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Electrochemical characterization of poly-(3,4 propylene-dioxythiophene) pseudo-capacitor

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Abstract. Every day use of appliances relies mostly in lithium-ion batteries to satisfy their energy requirements. However, the materials utilized and their lower power densities limit these batteries' desirability. An alternative to batteries is the supercapacitors, which are capable of storing energy in the electrical double layer (EDL) formed between the electrode material and the electrolyte. To reduce the gap in terms on energy and power density between batteries and EDL supercapacitor, pseudocapacitors has been used. In pseudo-capacitors a material that is capable of storing faradaic charge, such as metal oxides and conducting polymers, is deposited in the electrode surface, but its charge / discharge behavior approximate that of the EDL supercapacitor. Therefore, energy density is gained even though the faradaic nature of the process makes its power density decreases. In this paper, we use the conducting polymer, poly-(3,4 propylene-dioxythiophene) for the assembling of a pseudo-capacitor. We present the electrochemical characterization of the devices as a function of the amount of material accumulated in the platinum current collector, in terms of the capacitance, energy, and power density.

1. Introduction

Energy consumption worldwide increased from 495 kWh in 2007 with a projected amount of 739 kWh by 2035 [1]. From this total, countries belonging to the OECD (Organization for Economic Cooperation and Development) currently consumed 50 % (~ 230 kWh). However, when this number is estimated to remain constant for OECD's countries by 2035, the emerging economies will be accountable for the near-total increment in global energy consumption. This panorama calls for actions to improve the use and management of electrical energy resources.

In the USA, nearly 41 % of the energy produced goes into electric power, form which nearly a 50 % it used to provide electricity to residences and for commercial purposes [2]. Regardless of the challenges to obtain energy from renewable sources, a prominent one is to determine how to effectively storage the unused electric energy during low load periods. Energy storage devices (ESD) can present an alternative for the managing of electric energy. Also, ESD are important for the miniaturization of technologies such as those in demand for household electrical appliances, smart phones, personal computers, biomedical applications (pacemakers), and electric vehicles.

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Supercapacitors are just one of the approaches to storage energy, among others such as the Li-ion batteries, and fuel cells. Super-capacitors rely on the formation of the EDL between the material deposited in the electrode (regularly carbon based materials) and the electrolyte [3]. Different from batteries, in supercapacitors no chemical reaction is going on, therefore the cyclability of these ESD is higher as well as its power density. However, energy density is lower than that of the batteries which limits its uses in some applications. In pseudo-capacitor an electroactive material is placed in the electrode, in a configuration that permits the formation of the double-layer phenomena [3]. Pseudo-capacitors have appeared as alternative to reduce the gap between purely EDL super-capacitor and Li-ion batteries, by combining chemical phenomena and surface physics phenomena.

In this study we present the use of electro-active polymer poly-(3,4 propylene-dioxythiophene (p-ProDOT) as material for the construction of a pseudo-capacitor. There have been previous studies using p-ProDOT as conducting polymer for pseudo capacitors [4,5] however, none of these studies explore in depth the dependency of material accumulated in the electrode and capacitance. In the present studies we will discuss how the amount of material deposited over electrode's surface affect the characteristics of the device including, capacitance, energy and power density.

2. Materials and Instrumentation

2.1 Materials

3,4 propylenedioxythiophene (ProDOT), 99%, KCl and Propylene carbonate (PC), 99.7% anhydrous were obtained from Aldrich. Tetrabutyl ammonium perchlorate (TBAP), 99% was obtained from Fluka Chemical, Potassium ferricyanide, ACS grade, was from MP Biomedicals, LLC, diamond paste (No. 40-6244), Metadi fluid (No. 40-6032) were from Buehler Co., Water, D.I.U.F. was obtained from Fisher, an separator membrane from GorTEX®.

2.2 Instrumentation

A Bipotentiostat (model AFCBP1) by the PINE Instrument Company and a glove box from the LC Technology Solution Inc. have been used for all of the experiments. In addition, a potentiostat / Galvanostat (model 273 A) by the EG&G Princeton Applied Research was used for the platinum electrode surface area determination.

3. Methods

3.1 Electrode area calculation

A three-electrode cell, with platinum electrodes as the working electrode, Ag/AgCl (NaCl 3 M) and Nichrome wire as the reference and auxiliary electrodes respectively was used. All potentials are reported against the Ag/AgCl (NaCl 3 M), electrode. The Pt electrodes surface was polished with diamond paste/metadi fluid in a microcloth and rinsed with water. Subsequently, the electrode was cycled in 1 M H₂SO₄ solution from (-200 to 1200) mV at 100 mV/sec for 50 cycles, rinsed with water and air dried [6].

