Evaluation of Composite Electronic Materials Based on Poly (3, 4 – propylenedioxythiophene/Poly – (p – Naptheleneethynylene) Wrapped Single Wall Carbon Nanotubes for Supercapacitors

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Keywords

Supercapacitor

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ABSTRACT

Supercapacitors have emerged to do major advances in energy storage and technology. This paper summarizes the performance data of a specially designed poly (3, 4 – propylenedioxythiophene) PProDot based conducting polymer for use in a p-type supercapacitor. Performance data of these polymer composite electrodes are also compared with those of a poly (3, 4 – propylenedioxythiophene/poly – (p – naptheleneethynylene) wrapped single wall carbon nanotube supercapacitor. Longevity of the system was analyzed to determine life span and durability of both PProDot and PProDot/PNES/SWNT based devices. Both composites were characterized using Scanning electron microscopy (SEM).

1. INTRODUCTION

Electrochemical capacitors (EC) are new energy sources that have been under development for some time. Also known as “supercapacitors” or “ultracapacitors”, they can complement or replace batteries in electrical storage and harvesting, when high power delivery or uptake is needed.[1] Early electrochemical capacitors were rated at a few volts and had capacitance values from a fraction of farads to several farads.[2] But to meet higher requirements of future systems, their performance must be improved. One way to improve performance would be through the development of active storage devices using active materials (highsurface area carbons, electroactive polymers, and transition metal oxides and nitrides). Another way would be to modify the electrolytes using conventional aqueous and nonaqueous electrolytes, advanced

polymer electrolytes, or ionic liquids. Finally, device configurations, both symmetric and asymmetric, could be explored.

However, for such materials to be used in supercapacitors, they should fulfill the following requirements: (i) a high conductivity for assuring a high power density, (ii) an adequate pore size distribution and (iii) surface properties that could undergo redox reactions.[3]Such is the case of polymers and carbon nanotubes (CNTs) which have been reported in the literature. It has been demonstrated that carbon nanotubes can serve as a coating layer over ordinary current collectors to drastically enhance the electrode performance[4] and polymers have been shown to have very good cyclability and maximum capacitance.[5]

Due to the high requirements needed for better future systems, the region of the power vs. energy density plane of electrochemical capacitors was the goal of this investigation.. In this paper we present an electrochemical polymerization of a p-type supercapacitor device based on a poly (3, 4 – propylenedioxythiophene). Longevity of the system was analyzed to determine life span and durability of the electrochemical capacitor. Scan rate tests and oxidizing voltage window tests were also done. Scanning electron microscopy (SEM) characterization was done for the analysis of ProDot and CNTs morphologies. Also a poly – (p – naptheleneethynylene) wrapped single wall carbon nanotube supercapacitor was constructed to undergo the same analysis so that comparison of both systems was executed.

2. MATERIALS AND METHODS

2.1. *Preparation of solutions:*

A tetrabutylammonium hexafluorophosphate ($TBAPF_6$) electrolyte was prepared using 25 mL of propylene carbonate (PC) [Sigma-Aldrich, 99.7%] solution and 0.9796 g of $TBAPF_6$ [Fluka, 99.0%]. Also a *Poly (3, 4 – propylenedioxythiophene)/ Tetrabutylammonium hexafluorophosphate electrolyte* (PproDot/$TBAPF_6$/PC) was prepared. The polymer solution was done using approximately 30 mg of Poly (3, 4 – propylenedioxythiophene) [Aldrich, 97%] dissolved in 10 mL of $TBAPF_6$ solution.

2.2. Electropolymerization of ProDot in $TBAPF_6$/PC

For the electropolymerization of ProDot, the electrode setup was the following: platinum (Pt) working electrode from Bio Analytical Systems (BAS), silver wire (Ag) 99.9% (d = 2mm) reference electrode from Alfa Asar and platinum strip(Pt) (4 mm height, 6 mm wide) cut from commercial grade Pt foil from Sigma Cohn Corporation as an auxiliary electrode.

The working electrode was polished previously with 0.3 micron and 0.05 micron alumina slurry and rinsed with distilled water. The electrodes were sonicated for 10 minutes and rinsed with distilled water and dried with gas nitrogen (N_2). The Ag wire and Pt strip were gently polished with Carbimet paper disc and put in a 90 micron solution.

The electropolymerization was done in a glove box under an N_2 atmosphere. The cyclic voltammetry was done using Pine Instrument Potenciostat. A simple CV experiment was done using an initial sweep up direction with a total of 24 sweeps. The sweep potentials were from -1000 mV to 1600 mV and a sweep rate of 100 mV/s.

