



# Achieving efficient poly(3,4-ethylenedioxythiophene)-based supercapacitors by controlling the polymerization kinetics

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## ABSTRACT

In this study, we have prepared a series of poly(3,4-ethylenedioxythiophene) (PEDOT) with various molecular weight by using an inhibitor, imidazole (Im). The X-ray diffraction (XRD) results show that the PEDOT with larger molecular weight enhances the polymer chain ordering and stacking which leads to higher conductivity. With increasing the amount of Im, the conductivity of PEDOT can be increased from  $4.01 \text{ S cm}^{-1}$  (Im = 0.0 M) to  $153.6 \text{ S cm}^{-1}$  (Im = 1.8 M). Comparisons of the cyclic voltammetry (CV), it enables correlation between the conductivity and specific capacitance, which is important for understanding the electrochemical capacitive behavior of conjugated polymer for pseudo-capacitor application. The PEDOT prepared with 1.8 M Im shows a specific capacitance of  $124 \text{ F g}^{-1}$ , which is 2.2 times larger than the one without Im ( $57 \text{ F g}^{-1}$ ).

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## 1. Introduction

The growing demand for portable systems and electric vehicles which require high power in short term pulses have prompted a great interest in electrochemical capacitors, also known as supercapacitors [1]. As an electrode material for supercapacitor, the conducting polymers have an advantage over active carbon [2–4] or transition-metal oxides due to the fast, reversible redox reaction, mechanical flexibility and relative ease of processing. Among various conducting polymers, PEDOT has been applied in electricity storage devices, particularly supercapacitors for high pulsed power due to its good environmental and thermal stability, reversible and stable manner to relatively large potential window [5–8]. To date, most of the studies on PEDOT-based supercapacitors have been focused on enhancing their specific capacitances through increasing its surface area. For example, Liu et al. achieved a high specific capacitance of about  $140 \text{ F g}^{-1}$  by preparing PEDOT nanotube arrays through the cylindrical pores of an alumina template [9]. Li et al. enhanced the specific capacitance of PEDOT from  $36.8$  to  $109.1 \text{ F g}^{-1}$  by modulating the PEDOT morphology under different surfactant concentrations [10]. Kelly et al. reported a specific capacitance of  $106 \text{ F g}^{-1}$  by using PEDOT/microporous carbon composite [11]. For

the issue of poor conductivity, although much composites containing carbon nanotubes (CNTs) and PEDOT have been synthesized to promote the electrical conductivity but the enhancement comes only from the CNTs [12,13]. The correlation between conductivity of pristine PEDOT and its specific capacitance is still not clear so far.

In general, the conductivity of PEDOT can be enhanced by two different ways: (1) modulate the conformation of PEDOT from coil to expanded-coil or linear structure [14–16], (2) increase the molecular weight of PEDOT (longer polymer chains) [17]. It has been found that the conformation structure of PEDOT can be changed by treating with polyalcohols such as sorbitol [18], glycerol [19] and ethylene glycol [20]. Ouyang et al. proposed that the energy barrier among the PEDOT chains can be reduced with a linear conformation [14]. This can enhance the charge hopping along the polymer backbone leading to higher electrical conductivity. The longer polymer chains can be achieved by controlling the polymerization condition such as the ratio between monomer and oxidation agent, reaction temperature and addition of polymerization inhibitor. The longer polymer chains allow larger orbital delocalization and increase the conductivity.

In this study, we investigate the effect of conductivity of PEDOT on its capacitance property. The PEDOT was prepared by the oxidative polymerization with an inhibitor, Im, which can quench the polymerization kinetics and lead to higher molecular weight [21]. With different amount of Im, we can control the degree of polymerization of PEDOT and gain the polymer with different molecular weight.

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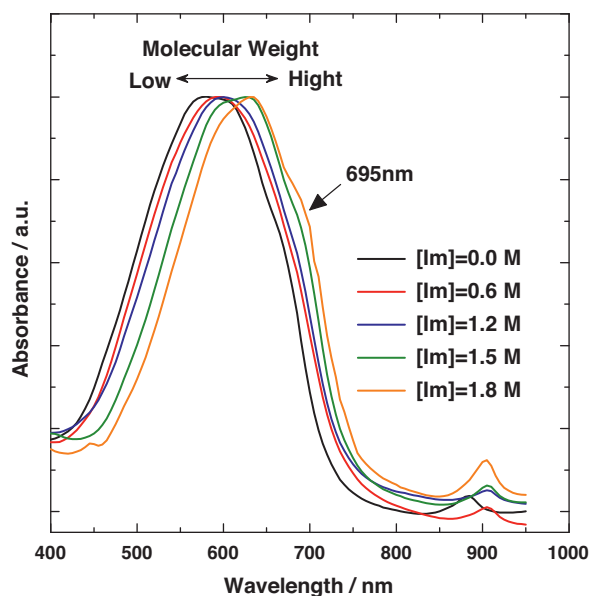


Fig. 1. UV-vis spectra of PEDOT films prepared with various Im concentrations.