To calculate the platinum electrodes area, the standard procedure [7] using potassium ferricyanide was employed. Chronoamperometry for a 1×10^{-3} M K₃Fe(CN)₆/ 0.1 M KCl solution was done. The resulting chronoamperogram is converted to the corresponding Anson Plot (charge vs time^{1/2}) and using the slope of the forward step and the derived Cottrell's equation (Equation 1, where m is the slope, n is the number of electrons transfer per mol, F is Faraday constant (96, 485.30 C (mol e⁻), C* the bulk concentration of K₃Fe(CN)₆, and D is the diffusion coefficient of K₃Fe(CN)₆ (7.63×10^{-6} cm²/s)) [8]. The above relation allows us to calculate the electrode area. This procedure was done three times for each electrode and the average area reported.

$$A = \frac{m\pi^{1/2}}{2nFC \cdot D^{1/2}} \quad (1)$$

3.2 Electro-polymerization and doping

Using a three-electrode cell as described above, cyclic voltammetry was performed using a 5 mM of ProDOT/0.1M TBAP/PC solution. The voltage window used was from -1000 mV to 1500 mV at a scan rate of 100 mV/s. The number of cycles went from 10- 50 in increments of 10. The same procedure was performed for two electrodes. The Coulombic efficiency was measured to assure that the electrodes do not differ from each other by more than a 30%. Once the electrochemical polymerization process was completed, the surface of the electrode was washed with a few drops of 0.1 M TBAP/PC to remove the excess un-reacted monomer that may be present on the surface. The electro-polymerization and doping chemical reactions are showed in figure 1.

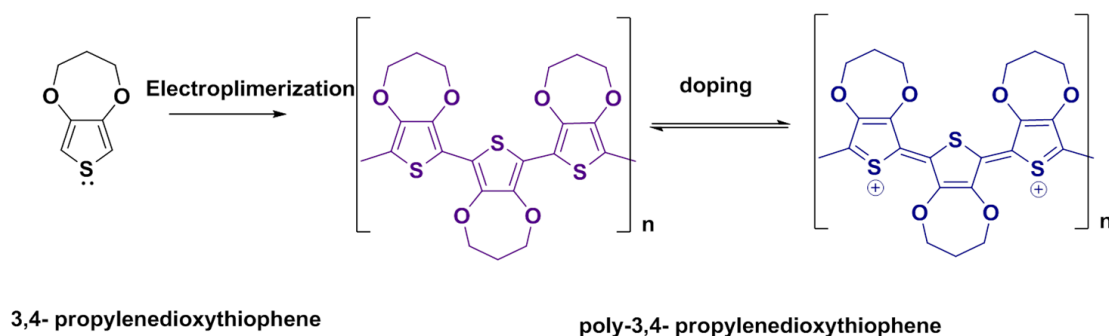


Figure 1. Electro-polymerization and doping reaction for poly-3,4-propylenedioxythiophene

Doping of the polymer is carried out in a similar three-electrode system with 0.1M TBAP/PC as the electrolyte. Out of one of the electrodes polymerized in the previous step, an oxidative reaction is utilized to create a positive charge. The setup is subjected to analog voltammetry sweep at a scan rate of 100 mV/s going from 0 to 700 mV. A complete oxidation of the polymer is accompanied by a color change from light shade of purple to a navy blue. This was considered as the stopping point for the oxidation process. The other electrode is neutralized by analog voltammetry sweep at a scan rate of 100 mV/s using a voltage window of -500 mV to 500 mV for 100 cycles, to ensure that there are no stray charges left on the polymer.

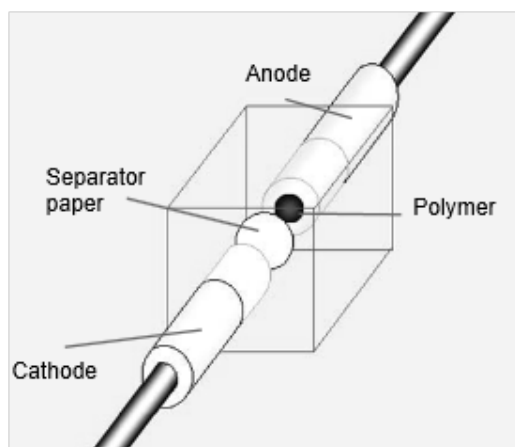


Figure 2. Pseudo-capacitor device configuration.