Cathode

2.3. Tests done on electrodes

Scan rate tests were done in a TBAPF6/PC solution using previously electropolymerized electrodes. The parameters used were the following: sweep rates: 25, 50, 100, 200, 250, 300, 400, 500, 750, 1000, 2500, 5000, 10000 mV/s, total sweeps: 6, sweep potentials: -1000 mV to 1000 mV, sweep up direction with 3 electrode setup mentioned.

Oxidizing voltage window tests were also conducted using a ProDot/TBAPF6/PC solution. Oxidizing tests were done using the following parameters:Sweep rate: 100 mV/s, total sweeps: 9, various sweep potentials. A sweep up direction CV with three electrode setup mentioned.

2.4. Charge capacities and Coloumbic Efficiencies

Anodic and cathodic charges were determined plotting each CV as a function of current vs. time (See Figure 1). The area below and above the curve is calculated by the same PineChem Software which gave us these values. Anodic and cathodic charges can not exceed a 30% limit difference. Columbic efficiency was determined by the ratio of cathodic to anodic charge capacity.

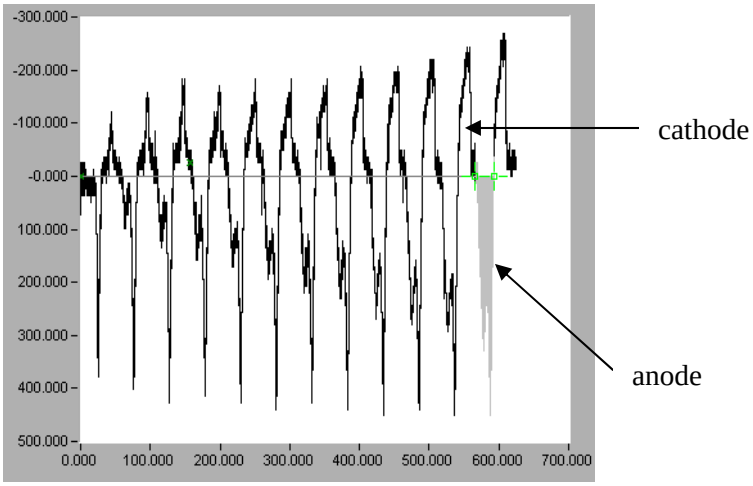


Figure 1: CV as a function of current vs. time

2.5. Supercapacitor assembley and testing based on the ProDot/TBAPF$_6$/PC system

The supercapacitor constructed is that of type I where the same p-doping polymer is used for both electrodes. One electrode contains ProDot in its neutral state and the other in its oxidized state. The same three electrode setup is used for the electropolymerization procedure and doping of both electrodes followed. The device was set up as shown in Figures 2 and 3.

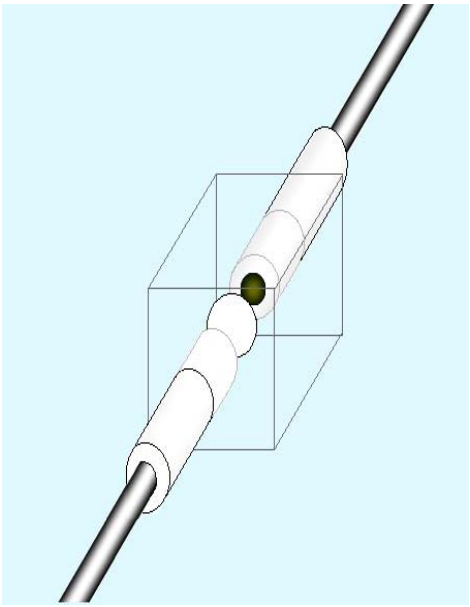
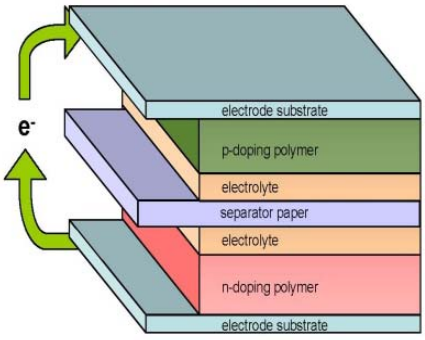


Figure 2: Supercapacitor device configuration



2.7.a

Figure 3: Supercapacitor device internal configuration

2.6. Supercapacitor Scan Rate Tests

After device construction scan rate tests were conducted using the following parameters:

Sweep rates: 250, 100, 50, 25, 500, 1000, 2500, 5000, 10000 mV/s, total Sweeps: 4 and a type I device potential of 0 mV to 500 mV. Charge potentials and columbic efficiencies were determined.

2.7. Integrating Poly – (p – Napthelenеethynylene (PNES) Wrapped Single Wall Nanotubes Composite

Same supercapacitor device was constructed but with the integration of PNES/SWNT. 8 µL of these SWNT were drop casted onto the platinum working electrodes. Same testing and experimental procedure was conducted.