## 2. Experimental

### 2.1. Monomer synthesis

The 5-tetradecyldioxeno[2,3-c]thiophene (EDOT-C<sub>14</sub>H<sub>29</sub>) was synthesized according to a reported procedure [22], 5-tetradecyldioxeno[2,3-c]thiophene-2,5-dicarboxylic acid (1 g, 2.3 mmol) and copper chromite (15% by mole) as a catalyst were mixed in 100 mL quinoline. Consequently, the mixture was reacted under 150 °C for 24 h. After the mixture was cooled to room temperature, 100 mL of pentane was then added and the catalyst residue was filtered. The quinoline was removed by repeated washing with 1 M HCl until the pH values of the aqueous layers were acidic. The organic layer was washed with 1 M NaHCO<sub>3</sub> and water until the pH became neutral. Finally, the organic layer was dried with anhydrous CaCl<sub>2</sub> and concentrated leading to a whitish gray solid. Yield = 0.2 g (25.3%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 0.88, 1.28, 1.34, 4.15, 4.45, 6.30. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm) 14.14, 22.75, 29.43–29.78, 31.99, 64.63, 76.85–77.49, 99.60, 141.82. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are also shown in the Supporting Information (Figs. S1 and S2), Elemental Anal. Calcd: C, 70.57; H, 10.32; S, 9.7. Found: C, 71.13; H, 10.61; S, 8.74.

### 2.2. General procedure for polymerization

The oxidative polymerization method was carried out according to the procedure reported in literature [21,15]. Firstly, the oxidant (iron(III) p-toluenesulfonate (Fe(OTs)<sub>3</sub>)) and weak base Im were dissolved separately in methanol solution. Then, the monomer was mixed with Im and Fe(OTs)<sub>3</sub> solutions and the molar ratio of Fe(OTs)<sub>3</sub>/monomer was controlled at 1.75:1. The mixture was heated at 100 °C subsequently for 48 h. Finally, the as prepared PEDOT or PEDOT-C<sub>14</sub>H<sub>29</sub> powder was rinsed by methanol and de-ionized water several times to remove the oxidative agent and Im and dried in N<sub>2</sub> atmosphere.

### 2.3. Characterization

NMR spectra were recorded on a Bruker AMX400 spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Gel permeation chromatography (GPC) analyses were

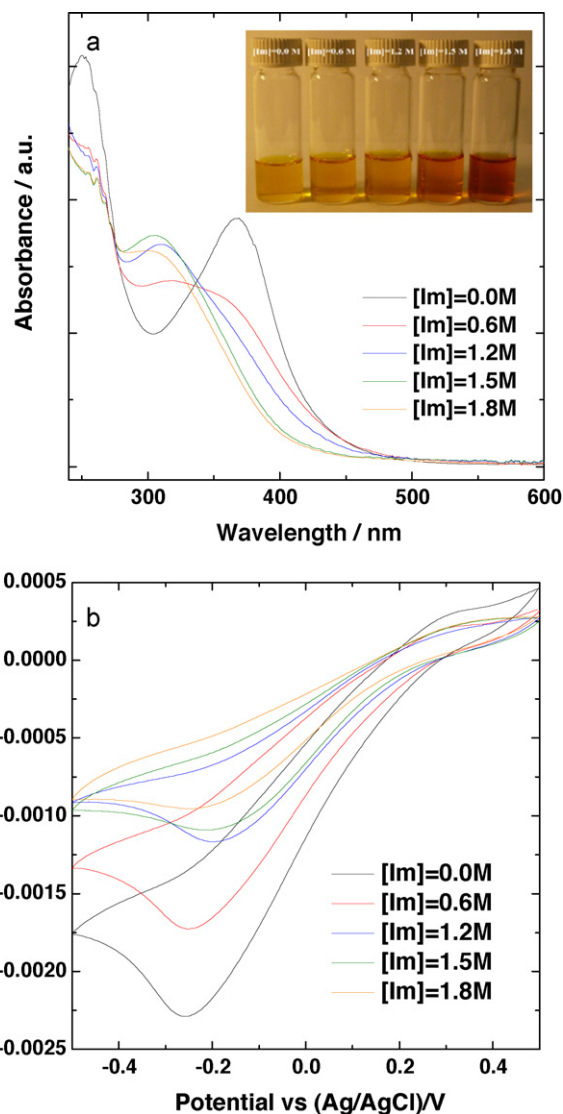


Fig. 2. (a) Absorption spectra of Fe(OTs)<sub>3</sub> with different Im amount. The coordination of Fe(OTs)<sub>3</sub> with Im around its shell leads to the shift of absorbance peak. Inset: photographs of the Fe(OTs)<sub>3</sub>/Im solutions with different blending ratios. (b) CVs of 0.1 M Fe(OTs)<sub>3</sub>/methanol with different Im amount.

