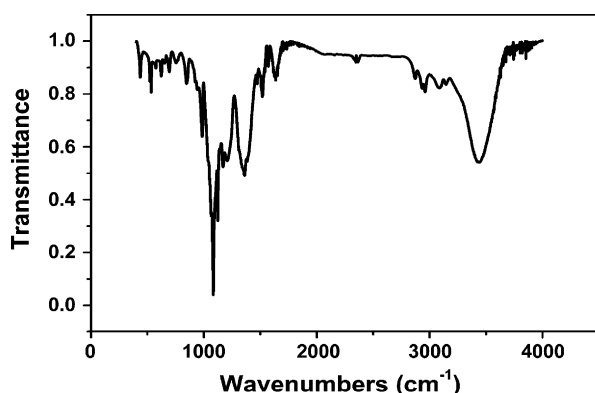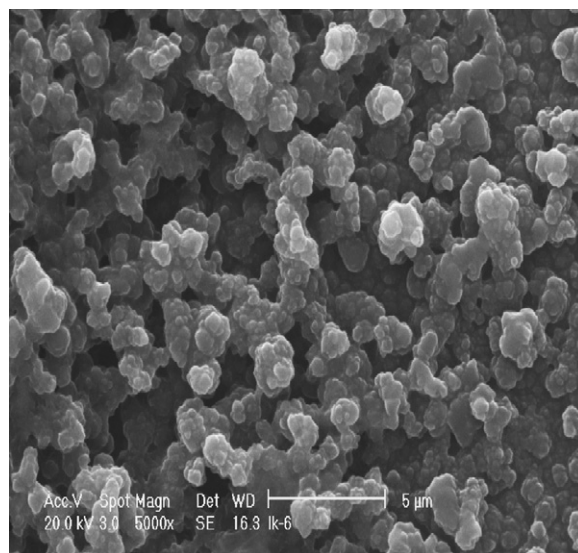


Fig. 4. ESEM image of PEDOT gained in [bmim][BF$_4$].

nearly 7 times of the film gained in acetonitrile electrolyte, which proves that ionic liquid can improve the polymer electroactivity. According to the current of PEDOT electrode [47], the specific capacitance achieved in [bmim][BF$_4$] is reckoned at the level of $130 \, F \, g^{-1}$.

In order to evaluate the validity of the specific capacitance calculated in cyclic voltammetry, electrochemical impedance spectrum (EIS) of PEDOT was studied. The relation between real ($Z'$) and imaginary ($Z''$) impedance components of PEDOT for a frequency range ($10^5$–$0.01 \, Hz$) is displayed in Fig. 6. The impedance plot is composed of a semicircle at high frequencies and a $45°$ capacitive slope at low and middle frequencies. The semicircle appeared at high frequencies is considered to owe to the charge–transfer resistance, which originates from the interface structure between the porous electrode surface and the electrolyte [48]. The linear part with $45°$ slope appearing in a transitory way next to the semicircle indicates the diffusion lim-
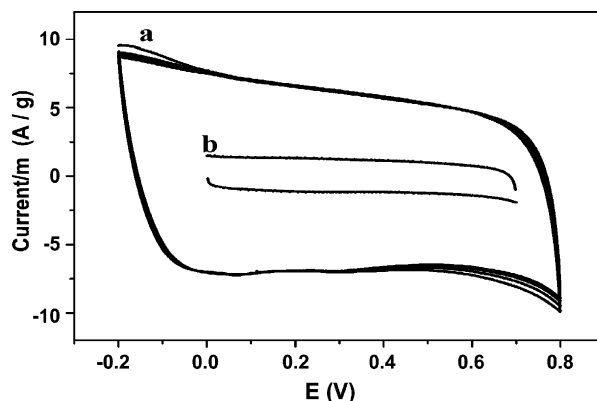


Fig. 3. . FT-IR spectra of PEDOT electropolymerized in [bmim][BF$_4$].