3. RESULTS

3.1. ProDot/TBAPF6/PC electrodes

After electroploymeriztion of Pt electrode was used for scan rate tests, cathodic and anodic charges were calculated.

Electrode 1 used for oxidizing voltage window tests had a cathodic charge of 12.21 mC and an anodic charge of 22.26 mC. Polymer film had a deep purple color and was well deposited over the working electrode.

Electrode 2 used for scan rate tests had a cathodic charge of 9.649 mC and an anodic charge of 16.17 mC. Polymer film also presented a deep purple color and was well deposited over the working electrode.

NOTE: Anodic and cathodic did not exceed the 30 % limit of difference.

Table 1: Scan Rate Tests on PproDot 1

Scan rate (mV/s)	*Lower limit (mV)*	*Upper Limit (mV)*	*Anodic Charge mC*	*Cathodic Charge mC*	*Coloumbic Efficiency(%)*
25	*-1000*	*1000*	*8.396*	*8.020*	*95.52*
50			*7.999*	*7.797*	*97.47*
100			*7.544*	*7.444*	*98.67*
200			*6.825*	*6.774*	*99.25*
250			*6.490*	*6.452*	*99.41*
300			*6.187*	*6.155*	*99.48*
400			*5.582*	*5.551*	*99.44*
500			*4.933*	*4.900*	*99.33*
750			*3.690*	*3.623*	*98.18*
1000			*2.925*	*2.778*	*94.97*
2500			*1.434*	*995.2 uC*	*69.40*
5000			*854.9 uC*	*411.0 uC*	*48.08*
10000			*496.5 uC*	*156.5 uC*	*31.52*

NOTE: Boxed scan rates have been graphed to show slow degradation of polymer film. These are the limits where the polymer film is still well adhered to the Pt electrode.

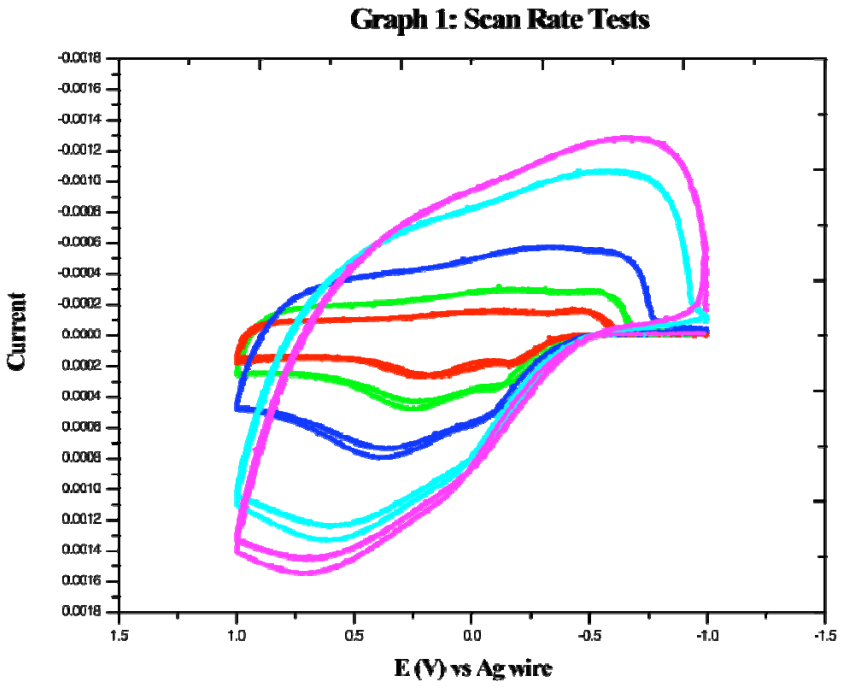
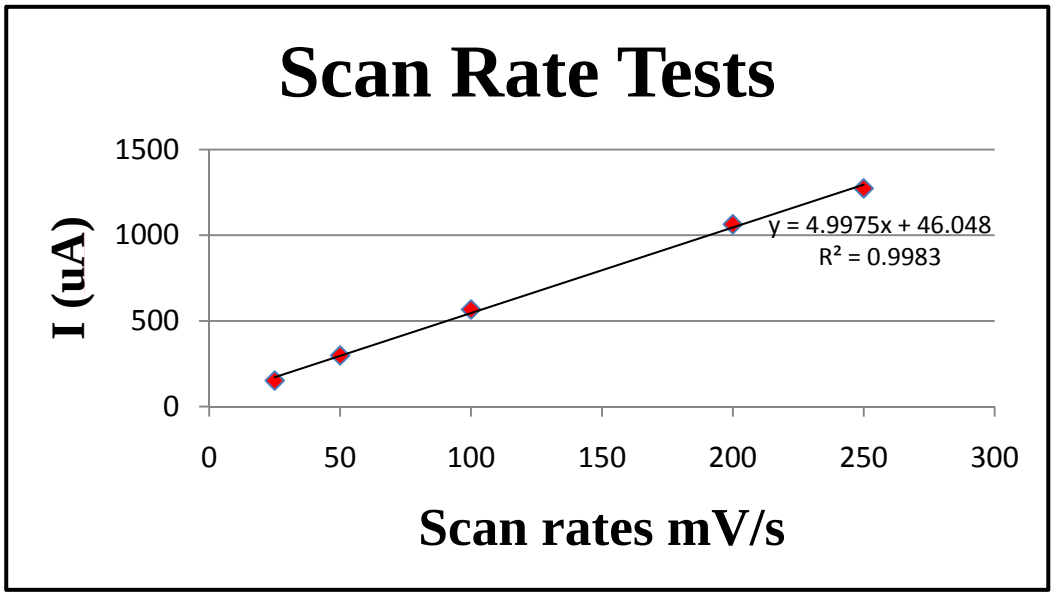