conducted on a Waters 1515 separation module using polystyrene as a standard and THF as an eluent. Spectral data was recorded on Shimadzu model UV-1601PC spectrophotometer. The UV-vis spectra were got from the PEDOT thin films which were prepared on glass substrates by following procedure. The mixture (monomer, Fe(OTs)<sub>3</sub> and Im) described above was spin-coated onto glass substrates and heated at 100 °C subsequently. Finally, the PEDOT film was rinsed by de-ionized water and methanol several times to remove the oxidative agent and Im and dried in N<sub>2</sub> atmosphere. Thermal gravimetric analysis (TGA) was conducted to characterize the thermal stability of PEDOT powder using DuPont 951 from the room temperature to 600 °C with a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. The surface morphology of polymer powders and films were examined using a scanning electron microscope (SEM, Hitachi S-800) and atomic force microscopy (AFM, Digital instrument NS 3a controller with D3100 stage), respectively. The crystal structures of the samples were characterized by X-ray diffraction (XRD) using a Philips X'Pert/MPD diffractometer. The conductivity of PEDOT films at different temperature was determined by a four point probe bench (sulfofocorder ET3000 Kosaka Laboratory).

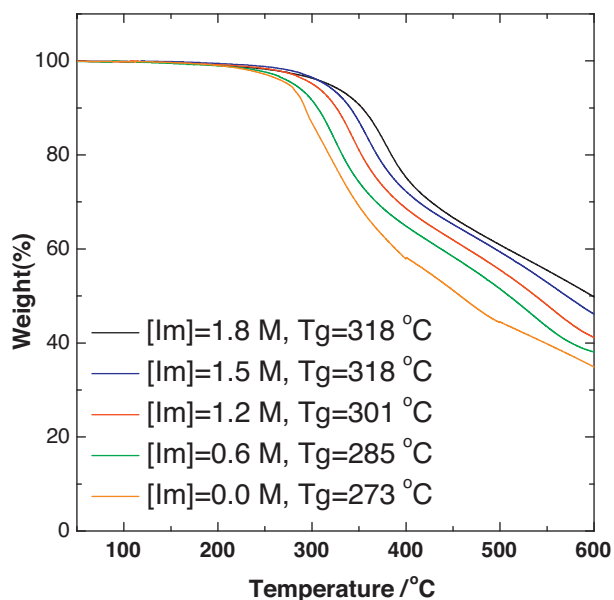


Fig. 3. The thermal stability of PEDOT prepared with various Im concentrations.

The supercapacitor test was conducted with three-electrode configuration. The electrodes were made of PEDOT powders with 10 wt% polytetrafluoroethylene (PTFE) binder. The mixture of PEDOT and PTFE was homogenized in water by being sonicated for 30 min, and then dried for 18 h at vacuum oven at 120 °C to remove water completely. The dried mixtures were pressed on a nickel foam with a pressure of 20 MPa as the electrodes. CV studies were performed with a three-electrode cell with 0.1 M LiClO<sub>4</sub> aqueous electrolyte using nickel foam as the working electrode, a platinum sheet as the counter electrode, and Ag/AgCl as the reference electrode.

### 3. Results and discussion

In this study, the PEDOT was synthesized via chemical polymerization. The polymerization kinetics can be controlled by adding the Im. However, the insolubility of PEDOT in any common organic solvents precludes the determination of the molecular weight of the polymers [21]. It is well known that the larger molecular weight of polymer leads to a larger orbital delocalization which causes a red-shift of UV–vis spectrum. Therefore we measure the UV–vis spectra of the as-prepared PEDOT films to semiquantify the degree of polymerization. The UV–vis spectra of the PEDOT films are shown in Fig. 1. The PEDOT films were polymerized under different Im concentration while fixing the molar ratio of the Fe(OTs)<sub>3</sub>/EDOT at 1.75:1. It can be seen that the maximum absorption of the PEDOT shifts from 580 to 635 nm while the Im concentration is increased from 0 to 1.8 M. This implies that a decrease in polymerization kinetics leads to a larger orbital delocalization with adding Im, namely red shifts of PEDOT absorption. Furthermore, for the PEDOT prepared with 1.8 M Im, a pronounced vibronic peak located at 695 nm appears. This indicates the longer polymer chains enhances the interchain interactions, which results in more delocalized conjugated  $\pi$  electrons and a lowering of the band gap between the  $\pi$  and  $\pi^*$  orbitals.

The effect of Im on the polymerization kinetics of PEDOT can be explained by Fig. 2. Spectroscopic studies show that a shift in the absorbance peak of Fe(OTs)<sub>3</sub> is observed with increasing Im concentration as shown in Fig. 2a. The spectroscopic shift comes from the substitution of Im replacing methanol ligand existing initially. The surrounding Im prevents the Fe(OTs)<sub>3</sub> and EDOT from reac-

Table 1

Summary of the molecular weight and polydispersities (PDI) of PEDOT-C<sub>14</sub>H<sub>29</sub> samples in this study.

