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# SOLID-STATE ULTRACAPACITORS FOR ELECTRIC VEHICLES AND CONSUMER ELECTRONICS

DE-FG02-96ER82138

## Final Report

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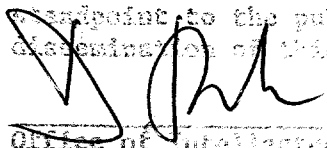
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### *Executive Summary*

Advanced ultracapacitors are described that are based upon conducting polymer technology. Both Type I and Type II capacitors were constructed in single cell and stacked arrays that had superior electrochemical properties. More specifically nanophase clay electrode supports were fabricated and the conducting polymers solvent deposited upon them. Both liquid phase and solid polymer electrolytes were evaluated as well.

Both single cell and multiple cell capacitors were prepared that exceeded the 15Wh/kg, 1500W/kg goals set by the United States Department of Energy. In addition, it was shown that different conducting polymer electrode configurations could be constructed that showed promise.

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## 1.0 PURPOSE OF THE RESEARCH

### 1.1 Introduction

Due to the increasing demand for portable power sources, there is a need to develop compact, lightweight, environmentally-friendly devices that deliver high power on demand. Electrochemical capacitors (ultracapacitors) are a good approach to meeting high power requirements. The construction of an electrochemical capacitor is similar to that of a battery. However, in most cases, the two electrodes in the capacitor are identical. The current at any electrode must be accounted for either by Faradaic reactions, surface charge transfer, or charging of the double layer. In a battery, the Faradaic reactions are dominant and the electrode material takes part in the reaction, with the effect of the double layer being minimal.

There are currently two types of electrochemical ultracapacitors under development; Electrochemical Double Layer Capacitors (EDLC) and electrochemical supercapacitors (ECC). EDLCs are usually composed of high surface area carbon and a suitable electrolyte (aqueous or organic). Electrostatic charge is stored on the surface of the carbon, so that the capacitance is limited by the available surface area of the carbon with the Faradaic current contribution being zero. The ions from the electrolyte approach the electrode but do not react with it, or are not absorbed into it. Energy densities of electrochemical capacitors based on carbon and graphite fibers, which have been under investigation for a long period of time, are much higher than those of ordinary electrolytic capacitors, (e.g. tantalum) but typically lower than those of advanced batteries (<10 Wh/kg). Unlike EDLCs, ECCs rely on actual Faradaic electrochemical reactions for energy storage. This process gives rise to the so called pseudocapacitance of an ECC. There are two types of pseudocapacitance possible in an ECC. In this report we confine ourselves to *Redox* pseudocapacitance which results from actual electrochemical oxidation and reduction reactions at active electrode sites. In these cases, the double layer can store much more charge than in the simple case of double layer capacitance. The total capacitance is therefore the sum of the double layer capacitance and a pseudocapacitance resulting from the charge transfer reactions. High power delivery with long cycle life derives mainly from the double layer capacitance, and the pseudocapacitance, which is diffusion related, contributes to a high energy density. Redox ECCs vary in their design, but the two most prominent approaches in current research are the metal oxide ECCs and conducting polymer ECCs.

For both parameters, one of the key requirements for high performance is the surface area of the electrode material. However, there are several characteristics that need to be taken into account for an electrochemical capacitor to perform well:

- Specific capacitance of the electrode material;
- Surface area of the electrode material;
- Electrode porosity, pore size distribution;
- Electrode density;
- Electronic conductivity of the electrode material;
- Ionic conductivity of the electrolyte;
- Conductivity of the current collector; and
- Contact resistance between the electrode and the current collector.

The use of ultracapacitors can be envisioned in battery operated vehicles. For example, the capacitor could be used at start-ups, acceleration and hill climbing in parallel with the battery. The capacitor can then be recharged when traveling at a constant speed or by regenerative braking. In such applications, the battery will not be used for pulsed power and would have a longer life. Also, these capacitors with high power densities and energy densities will find uses in portable electronic equipment such as computers, cellular telephones and other consumer electronics. Another important use will be as backup power devices for computers, displays and camcorders. In some military applications, short time scale power delivery (milliseconds to microseconds) are required. For all of these applications, performance and packaging characteristics are important. Furthermore, the exponential growth of consumer electronics, coupled with concerns about the environment, has created a significant demand for new energy sources that possess higher specific energies and energy densities in an environmentally benign fashion.