Table 1 and Graph 1 show that as the scan rate increases there is an evident increase of columbic efficiency and consequent degradation of polymer film.

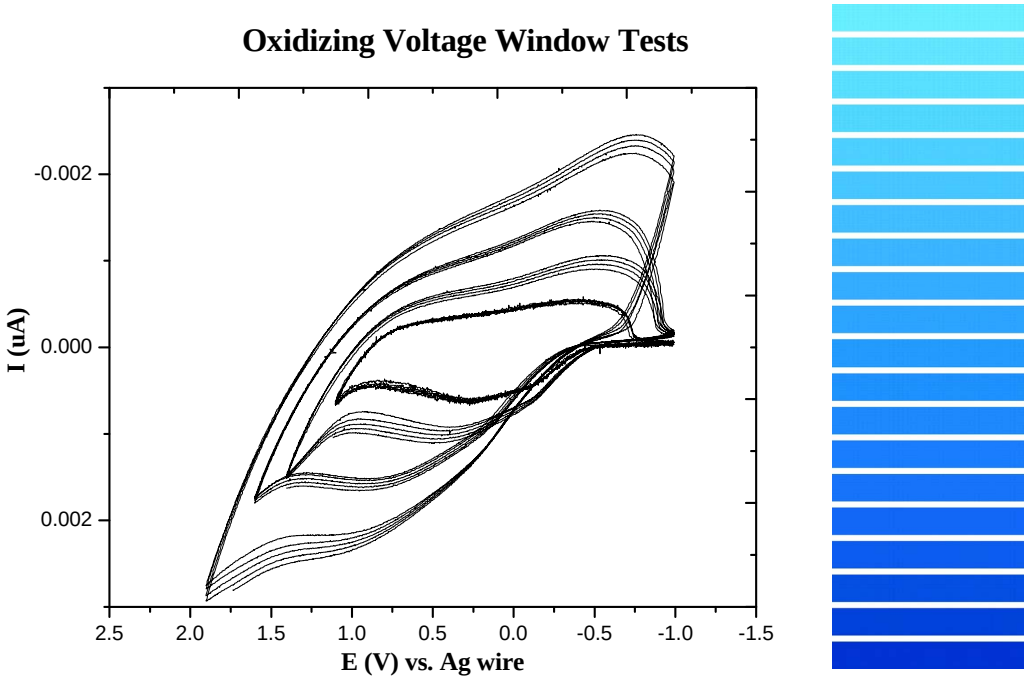
Graph 2: Peak Height vs Scan Rate Tests



This graph evinces immobilized polymer film from the 25 mV/s to 250 mV/s scan rate

Table 2: Oxidizing Voltage Window Tests

Sweep rate (mV/s)	*Lower limit (mV)*	*Upper limit (mV)*	*Anodic charge*	*Cathodic charge*	*Coloumbic Efficiency (%)*
100	-1000	900	10.13	9.295	91.76
		1000	10.45	9.710	92.92
		1100	7.741	6.680	86.29
		1200	10.28	8.160	79.38
		1300	13.81	10.44	75.60
		1400	18.65	13.78	73.89
		1500	21.59	17.18	79.57
		1600	26.70	21.81	81.69
		1700	32.30	26.28	81.36
		1800	39.16	31.39	80.16
		1900	48.23	38.28	79.37
		2000	56.01	44.85	80.07
		2200	70.93	54.35	76.62
		2400	89.80	66.05	73.55



Oxidizing voltage window tests show a decrease in coloumbic efficiency as the potential limit increases meaning degradation of polymer film. As the potential limit increases, the polymer film changes from a light blue color to a navy blue, as shown at the right side of the graph.

