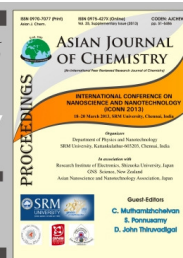




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A Comparative Study of Capacitance Properties with Different Polydioxithiophene†

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Polydioxithiophenes such as 3,4-ethylenedioxithiophene (PEDOT), 3,4-propylenedioxithiophene (ProDOT) and dimethyl-3,4-propylenedioxithiophene (dimethyl-ProDOT) had been electrodeposited by potentiostatic method over indium tin oxide (ITO) surface for comparative electrochemical capacitance measurement. Weight of the polymer deposited by potentiostatic method is estimated by determining the charge consumed during the process. A symmetrical parallel plate electrochemical cell was used for capacitance measurement. The solvent and electrolytes used were propylene carbonate (PC) and tetrabutylammonium perchlorate (TBAP), respectively. Value of capacitance is highest in case of PEDOT followed by ProDOT and dimethyl-ProDOT, however, power density follows the reverse trend. High capacitance of PEDOT with slow charge/discharge is because of compact coiled nature of the polymer film. This facilitates the movement of the ion in and out of the polymer film. In contrast to that ProDOT and dimethyl-ProDOT has porous nature which allows the fast movement of ion through the polymer film. Fast movement of the ion reduce the stability of polymer in case of ProDOT and dimethyl-ProDOT, however, in case of PEDOT capacitance remain stable after several redox cycle. A comparative analysis of all the three polymers reveals that PEDOT is better in terms of energy density, when compared to ProDOT and dimethyl-ProDOT that exceed in term of power density, for future capacitor fabrication.

Key Words: Polydioxithiophenes, Electrochemical polymerization, Supercapacitor, Power density, Energy density.

INTRODUCTION

Supercapacitor is one of the newly growing area and has received extensive interest because of huge demand for energy storage devices with high power density for electronic machines¹⁻³. Two type of charge storage mechanism participate in the supercapacitor which distinguish them in two category *i.e.*, electrochemical double-layer capacitor (EDLC) through non-faradaic process, resulting into the formation of double layer at the interface of the electrolyte and porous electrode and second is faradaic process through redox active^{4,5}. Energy density of redox supercapacitor is comparatively higher than EDLC based capacitor. For this purpose conductive polymers⁶⁻⁸ is widely studied because they can be readily converted between oxidized (doped) and reduced (dedoped) states by simply varying the applied potential. In addition, various intrinsic properties of conductive polymers like excellent redox property, fast redox cycle, doped conducting state, mechanical flexibility, environment friendly nature and low cost adds in their applicability for supercapacitor application. Due to high redox stability, poly(3,4-ethylenedioxithiophene) (PEDOT) is a type of dioxithiophene that got a special attention in the field of conducting polymer based supercapacitor⁹⁻¹⁴. In redox capacitor the achieved energy density or specific capacitance is very high. However, there is a gap in term of power density between supercapacitor and other energy storage devices which still requires extensive research in this area. The conversion between redox states is controlled by mass transfer process of counter-ions¹⁵. The high power demand requires fast charge/discharge process. Difficulty in keeping pace with high power demand will result into degradation of electrode materials. Various methods have been adopted to increase the power density of supercapacitor based on conducting polymers *i.e.*, by making nanostructure and by increasing the size of monomer. In case of dioxithiophene, the size of monomer can be increased by either enhancing the ring size or by functionalization using different group. It was observed that, both the above method help in enhancing the charge/discharge rate of dioxithiophene. But there is no literature available which deals with the comparative studies of different type of dioxithiophene modified by ring expansion followed by functionalization. Here, we have selected three monomer *i.e.*, EDOT, ProDOT and dimethyl-

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ProDOT for their comparative electrochemical properties. Impedance spectroscopy and cyclic voltammetry used for the capacitance measurement, however, the stability of polymers is estimated by chronamperometry technique.