## 1.2 Phase II Research

The Phase II program was undertaken to investigate the use of conducting polymers in capacitor designs to demonstrate the current and power density possibilities of these devices. Electrochemical capacitors using conducting polymer electrodes operate on the now well-known concept of doping and undoping of these polymers. The ultracapacitors operate similar to a battery, except that the nature of charge storage in the electrode material is capacitive, *i.e.*, the charge and discharge processes consist of the transformation of ionic and electronic charges into electronically and ionically conducting domains respectively. The charge/discharge processes consist of doping/undoping of the polymer by electron donors or acceptors. Both processes are reversible and this forms the basis for the capacitor design. During the doping and undoping processes at conducting polymer electrodes, the reaction takes place through the bulk of the material. Doping levels as high as one electron per two monomeric repeat units in the polymer chain can be achieved in the case of polyaniline. This is a major advantage of these polymers compared to carbon or other electrode materials. A capacitor which utilizes polypyrrole as both anode and cathode has been

described. Shuttling of the perchlorate ion between two electrodes provides a capacitor-like dependence of voltage on charge. The inter-electrode voltage was zero when both electrodes were charged to the same extent with the perchlorate ion. Deviation from this situation resulted in a voltage which increased in proportion to inter-electrode dopant transfer. Similar work was performed using polypyrrole and polythiophenes<sup>1</sup>. Capacitors with an energy density of 200-300 J/cm<sup>3</sup> operating at frequencies up to 100Hz, were claimed early on<sup>2</sup>. This exceeds by far that of conventional capacitors which is about 1 J/cm<sup>3</sup>.

There are several advantages to using intrinsically conducting polymers in electrochemical capacitors compared to carbon-based or mixed metal oxide electrodes. Conducting polymers can be synthesized directly on the current collector resulting in a minimal contact resistance. The electrode material can be formed as sub-micron coatings (double layer capacitance), thick films or powders (pseudocapacitance). With a diffusion constant of the dopant in the range of 10<sup>-5</sup>-10<sup>-6</sup> ion/cm<sup>2</sup>, sub-micron coatings should result in microsecond response times. Intrinsic conductivity is high (10 to several hundred  $\Omega\cdot\text{cm}^{-1}$ ) for high power density. High surface area is possible for both high power and high energy densities. The ions shuttle between the polymer and the double layer efficiently and fast by doping/undoping of the polymer and conducting polymers can be produced on a large scale at low cost. With these characteristics in mind, we chose to continue the work of our initial feasibility study by exploring the use of new conducting polymers for use in ECCs.

## 2.0 PHASE I RESEARCH CARRIED OUT

### 2.1 Objectives

The objective of this work was to take advantage of the emerging conductive polymer technology for the fabrication of high energy and power density, solid-state, compact ultracapacitors. The flexible construction design will have an overall performance that will take into account DOE's specific requirements and exceed that of existing technology. The specific goal addressed in Phase I work which were fully achieved at the end of Phase I were:

- *High energy density:* > 15 Wh/kg;
- *High power density:* > 1600 W/kg;
  - *Modest cost:* < \$100/Wh;
- *Low self-discharge rates:* 1 - 2 years;
- *Long lifetime:* up to 5 years (shelf + operational); and
  - *Convenient packaging.*



The specific objectives of the Phase II program were to:

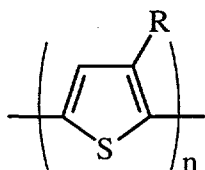
- ◇ Optimize the conducting polymer coatings and membranes towards an increased surface area to maximize energy and power densities;
- ◇ Evaluate the use of thin clay layers as the electrode support materials;
- ◇ Develop and optimize the two construction designs which consist of the multilayer (stacked cell) design and the laminated design;
- ◇ Evaluate a process design which includes of a solid polymer electrolyte;
- ◇ Demonstrate superior capacitor performance;

All of these objectives were met. We succeeded in demonstrating that certain conducting polymers can be used successfully in combination with clays to yield a capacitor that exceeds the 15Wh/kg, 1500W/kg goals set by the US Department of Energy.

The work conducted in the Phase II effort is summarized in the following sections.

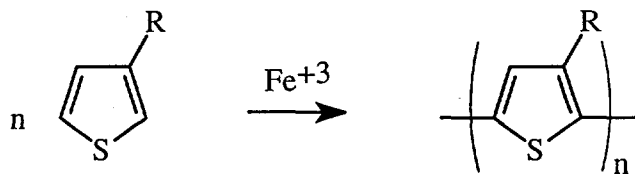
## 2.2 Conducting Polymer Preparation

A number of conducting polymers were evaluated for use in capacitors, both in symmetric and asymmetric constructions. We focused upon the poly-3-butyl- and poly-3-hexylthiophenes, shown below, since these represent more practical candidates, and they can be solvent deposited onto a variety of substrates.