3.2. ProDot/TBAPF6/PC Supercapacitor Device

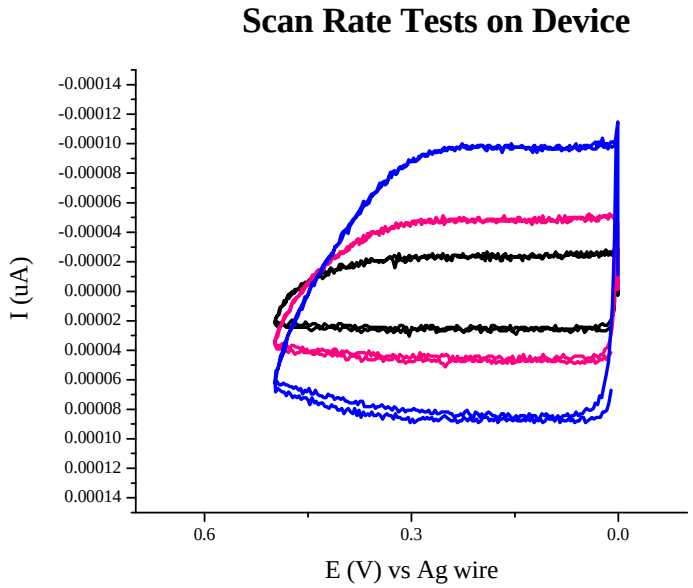
After electroploymeriztion of the Pt working electrode that was used for scan rate tests, cathodic and anodic charges were calculated.

Electrode 1 had an anodic charge of 12.74 mC and a cathodic charge of 8.467 mC. It was doped to its oxidized state and recovered an anodic charge of 5.109 mC and a cathodic charge of 4.985 mC. Its polymer film turned from a deep purple to a blue color after oxidation.

Electrode 2 had an anodic charge of 13.05 mC and a cathodic charge of 8.238 mC. It was doped to its neutral state and recovered an anodic charge of 1.010 mC and a cathodic charge 973.1 µC. Its polymer film remained a deep purple color after neutralization.

Table 3: Supercapacitor Scan Rate Tests

Scan rate (mV/s)	*Lower limit (mV)*	*Upper Limit (mV)*	*Anodic Charge mC*	*Cathodic Charge mC*	*Coloumbic Efficiency(%)*
25	-1000	1000	8.396	8.020	95.52
50			7.999	7.797	97.47
100			7.544	7.444	98.67
200			6.825	6.774	99.25
500			4.933	4.900	99.33
1000			2.925	2.778	94.97
2500			1.434	995.2 uC	
5000			854.9 uC	411.0 uC	48.08
10000			496.5 uC	156.5 uC	31.52



Scan rate tests on the device demonstrated an evident decrease on columbic efficiency while there was an increase in scan rate. The graph of scan rates done on the device show degradation of the polymer film while the speed of the system is increasing. In other words increase of scan rate is an increase of degradation of polymer film.

3.3. ***ProDot/PNES/SWNT electrodes***

After drop casting SWNT and electroploymeriztion of Pt electrode was used for scan rate tests, cathodic and anodic charges were calculated.

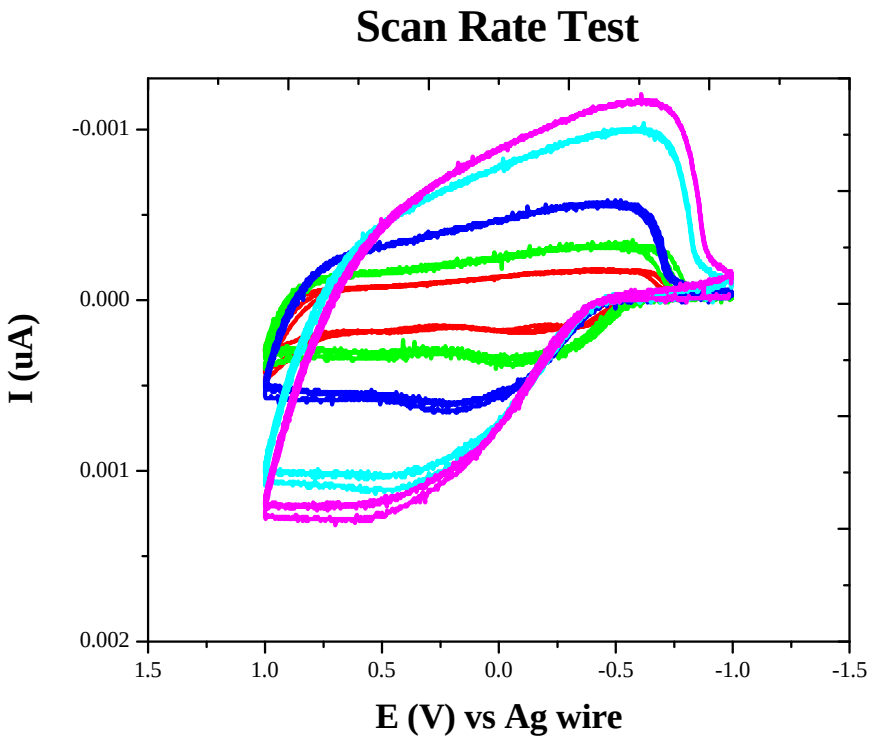
Electrode 1 used for oxidizing voltage window tests had a cathodic charge of 9.200 mC and an anodic charge of 15.97 mC. Polymer film had a deep purple color and was well deposited over the working electrode.