Fig. 5. Cyclic voltammograms of PEDOT-modified electrode in $1 \, mol \, L^{-1}$ $H_2SO_4$ solution: (a) PEDOT electropolymerized in [bmim][BF$_4$] containing $0.1 \, mol \, L^{-1}$ EDOT; (b) PEDOT electropolymerized in acetonitrile solution containing $0.1 \, mol \, L^{-1}$ EDOT $+0.1 \, mol \, L^{-1}$ $LiClO_4$, the other polymeric conditions were the same as the film obtained in [bmim][BF$_4$]. Scan rate: $50 \, mV \, s^{-1}$.
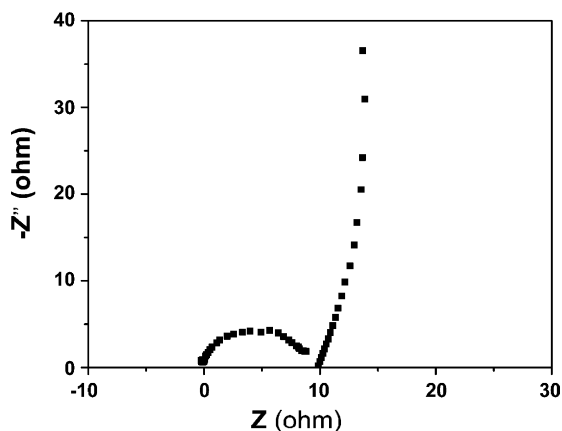
Fig. 6. Electrochemical impedance spectrum of PEDOT electropolymerized in [bmim][BF$_4$].



Fig. 8. Cycle test of PEDOT achieved in [bmim][BF$_4$] using 1 mol L$^{-1}$ H$_2$SO$_4$ as electrolyte. The inset shows the cycle test of PEDOT obtained in acetonitrile electrolyte. Scan rate: 5 mV s$^{-1}$.

itation in the doping/undoping process [48]. At low frequencies, the impedance plot becomes a near vertical line, which is indicative of a redox layer produced by the ac stimulation penetrating the entire depth of the polymer film [22]. The specific capacitance can be calculated according to the following formula: $Cp = -1/(\omega Z''m)$ where $\omega$ is the angular frequency, which has the relationship with frequency as follows, $\omega = 2\pi f$, $Z''$ is the imaginary impedance of impedance spectrum, $m$ is the mass of the polymer. In Fig. 6, the specific capacitance of 122 F g$^{-1}$ can be gained at the frequency of 11.8 mHz, which is nearly close to the value computed from cyclic voltammogram.

The representative charge–discharge curve of the PEDOT electrode within a potential window of 0–1.0 V (versus SCE) at a constant current density of 12.5 mA cm$^{-2}$ is shown in Fig. 7. It behaves as triangular profile during the charge–discharge process, which indicates that this material has good charge–discharge reversibility.

As it is well-known, the long-term stability of conducting polymers is an important consideration for their applications in electrochemical capacitors. In order to test the cycle-life of PEDOT, consecutive voltammetric scans were performed in 1 mol L$^{-1}$ H$_2$SO$_4$ solution, where a cycle is defined as scan-