Sample	$M_n$ (kg mol <sup>-1</sup> ) <sup>a</sup>	$M_w$ (kg mol <sup>-1</sup> ) <sup>a</sup>	PDI <sup>a</sup>
0.0 mol l <sup>-1</sup> Im	17.3	41.7	2.4
1.0 mol l <sup>-1</sup> Im	41.2	141.6	3.4

$M_n$ , number average molecular weight;  $M_w$ , weight average molecular weight.

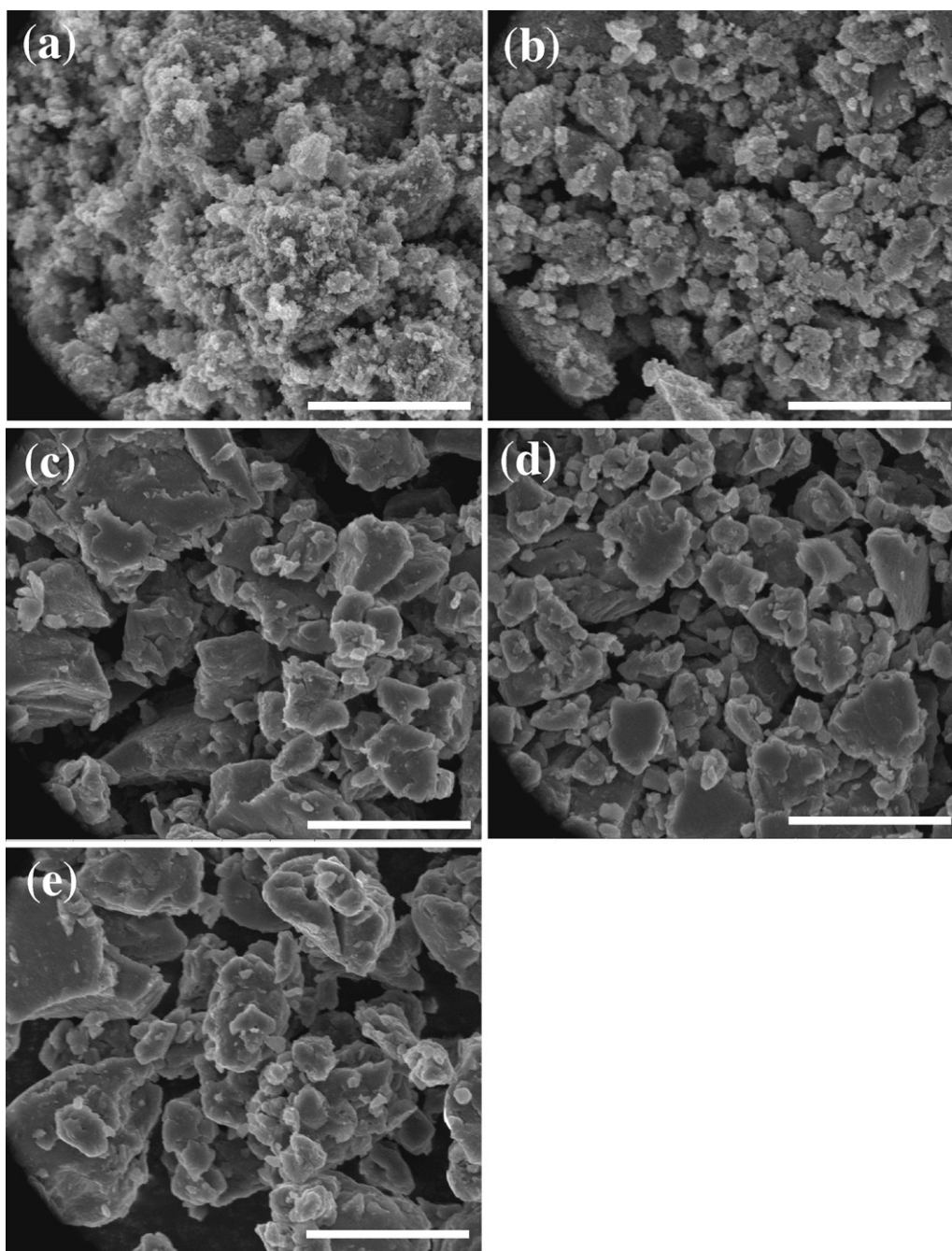
<sup>a</sup> Molecular weights and polydispersity were measured by GPC, using THF as an eluent and polystyrene as a standard.

tive collision leading to decreasing the reactivity [23–26]. Another important effect of added amine on the reactivity of Fe(OTs)<sub>3</sub> proposed by de Leeuw et al. is the variation of pH in the reaction media [27]. They found that the activity of Fe(OTs)<sub>3</sub> is reduced by increasing the pH after adding amine. This can be further proven by measuring the reduction peak of Fe(OTs)<sub>3</sub> with various Im concentration as shown in Fig. 2b. It can be seen that the reduction current of Fe(OTs)<sub>3</sub> decreases with increasing the concentration of Im. While the polymerization reaction proceeds, Fe(OTs)<sub>3</sub> get reduced and EDOT get oxidized. The smaller reduction peak of Fe(OTs)<sub>3</sub> indicates weaker capability to oxidize EDOT which leads to a decrease of polymerization rate.