Electrode 2 used for scan rate tests had a cathodic charge of 10.02 mC and an anodic charge of 16.10 mC. Polymer film also presented a deep purple color and was well deposited over the working electrode.

NOTE: Anodic and cathodic did not exceed the 30 % limit of difference. Same tendencies on all tests were seen.

Table 4: Scan Rate Tests

Scan rate (mV/s)	*Lower limit (mV)*	*Upper Limit (mV)*	*Anodic Charge mC*	*Cathodic Charge mC*	*Coloumbic Efficiency(%)*
25	*-1000*	*1000*	*10.28*	*8.391*	*81.62*
50			*8.333*	*7.804*	*93.65*
100			*7.008*	*6.802*	*97.06*
200			*6.032*	*5.918*	*98.11*
250			*5.557*	*5.485*	*98.70*
300			*5.333*	*5.244*	*98.33*
400			*4.759*	*4.696*	*98.68*
500			*4.337*	*4.282*	*98.73*
750			*3.455*	*3.385*	*97.97*
1000			*2.778*	*2.683*	*96.58*
2500			*1.332 uC*	*1.018 uC*	*76.43*
5000			*910.0 uC*	*793.0 uC*	*87.14*
10000			*460.1 uC*	*166.9 uC*	*36.27*



Peak Height vs Scan Rate

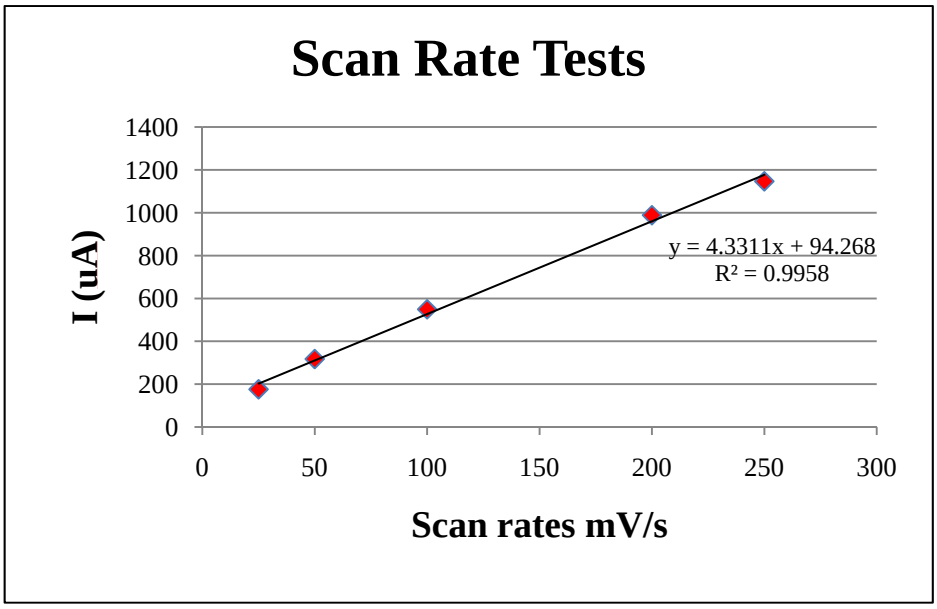
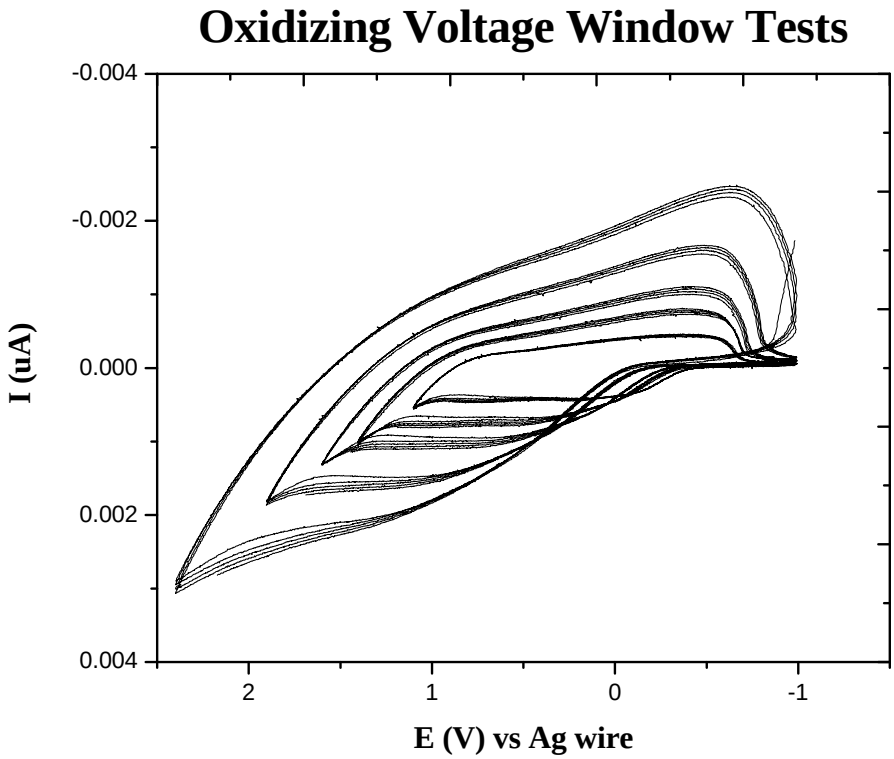