EXPERIMENTAL

EDOT, ProDOT and dimethylProDOT purchased from sigma aldrich. TBAP and dichloromethane were obtained from Merck, India. ITO coated glass of 30 Ω cm sheet resistance procured from sigma Aldrich. All other chemicals used were of analytical grade. Double distilled deionized water was used in all the experiments. Electrochemical characterizations were carried out using electrochemical workstation (Model CHI7041C), CH-Instrument Inc., Tx, USA. Electrochemical experiments were performed in a single-compartment cell using three electrodes assembly with a polymer coated ITO electrode as working electrode, a Pt plate as an auxiliary electrode and Ag/AgCl as reference electrode. Polymer was casted over FTO glass through potentiostatic technique at 1.2 V potential in monomer and 0.1 M TBAP solution followed by cyclic voltammetry in 0.1 M TBAP in dichloromethane for scan rates 0.05 V/s versus Ag/AgCl. Chronamperometric technique for stability test was carried out in TBAP solution in dichloromethane at 1 mA current density. Impedance spectroscopy was carried out at potentiostatic method with varying frequency. Scanning electron microscopy (SEM) images were taken using JEOL JSM-840 on dried silica deposited on the stubs and coated with gold to minimize charges.

RESULTS AND DISCUSSION

Calculation of capacitance per gram or specific capacitance of a material is very important specially when conducting polymers are taken as possible supercapacitor materials. Singnificance, of a variety of conducting polymers as super-capacitor materials will only be considered when an accurate calculation of this value is estimated. In case of dioxothiophene polymerization was carried out by potentiostatic technique. Applied potential and time for polymerization was 1.3 V and 30 s, respectively. Concentration of monomers and TBAP is 30 mM and 0.1 M, respectively. The mass of the deposited polymers is determined by charge consumed during the process using the following formula:

$$Q = NnF = N \left(\frac{M}{\text{Meq}} \right) F$$

where, F is Faraday's constant, Q the deposition charge, n the number of electrons, N the number of moles reacted, M the mass of the deposited polymer and Meq the equivalent polymer mass per electron transferred during polymerisation. It was found that the consumed charge is 14.0 and 20.8 mQ in case of PEDOT and PProDOT, respectively. However, it was highest in case of dimethylPProDOT *i.e.*, 60 mQ. This corresponded to the calculated value of the weight deposited which is 2.04×10^{-2} , 3.52×10^{-2} mg and 0.219 mg. The increasing trend of mass deposition with increase in size of the monomer supports high degree of polymerization.

Electrochemical characterization

Cyclic voltammetry: For the cyclic voltammetry measurement, a parallel plate assembly is made where two symmetrical

size polymers coated FTO are kept in front of each other. Study was carried out at 50 mV/s scan rate for each monomer system. It was found that the current density decreased from PEDOT to dimethylPProDOT even the deposited mass was in reverse order as shown in Fig. 1, because of less conducting nature of modified polymer. It is also assumed that as the size of monomer increased, density of the polymer film decreased resulting in less ion exchange with the electrolyte solution. In addition, with functionalization and ring expansion the solubility of the polymer also increased which causes less current density of dimethylPProDOT and PProDOT in comparison to PEDOT. Capacitance measurement through cyclic voltammetry was carried out using the following formula:

$$C = \frac{i}{\text{Scan rate}}$$

where "i" is the average current density in cyclic voltammetry. Specific capacitance was measured by dividing the mass of the polymer. The value of specific capacitance in case of PEDOT, PProDOT and dimethylPProDOT is 70, 51 and 25 F/g.