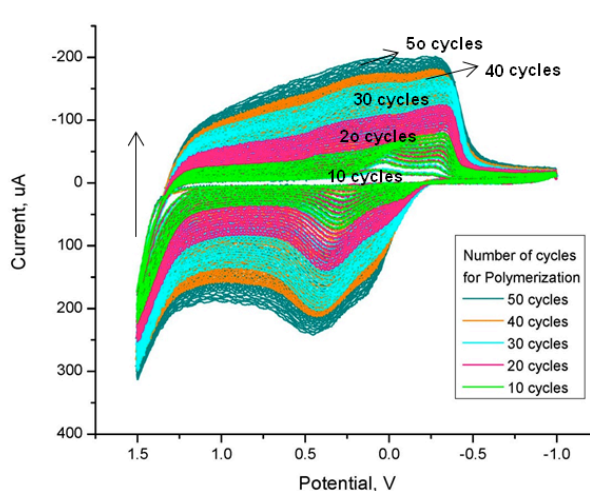


Figure 3. Cyclic voltammograms for the electro-polymerization of 5 mM 3,4-propylenedioxythiophene at 100 mV/s in 0.1 M TBAP/ PC at different polymerization cycles.

3.3 Device Test

The two electrodes are then put together in an assembly shown in figure 2. A few drops of 0.1 M of TBAP are used as electrolyte and a separator paper is used in between the electrodes. For the device test cyclic voltammetry (4 cycles) at different working windows (1 V, 1.5 V, and 2 V) is done at different scan rates (25 mV/s-10,000 mv/s). From the results the capacitance, energy density, power density and device life was determined.

4. Results

4.1 Electropolymerization and doping

Calculated Pt electrodes' area ranged from (0.018-0.020) cm². Figure 3 shows the cyclic voltammograms as function of polymerization cycles obtained for the electro-polymerization of poly-3,4-propylenedioxythiophene. The trace crossing of the reverse scan, associated with the initiation of the nucleation process that occur as initial products are formed (dimers, oligomers, and bipolarons), is observed in the first cycle, as reported previously for conducting polymers [8]. The amount of material deposited in the electrode was calculated using the equation for quantitative estimate of the surface coverage for adsorbed species ($\Gamma=Q/(nFA)$) [9,10] where Q is the charge in coulombs (obtained from the integration of the voltammetric wave), A is the area of the electrode in cm², F is the Faradays' constant (96,487 coulombs/ mol), and n is the number of electrons per mol of reaction that, for p-PRODOT, yields 2.25 electron/monomer [5]. By simply multiplying by the monomer molecular weight, the mass of material deposited in the surface can be calculated. Table 1 shows the mass in micro grams of the material deposited over the electrode as a function of polymerization cycles. As cycling is increased the amount of material deposited in the electrode increases, as expected. However, it can be appreciate from the table that the tendency is to reach a plateau as the numbers of cycles approach 50 cycles.

We attribute this result to a diffusion limitation, as more material is deposited, few monomer molecules from the solution can accesses the electrode surface and therefore the current (which have a direct dependence with the square root of diffusion coefficient [9,10], is reduce). This can be observed from the voltammograms in figure 2. Going from 30 to 50 polymerization cycles, the increment in current is considerably reduced. Also, a close look to the oxidation wave show a shift to more positive potentials as polymerization cycles are increased, which denotes that the oxidation process becomes more difficult as more material is grown in the surface [11].

Table 1. Mass of the material accumulated as a function of polymerization cycles

Number of Cycles	Mass, μg
20	0.68
40	1.19
60	1.66
80	1.93
100	2.09

The doping time dependence with number of cycles, and therefore amount of material deposited was also determined. It can be observed in figure 4, that as the amount of cycles are increased, the time for doping increases exponentially. As more material is deposited in the electrode, the accesses of the electrolyte to all the oxidation sites become harder and therefore, the oxidation time increases.

4.2 Device test

The cyclic voltammograms for the device test of the p-ProDOT pseudocapacitor using a one-volt window at different scan rates are shown in figure 5. The voltammograms showed the expected

square-shape for a super capacitor. As working window is opened (results not showed) the square shape is lost at lower scan rates.