Table 5: Oxidation tests on PproDot/PNES/SWNT 1

Sweep rate (mV/s)	*Lower limit (mV)*	*Upper limit (mV)*	*Anodic charge*	*Cathodic charge*	*Coloumbic Efficiency (%)*
100	-1000	900	4.549	4.235	93.10
		1000	5.079	4.704	92.62
		1100	6.185	5.356	86.59
		1200	8.259	6.594	79.84
		1300	10.81	8.448	82.98
		1400	18.65	13.78	73.89
		1500	12.34	10.00	81.04
		1600	14.93	11.96	80.11
		1700	18.06	14.39	79.67
		1800	21.57	17.27	80.06
		1900	25.02	20.32	81.22
		2000	28.90	23.70	82.00
		2200	42.61	33.57	78.78
		2400	53.71	40.64	75.67



3.4. ProDot/PNES/SWNT Supercapacitor Device

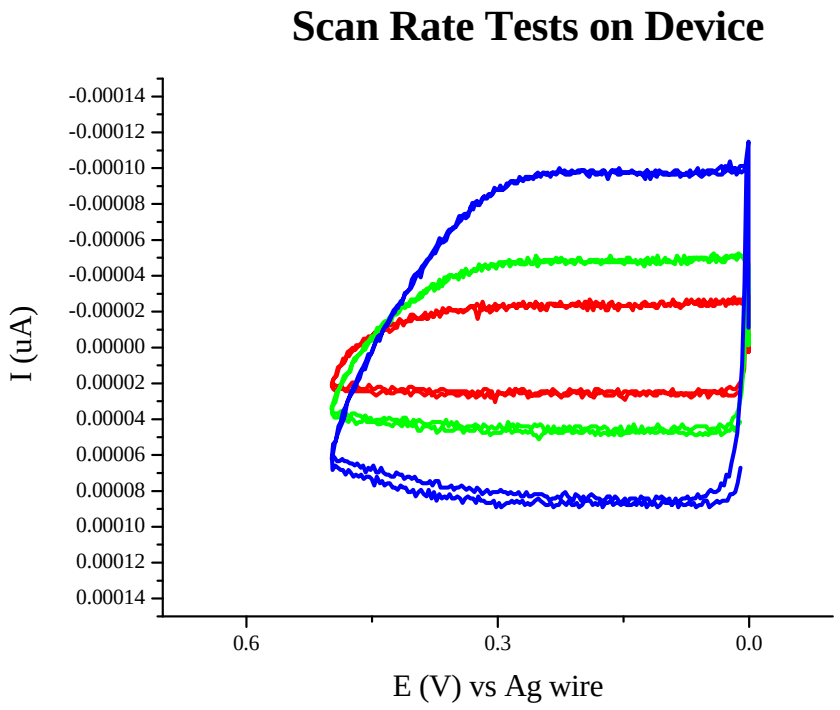
After electroploymeriztion of the Pt working electrode that was used for scan rate tests, cathodic and anodic charges were calculated.

Electrode 1 had an anodic charge of 9.745 mC and a cathodic charge of 6.370 mC. It was doped to its oxidized state and recovered an anodic charge of 3.259 mC and a cathodic charge of 3.259 mC. Its polymer film turned from a deep purple to a blue color after oxidation.