In order to further confirm the decrease of polymerization kinetics of PEDOT induced by the Im, TGA thermograms (Fig. 3) were recorded under nitrogen atmosphere for the as-prepared PEDOT powders to compare the molecular weight. A drastic weight loss was observed in the temperature higher than 285 and 350 °C for the PEDOT prepared with 0.0 M and 1.8 M Im, respectively. The onset temperature of 5% weight loss ( $T_d$ ) for the polymer is found to increase with increasing the concentration of Im. The  $T_d$  is independent of the degree of crystalline, therefore we can conclude that the higher  $T_d$  of PEDOT is totally contributed from the higher molecular weight. The increasing thermal stability with higher molecular weight has been observed in many other polymer systems [28].

Although the PEDOT prepared from higher Im concentration reveals pronounced red-shift of UV–vis spectra and higher  $T_d$ , however these results are still indirect evidence and not strong to conclude the increase in molecular weight. Since PEDOT is not soluble and its molecular mass cannot be measured directly, we have decided to synthesize its soluble analogue, namely EDOT-C<sub>14</sub>H<sub>29</sub>, and measure its molecular weight by GPC. We polymerized the EDOT-C<sub>14</sub>H<sub>29</sub> with the same procedure. The molecular weights of the PEDOT-C<sub>14</sub>H<sub>29</sub> with 0 and 1.0 M Im are shown in Table 1. The GPC spectra are shown in the Supporting Information (Fig. S3). The molecular weights of PEDOT-C<sub>14</sub>H<sub>29</sub> prepared from 0.0 and 1.0 M Im are 4.1 and 14.1 kg mol<sup>-1</sup>, respectively. The higher molecular weight of PEDOT-C<sub>14</sub>H<sub>29</sub> indicates that the imidazole indeed can act as the polymerization inhibitor to increase the length of polymer chains (Fig. 4).

The nature of PEDOT powders obtained with different Im concentrations was examined by SEM. It is seen that without adding Im, the PEDOT powder is mostly globular-like particles with a diameter of 1.5  $\mu$ m and aggregated together. With increasing the concentration of Im, the particle size increases gradually. For the PEDOT obtained with 1.8 M Im, it reveals very large-sized particles with broken pieces. The polymerization is retarded by the addition of Im which reduce the nucleation rate of PEDOT in the solution. Because the amount of EDOT is fixed, for the case of slower nucleation rate (larger Im concentration), most of the monomer is consumed on the growth of PEDOT particle. Based on the kinetics of nucleation and growth, the particle size of PEDOT increases with increasing amount of Im. It is worthy to mention that PEDOT cannot be polymerized anymore if the concentration of Im is higher than 1.8 M. The polymerization cannot be proceeded at all in the presence of high imidazole concentrations.



**Fig. 4.** The SEM images of PEDOT powders prepared from different Im amount. (a) [Im] = 0.0 M, (b) [Im] = 0.6 M, (c) [Im] = 1.2 M, (d) [Im] = 1.5 M and (e) [Im] = 1.8 M. Scale bar: 20  $\mu\text{m}$ .

Fig. 5 shows the XRD pattern of the PEDOT powders obtained from various Im concentrations. The PEDOT features three main peaks at a scattering angle  $2\theta \sim 6.2^\circ$ ,  $12.4^\circ$  and  $25.8^\circ$  which corresponds to (1 0 0), (2 0 0) and (0 2 0) reflection, respectively [29,30]. The increase in intensity of the peak at  $2\theta \sim 6.2^\circ$  is observed in the PEDOT oxidized with higher Im concentration. The more intensive and narrow peaks of PEDOT indicates the improvement of the polymer chain ordering. Furthermore, it can be seen as a pronounced shift of the (0 2 0) reflection from  $25.6^\circ$  (Im = 0.0 M) to  $26.4^\circ$  (Im = 1.8 M). Substitution of these data into the Bragg equation yields a mean interlayer spacing for the PEDOT prepared with 1.8 M Im of 0.330 nm, which is 0.015 nm less than that obtained without Im. This stacking distance is attributed to the face-to-face packing of the thiophene rings. The improved crystallinity and packing

of the PEDOT chains result in improving interchain and intrachain transport. These results illustrate that lower rate of polymerization enhances crystallinity and polymer chain stacking of PEDOT which is in good agreement with the SEM images. This phenomenon has also been reported in the polyaniline system [31].