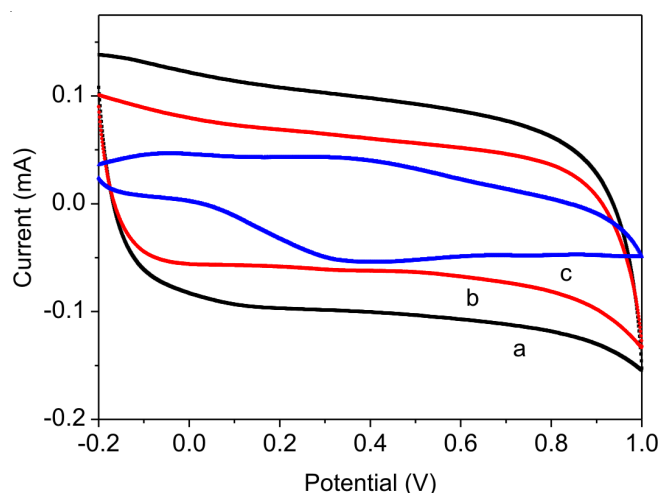


Fig. 1. Cyclic voltammogramme of electropolymerized (a) PEDOT (b) PProDOT and (c) dimethylPProDOT in dichloromethane solution of TBAP

Impedance studies: Impedance measurement was carried from 0.1-10⁴ Hz frequency range in TBAP solution of propylene carbonate at open circuit potential for each polymer film. Nequest plot shows the two regions of frequency first is the high-frequency wing of such spectra in the form of an arc, which is composed of two parallel combined component *i.e.*, C_{dl} (double layer capacitance) and R_{ct} (charge transfer resistance). At lower frequencies region, the spectra looked like a straight line with a particular angle denoted as anomalous diffusion element Z_D as shown in Fig. 2. It was observed that the value of diffusion onset is higher in case of dimethylPProDOT followed by PProDOT and PEDOT which supports higher charge transfer resistance of polymer. From the diffusion part it reveals that PProDOT has higher degree of diffusion than PEDOT, may be due to lesser degree of doping. In case of PEDOT, the existing dopant repel the ion coming through the process of diffusion. However, in case of PProDOT it allows the movement of ion through the polymer film. Secondly, it may

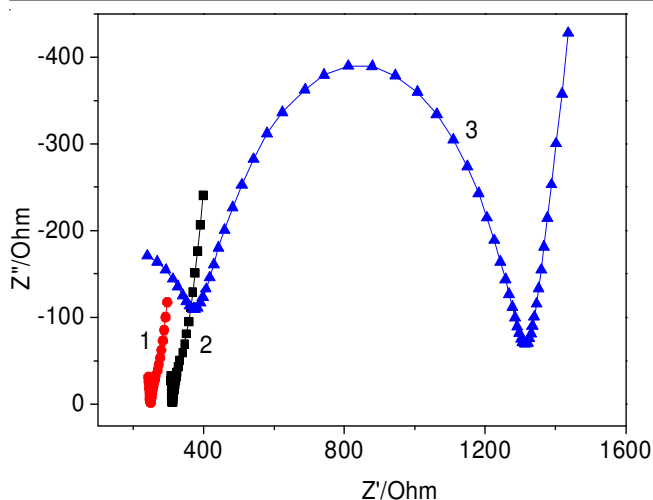


Fig. 2. Nyquist plot of electropolymerized (1) PEDOT (2) PProDOT and (3) dimethylPProDOT in dichloromethane solution of TBAP in parallel plate three electrode assembly

also be due to high porous nature of the PProDOT film. In case of dimethylPProDOT, there is two charge transfer resistance formed due to less degree of doping and highly porous nature of the polymer film as shown in Fig. 2. Due to the less doped/oxidized form of polymer there is fast diffusion that takes place through the polymer film which creates an additional resistance for the ion coming through diffusion process. This phenomenon is well in accordance with cyclic voltammetry where both PEDOT and PProDOT depict the capacitive current; however, dimethylPProDOT shows diffusive current. Following is the formula used for capacitance calculation:

$$C = \frac{1}{2\pi f Z''}$$

where, Z'' and f , is an imaginary impedance at lowest value of frequency. Value of the calculated capacitance is 72, 47 and 22 F/g for PEDOT, PProDOT and dimethylPProDOT.

Chronoamperometric studies: Chronoamperometric technique is carried out to check the stability and power density of the polymer. Study was carried out at constant current (1 mA) for the potential range of 0-1 V. At the constant current density rate of ion exchange with surrounding was studied. It was found that rate is highest in case of dimethylPProDOT followed by PProDOT and PEDOT again due to less conducting and porous nature of modified polymers which correlates well the impedance and cyclic voltammetry data as shown in Fig. 3. Value of capacitance estimated through this technique is found, similar to that of CV and impedance.