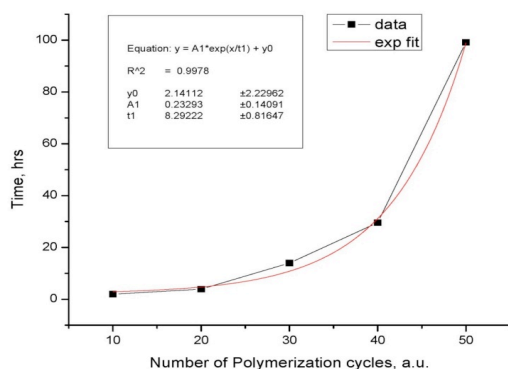


Figure 4. Oxidation time dependence with amount of polymer deposited (polymerization cycles).

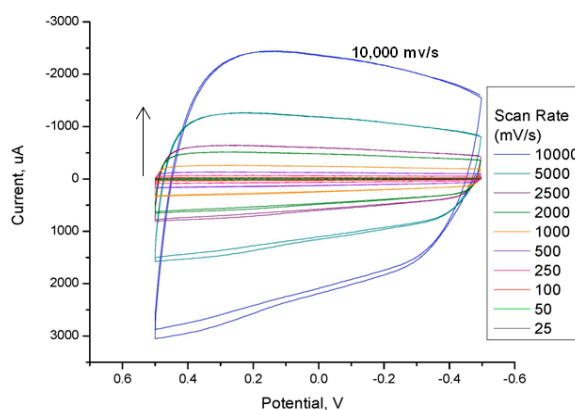


Figure 5. Cyclic voltammetry for device test at different scan rates

It can also be appreciated as expected, an increment in current as the scan rate is increased. The capacitance as a function of scan rate and frequency, and dependence on polymerization cycles for a working window of 2 volts is shown in figure 6. The capacitance is determined from the charge of capacity ($C_{1/2}$) and the device voltage (V_d) and corrected for the amount of material in the electrodes. The capacitance profiles for all the devices show the expected decay in capacitance as scan rate is increased.

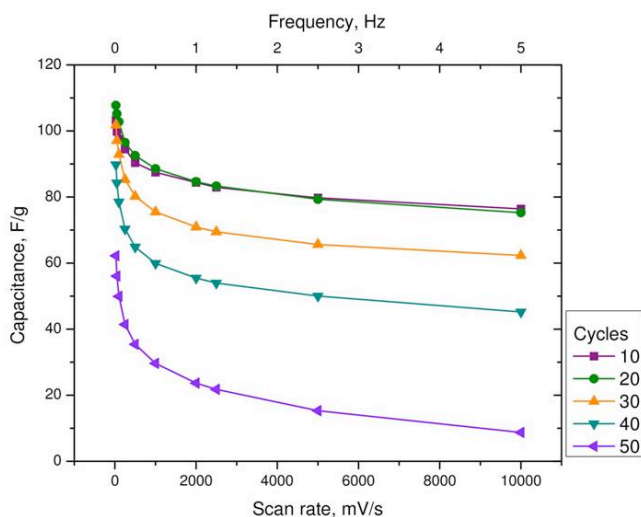


Figure 6. Capacitance as a function of frequency and scan rate for 2 volts working window for different polymerization cycles

The finer details can be seen more clearly from the plot of capacitance with the log of scan rate (figure 7A). This transformed the results plot into a linear decay, and from the slope for these lines it can be observed that as the polymerization cycles are increased, the slope increases (2.29 ± 0.59 to 4.46 ± 1.20), meaning that the discharge for the higher polymerization device is more dramatic as frequency increases. The capacitance for 10 and 20 cycles of polymerization is similar, with a slightly difference of 4 F/g (103.3 F/g vs 107.8 F/g) at lower frequencies with a lost in capacitance of approximately 30 F/g from scanning all the frequencies ranges. For 30 cycles we see a difference ranging from 101.8 F/g to 62. F/g. The most dramatic is for 40 and 50 cycles, that even at low

frequencies there is a difference in capacitance of up to 40 F/g in comparison with the other devices, and for the 50 cycles we see that at the highest frequency the capacitance abruptly decreases (8.7 F/g). Similar tendencies are observed in figure 7B and 7C for power and energy respectively. These observation can be explain based in diffusion limitations, even when as more material is deposited in the electrode and therefore more possible charges, accessing them is more difficult. Since capacitance is a surface phenomenon between the electrolyte and the electrode material, it is essential for the electrolyte to be in contact with the electrode. Sulaiman and Katakya [8] reported that the morphology of electro-polymerized p-ProDOT, different from PEDOT that posses a rough dense morphology, have a very porous surface with micro-sized holes. Based on this observation we conclude that as more material is accumulated in the electrode surface, the accesses of the electrolyte to these holes during the experimental time frame becomes more difficult, therefore reducing the device overall capacitance.