In order to measure the conductivity of PEDOT, the polymer films were also prepared by spin-coating. The active layer was obtained by spin-coating the blend of EDOT,  $\text{Fe}(\text{OTs})_3$  and Im (dissolved in methanol) at 3000 rpm for 60 s. Subsequently, the films were annealed on the top of hotplate at  $150^\circ\text{C}$  for 3 min. The resulting films were thoroughly washed with methanol to remove the unreacted monomer,  $\text{Fe}(\text{OTs})_3$  and Im. The morphology of the polymer films were studied by AFM. The PEDOT films prepared without and with 1.8 M Im were shown in Fig. 6a and b, respectively. Unlike

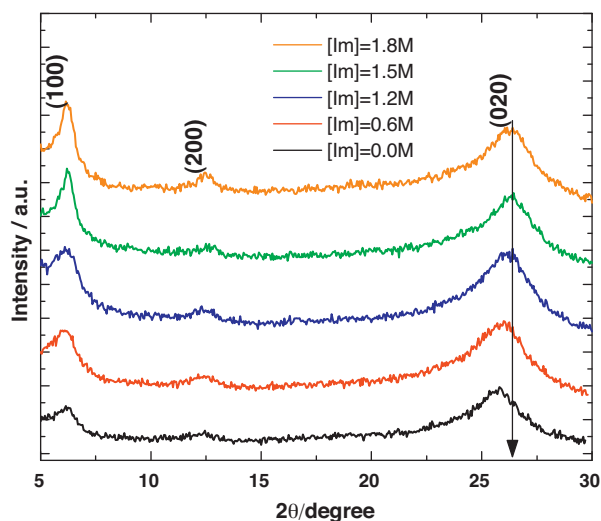


Fig. 5. XRD spectra of the PEDOT powders prepared from different Im concentrations.

the SEM images, the PEDOT films reveal smoother morphology while adding Im. The PEDOT obtained without Im shows very large aggregation compared with the one prepared with the Im. The former films have a root mean square roughness of 68.9 nm, compared to 5.3 nm for the latter films. The presence of Im prevents EDOT from oxidation after spin-coating. Oxidative polymerization occurred at elevated temperature after spin-coating leads to a smooth surface which is particularly important for optoelectronics devices. Again, this proves that Im acts as a polymerization quencher. The difference in thickness of the PEDOT films also indicates the quenching function of Im in the polymerization reaction. Compared with the thickness of these polymer films, films prepared without Im is much thicker ( $\sim 110$  nm) than that with 1.8 M Im ( $\sim 40$  nm). This is due to the polymerization rate after quenching with Im is much slower than the rate of solvent evaporation. Once the solvent was evaporated completely (within 5 s) at  $150^\circ\text{C}$ , polymerization was terminated and the residual EDOT was washed away leading to a thinner film.

Fig. 7 shows the effect of Im and temperature on conductivity of PEDOT. A significant increase of the conductivity by an order of magnitude is seen for adding Im. The conductivity approaches

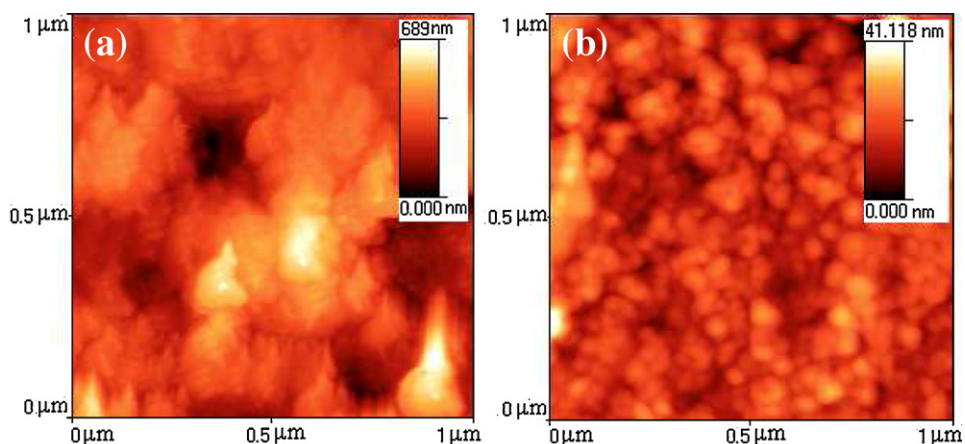


Fig. 6. AFM images of the PEDOT films cast (a) without Im and (b) with 1.8 M Im.