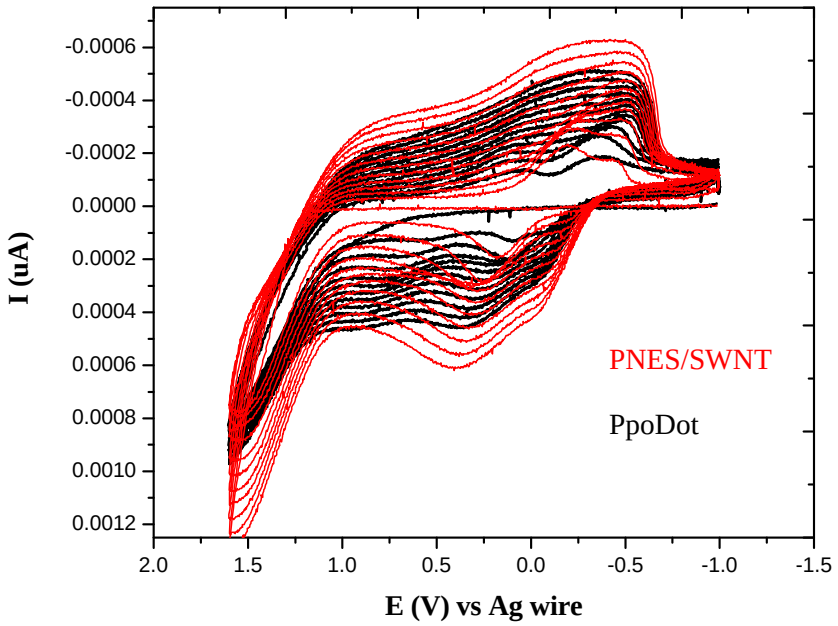
Electrode 2 had an anodic charge of 8.061 mC and a cathodic charge of 5.809 mC. It was doped to its neutral state and recovered an anodic charge of 828.0 uC and a cathodic charge 872.6 µC. Its polymer film remained a deep purple color after neutralization.

Table 6: Supercapacitor Scan Rate Tests

Scan rate (mV/s)	*Lower limit (mV)*	*Upper Limit (mV)*	*Anodic Charge uC*	*Cathodic Charge mC*	*Coloumbic Efficiency(%)*
25	-1000	1000	340.7	330.8	97.09
50			382.3	368.7	96.44
100			407.8	390.2	95.68
200			429.4	402.5	93.74
500			285.8	279.0	97.62
1000			233.1	226.9	97.34
2500			151.9	142.3	93.68
5000			100.9	82.64	81.90
10000			69.16	39.76	57.49



Comparison PproDot vs PproDot/PNES/SWNT



DISCUSSION

In the construction of a supercapacitor various properties should be considerate. In the making of the ProDot/$TBAPF_6$/PC capacitor, the polymer and the whole electrolyte solution were studied before the construction of the device. ProDot or poly (3, 4 – propylenedioxythiophene) is an electronically conducting polymer (ECP) and provided higher capacitance and/or high power capability. ECP's have the ability to tailor conductivity, voltage window, storage capacity and chemical stability. On the other hand $TBAPF_6$ has a small ionic radius. This permitted the constant movement of ions in the electrochemical process which is crucial in the electropolymerization of electrodes and accumulation of charge. Each electrode accumulated more cathodic and anodic charge compared to the ProDot /$TEABF_4$/PC supercapacitor previously constructed (approximately an increase of 50% accumulation of charge).

Device configurations, both symmetric and asymmetric are very important in the construction of a device. This study focused on a Type I symmmetric capacitor containing the same p-doping polymer. Increasing storage capacity and the operating potential differs from type to type. N-polymers are inherently less stable than p-doping polymers. As a consequence, p-doping polymers were used. This added atoms that increased the number of free positive charge carriers. Page: 16

Scan rate tests of the electropolymerized electrodes showed that as the scan rate increases there is an evident increase of columbic efficiency and by consequence degradation of polymer film. Scan rate tests are primarily done to experiment how fast a system can operate without damaging some aspect of functionality. Ions tend to gain more kinetic energy as scan rate increases. Scan rate tests were also done to the whole device and responded the same way as did the electropolymerized electrode. Peak height was plotted versus scan rate where a nice correlation line demonstrates immobilized polymer film. Also oxidation tests were conducted and effectively showed a degradation of the polymer film while coloumbic efficiency decreased and potential limit increased. By changing the sweep potentials, identification of how far the oxidation state can be taken. What helped in the determination in the over oxidation of the polymer film was the surface appearance and color of the electropolymerized Pt electrode. When over oxidized the polymer film changed from a light blue to dark blue color. Also tearing and scratching of polymer film was observed.

Integrating PNES/SWNT gave similar results on scan rate tests and oxidizing tests. Scan rate tests done on device show very good distribution on charge. The scan rate test CV resembles a rectangular form which confirms a very good distribution of charge. Comparing cyclic voltammagrams of PproDot/TBAPF6/PC device and the PproDot/PNES/SWNT we see a major capacitance using the SWNT composite than that using PproDot only. A 3% difference is obtained.

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