Morphological studies: The electrochemical properties of conducting polymers are strongly dependent on their morphology and structure. PEDOT and modified polymer were synthesized in the form of thin film and thus directly used for scanning electron morphology investigation as illustrated in Fig. 4. PEDOT (Fig. 4A) resembled as compact and very regular polymer aggregates, however, PProDOT and dimethylPProDOT shows loss and porous morphology, Fig. 4B-C. These results are in well accordance with the expected feature.

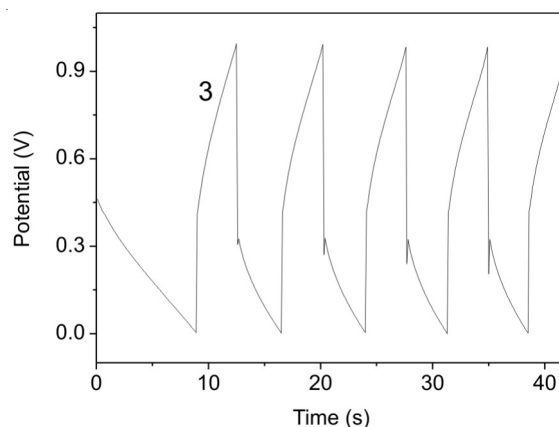
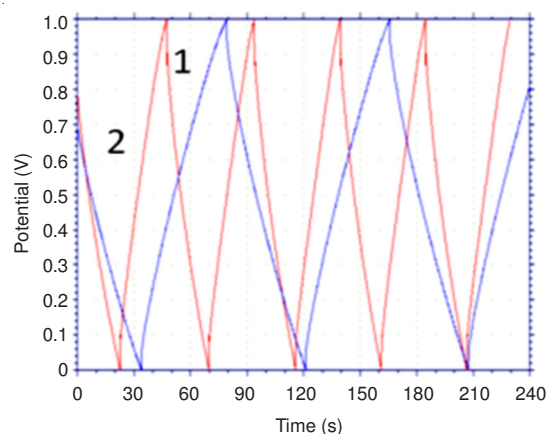


Fig. 3. Chronoamperometric plot of electropolymerized (1) PEDOT (2) PProDOT and (3) dimethylPProDOT in dichloromethane solution of TBAP in parallel plate three electrode assembly

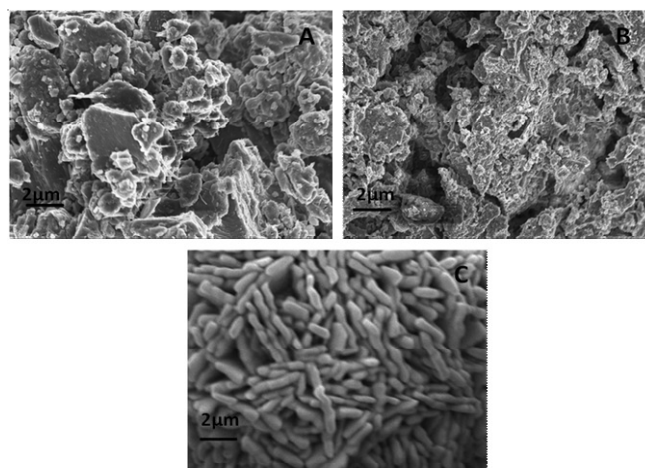


Fig. 4. SEM images of electropolymerized (A) PEDOT (B) PProDOT and (C) dimethylPProDOT thin film

Conclusion

Here we have demonstrated the comparative capacitive properties of different dioxathiophene. It has been found that, increase in both the ring size and functional groups present on polymer film, results in more porous and less conducting polymers, furthermore enhancing the charge/discharge rate. Thus it would be easy to tune the capacitive properties (energy density or power density) of polydioxathiophene for future supercapacitor fabrication.

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