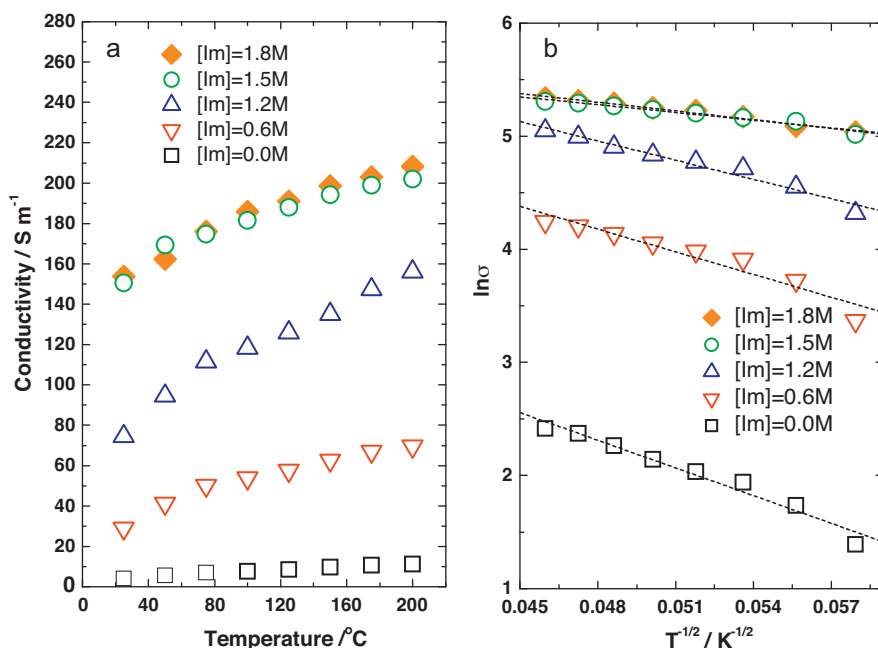


Fig. 7. (a) Temperature dependence of conductivity and (b) temperature dependence of conductivity of PEDOT plotted as  $\ln \sigma$  vs.  $T^{-1/2}$  prepared with various Im concentrations.

saturation while  $I_m$  concentration is larger than 1.5 M. The conductivities ( $\sigma$ ) of PEDOT at room temperature are 4.01, 28.9, 74.4, 150.5 and 153.6 S cm<sup>-1</sup>, respectively, while the  $I_m$  concentrations are increased from 0 to 1.8 M. The enhancement in conductivity is due to the better polymer chain ordering and tighter stacking which enhances the charge transport. The conductivity of PEDOT gradually increases at an elevated temperature, indicating typical organic semiconducting behavior. The one-dimensional variable range hopping model [32] can describe the temperature dependence of conductivity of PEDOT which is given as:

$$\sigma(T) = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/2} \right] \quad (1)$$

Here,  $T_0$  can be interpreted as the energy barrier between localized states, and can be written as  $T_0 = 16(k_B N(E_F) L_{||} L_{\perp}^2)^{-1}$ , where  $k_B$  is the Boltzmann constant,  $N(E_F)$  is the density of the states at the Fermi level, and  $L_{||}(L_{\perp})$  are the localization length in the parallel (perpendicular) direction to the polymer chains. The fitted values of  $T_0$  are 6669, 4476, 3223, 543 and 526 K for the  $I_m$  concentrations increased from 0 to 1.8 M. It is seen from Fig. 6b that the value of  $T_0$  drops from 6669 K (without  $I_m$ ) to 526 K ( $I_m = 1.8$  M), which suggests that the effective energy barrier for charge hopping decreased by extension of the localization length ( $L_{||}(L_{\perp})$ ).

The dependence of specific capacitance with potential of the PEDOT powder with various  $I_m$  concentrations in 1.0 M LiClO<sub>4</sub> aqueous solution at a scan rate of 10 mV s<sup>-1</sup> are shown in Fig. 8. All the scans were performed in a potential range from -0.2 to 0.8 V (vs. Ag/AgCl). The shape of the capacitance loop of the supercapacitor implies the resistance of electrode material [33]. The shape of capacitance loop closes to a rectangular while the electrode material with low resistance. In contrast, the electrode material with high resistance distorts the rectangular shape with an oblique angle [34]. As shown in Fig. 8, the curve of PEDOT prepared without  $I_m$  reveals a distorted shape. With increasing the  $I_m$  amount, the capacitance shapes become more and more rectangular, which

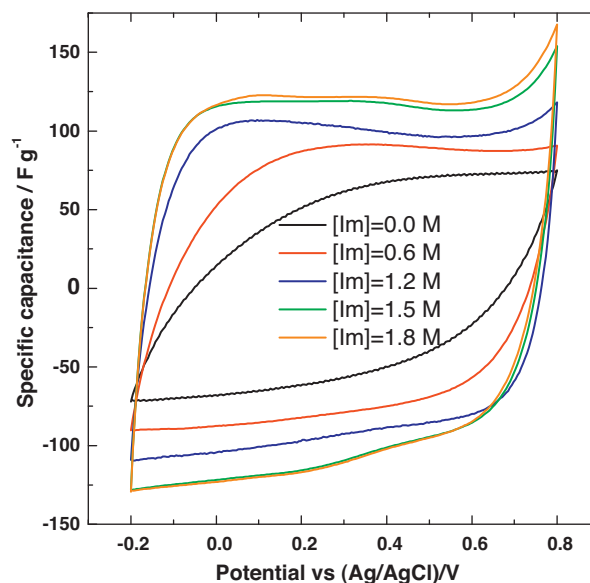


Fig. 8. The dependence of specific capacitance with the potential for the PEDOT powders prepared from different  $I_m$  concentrations.

agrees with the conductivity measurements. It is worthy to note the loop of the PEDOT prepared with 1.5 and 1.8 M  $I_m$  are nearly overlapping, indicating the properties of the PEDOT powders are almost the same. The capacitance loop of PEDOT prepared with 1.8 M  $I_m$  is very close to being rectangular, indicating an excellent capacitance behavior and low internal resistance in the capacitors.