The device cyclability was also calculated for 10,000 cycles, for 20, 30, and 40 polymerization cycles devices. At a scan rate of 100 mV/s and a working window of 2 V (figure 7D), the results show that after 5 % of the initial current lost or less, the device keeps stable during the time scale of the experiment for all the tested parameters.

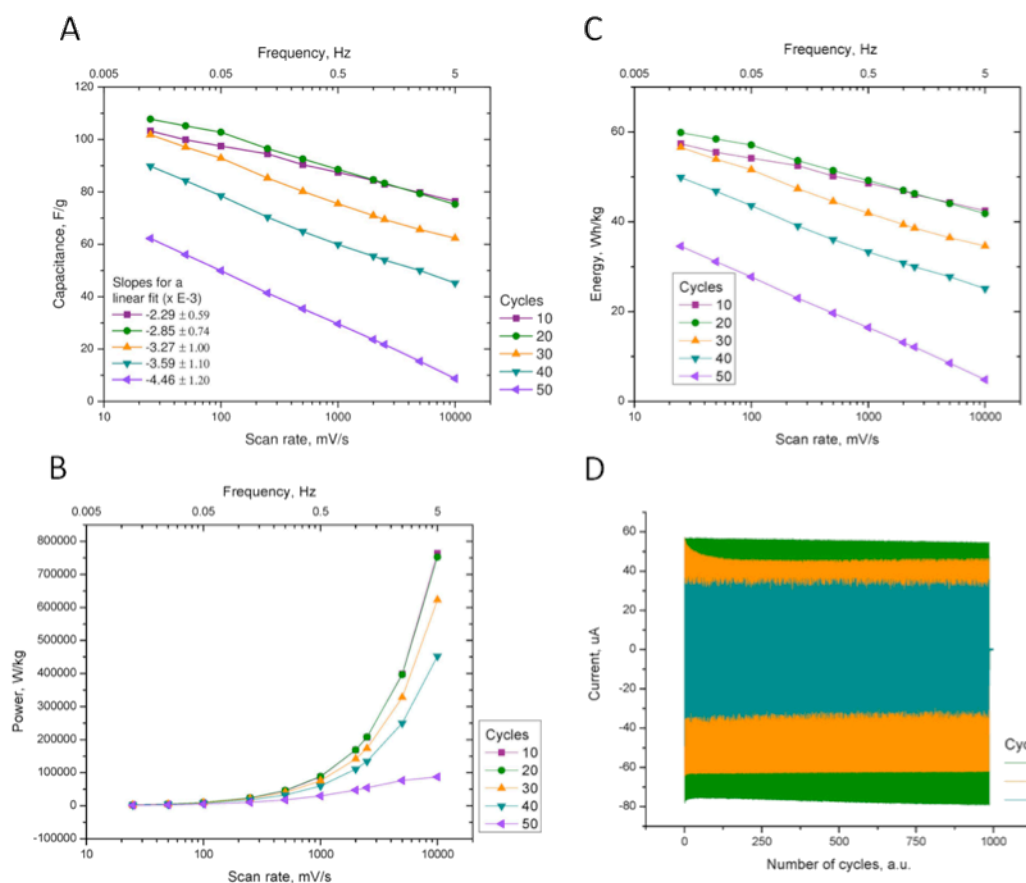


Figure 7. Device Characteristics for 2 Volts working window A) Capacitance as a function of frequency and log scan rate B) Power as a function of frequency and log scan rate C) Energy as a function of frequency and log scan rate D) Stability of the device for 1000 cycles as a function of the polymerization cycles.

5. Conclusions

The dependence of p-ProDOT pseudo capacitor characteristics upon the amount of material deposited in the electrode has been investigated. The results show an increment in capacitance as function of frequency after 30 polymerization cycles. The slope of the device for 50 polymerization cycles experiences a two folds increment in comparison to 10 and 20 polymerization cycles. This behavior has been attributed to a diffusion limitation of the electrolyte to access all the sites in the polymer as the amount of material is increase.

Acknowledgements

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