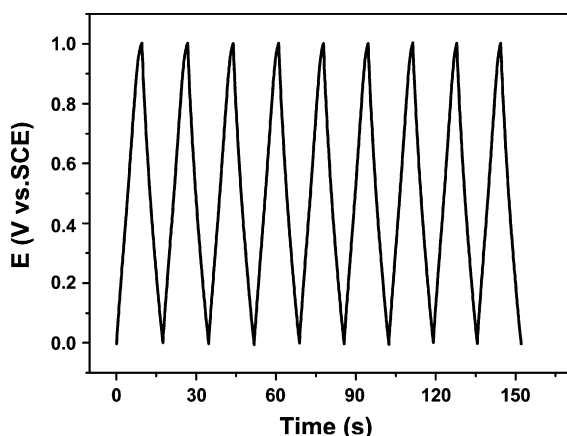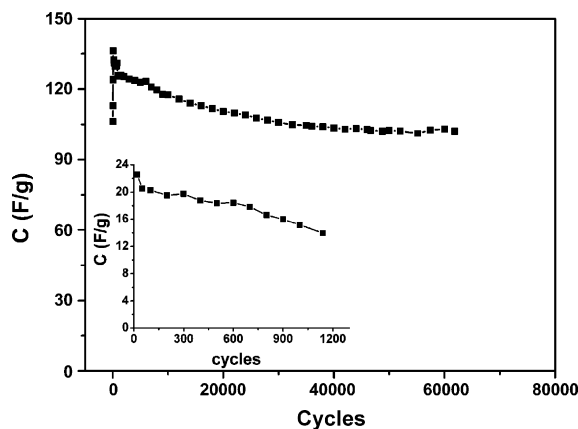ning from −0.2 to 0.8 V and then back to −0.2 V at a scan rate of 5 mV s$^{-1}$. Fig. 8 depicts that the specific capacitance of the polymer electrode changed along with the cycles. It is interesting to note that the specific capacitance of the electrode increased from 106 to 136 F g$^{-1}$ during the initial 100 cycles, this surprising increase should attribute to the porous structure along with a swelling of the material due to solvent and salt retention [49]. At subsequent 1000 cycles, no drift of specific capacitance could be observed, and the value remained constant at around 130 F g$^{-1}$. After continuous cycles, the specific capacitance decayed slowly from the 125 F g$^{-1}$ at 1000th cycle to 110 F g$^{-1}$ at 20,000th cycle. This just meant that the capacity fade at 1000th and 20,000th cycle for PEDOT electrode is just 3.85% and 15.4%, respectively. But following the next cycles, the drift rate of the specific capacitance was measured to be lower than 1 F g$^{-1}$ per 2000 cycles for the PEDOT electrode. When the cycle reaches to 70,000th cycle, the specific capacitance still kept on nearly 100 F g$^{-1}$; it descends only 25% in comparison to original value. Under the same condition, the PEDOT obtained in acetonitrile electrolyte only achieved a specific capacitance of 20 F g$^{-1}$, and lost its capacitive property after 1000 cycles (as can be seen in the inset of Fig. 8). In comparison with other polymers, this lifetime is markedly improved. For the lifetimes of conducting polymers are usually short with a maximum lifetime of up to 10,000 cycles that was obtained by poly[3-(3,4-difluorophenyl)thiophene] cycled in tetraethylammoniumbis(trifluoromethanesulfonyl)imide and retained 70% of their initial charge after 10,000th cycles [50]. This increasing stability of the PEDOT electrode can be attributed to the following reasons: (1) the electrochemical activity of the polymer grown in ionic liquids is less affected by the nature of the cycling solvent than the polymer achieved in other solutions [51]; (2) the porous structure of polymer offers a higher specific surface area that is convenient for dopant ions accessing into the polymer matrix and inducing higher charge to keep stable [50]; (3) a simultaneous p-doping reaction occurred during the polymeric process, and in comparison to n-doping, p-doping polymer is more stable [52].



Fig. 7. Galvanostatic charge–discharge cycles in 1 mol L$^{-1}$ H$_2$SO$_4$ solution between 0 and 1.0 V at 12.5 mA cm$^{-2}$ for PEDOT obtained in [bmim][BF$_4$].

## 4. Conclusions

In this study, non-electrochemical responsible ionic liquid [bmim][BF$_4$], which can be directly used as electrolyte, is obtained through the potentiostatic electrolysis. Cyclic voltammetry and galvanostatic charge–discharge test shows that the PEDOT electropolymerized in neat [bmim][BF$_4$] possesses excellent capacitive characteristic. Especially that it has a long time of redox cycling, which is up to 70,000 cycles. This good level of stability for PEDOT has been close to the stability of carbon electrode material with a general lifetime of 100,000 cycles, and exceeded the life of amorphous hydrous ruthenium oxide, which was the most excellent inorganic metal electrode material with a maximum cycles of 60,000 times up to now [53]. Therefore, this highly stable polymer electrode material is of particular interest and may be used to develop high-performance supercapacitor.

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