Galvanostatic cycling of supercapacitor electrodes is performed at various current density. As seen in Fig. 9, the charge/discharge curves of the PEDOT (prepared from 1.8 M  $I_m$ ) electrodes are linear in the total range of potential with constant slopes, indicating excellent capacitive behavior. The specific capacitance is evaluated

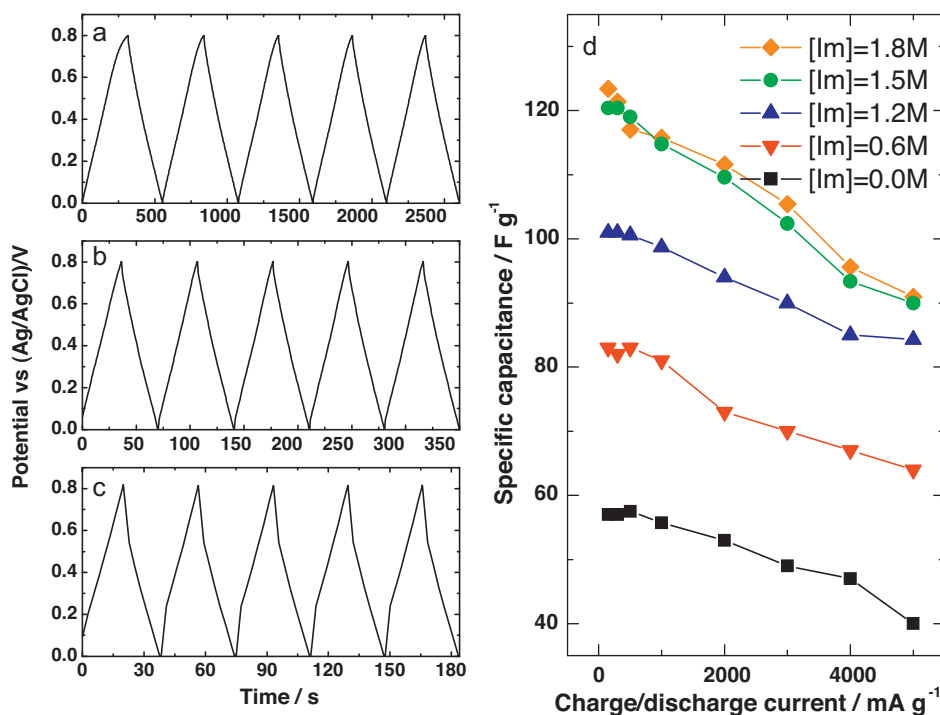


Fig. 9. Galvanostatic charge/discharge curves of PEDOT ( $[I_m] = 1.8$  M) scanned with different current density (a) 0.5 A g<sup>-1</sup>, (b) 3.0 A g<sup>-1</sup>, (c) 5.0 A g<sup>-1</sup> and (d) plots of PEDOT specific capacitance versus current density.

from the slope of the charge–discharge curves, according to the following equation:

$$C = \frac{I \Delta t}{m \Delta V} \quad (2)$$

where  $I$  is the applied current and  $m$  is the mass of each electrode. As shown in Fig. 8d, the specific capacitance of PEDOT obtained without Im is  $57 \text{ F g}^{-1}$  at a constant current of  $150 \text{ mA g}^{-1}$ . With increasing the conductivity, the capacitances of PEDOT are also increased. For the PEDOT prepared from  $1.8 \text{ M Im}$ , the specific capacitance increases to  $124 \text{ F g}^{-1}$ . The enhancement is contributed from the reduction of internal resistance between the PEDOT particles. In Fig. 9d, all the PEDOT samples reveal a decrease in specific capacitance with an increase in the input current. Galvanostatic cycling at high current typically causes the electrolyte ions to reach the outer surface only, and lead to a decrease in the capacitance. Therefore, the specific capacitance of PEDOT with  $1.8 \text{ M Im}$  shows that specific capacitance decreases from  $124$  to  $91 \text{ F g}^{-1}$ . This phenomenon is attributed to the uncompleted charging/discharging of the electrode material caused by the limited ionic diffusion.

#### 4. Conclusions

In this study, the molecular weight of PEDOT was modulated by adding inhibitor. These results show that the inhibitor could reduce the polymerization kinetic to get a PEDOT with longer polymer chains. The PEDOT with larger molecular weight can enhance the stacking of polymer chains leading to higher conductivity. The increase of conductivity reduces the internal resistance of PEDOT powders. This not only forms a more rectangular capacitance curve of PEDOT but also enhance the current density. For the PEDOT prepared with  $1.8 \text{ M Im}$ , the specific capacitance is  $124 \text{ F g}^{-1}$  which is almost 2.2 times larger than the one without Im ( $57 \text{ F g}^{-1}$ ).

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.electacta.2011.03.044](https://doi.org/10.1016/j.electacta.2011.03.044).

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