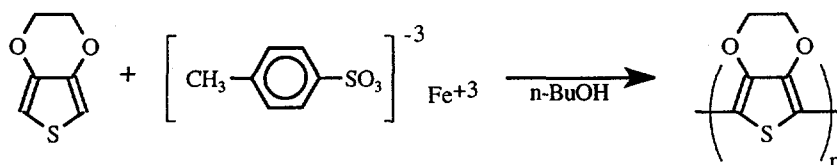


$R = n\text{-butyl or } n\text{-hexyl}$

Both of these substances are p-dopable conducting polymers that are conveniently synthesized as follows:

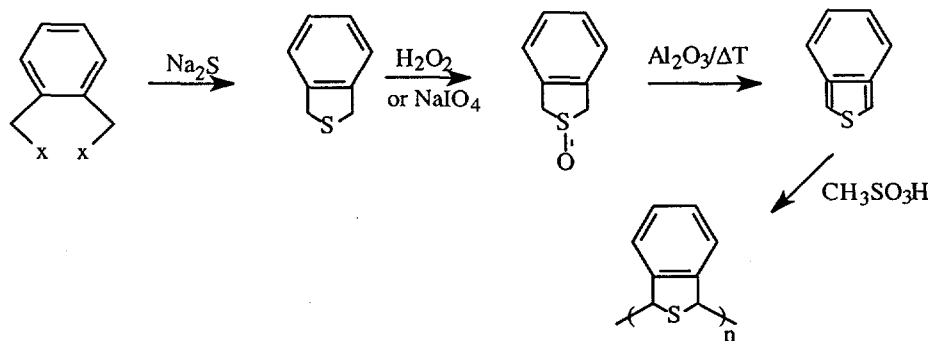


A third conducting polymer evaluated was poly(ethyl-3,4-dioxy)thiophene (PEDT). PEDT is a commercially available conducting polymer which is available from Bayer, Inc. Pure PEDT comes as a two component material which is prepared according to the manufacturer's instructions. The reaction of the monomer and the catalyst results in the polymer as follows:



The reagents, both dissolved in n-butanol were mixed in 1:1 ratio (25mL:25mL) and stirred for 24 hours under nitrogen atmosphere. To the dark bluish black solid gel like material, 100mL of isopropanol was added. The solution was then sonicated in a 100W ultrasonic bath to breakup the solid particles. After the polymer forms a fine dispersion, it was collected by vacuum filtration. The product polymer is then washed several times with isopropanol and ethanol, until the wash solvent is clear. This was followed by a drying step under vacuum at 80°C.

A fourth polymer tested was polyisothionaphthalene (PITN). PITN is a low band gap conducting polymer. This class of conducting polymer is of interest because these materials may show intrinsic conductivity without the necessity of oxidation or reduction by a dopant, possibly resulting in superior environmental stability. In addition, the low band gap of this material may make it suitable for use as an n-doping conducting polymer. PITN was prepared according to the procedure of von Asselt et al<sup>3</sup>:



Preparation involved mixing 6.2g of phthalic anhydride (42mmol) and 13.31g P4S10 (30mmol) in 50 ml xylene under refluxing conditions. After 17 hrs, the mixture was cooled to 20°C and filtered. The resulting solid product was dispersed in 50ml MeOH and heated to reflux for one hour. The mixture was then filtered and the residue refluxed once more in 50ml MeOH for one hour. Following filtration, the black solid was transferred to a Soxhlet apparatus and continuously extracted successively with THF (20 hrs), chloroform (8 hrs), and petroleum ether 40-60 (2 hrs).

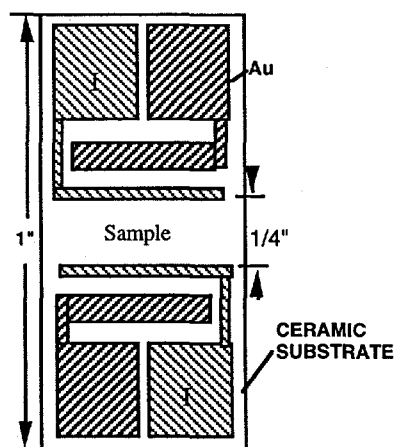
## 2.3 Conducting Polymer Characterization

### 2.3.1 General Analytical

In general the reaction sequences were followed using classical FTIR techniques on a Perkin Elmer Paragon Model 1000 instrument. Since all of the monomers and polymers were previously known, comparisons with data reported in the literature established the identity of all of the compounds described. In some cases FT-NMR was also used. The latter were run on a 90Mhz JEOL instrument.

### 2.3.2 Conductivity Measurements

Four probe conductivity measurements were performed on several of the candidate conducting polymers to compare their relative conductivity. The ionic conductivity of the conducting polymers was determined using a four-probe test apparatus as shown in the following figure.



**Figure 1** Membrane Conductivity Measurement Apparatus

To apply the conducting polymer to the chip, the polymer was first dissolved in an appropriate solvent and the solution was dried at room temperature. The test material was applied in a uniform layer on the chip in the area marked *Sample* in the preceding Figure. This was accomplished using spin coating of each solution to ensure that the test layer coating was uniform and thin. We measured the coating thickness using a digital micrometer. The conductivity measurement was accomplished by applying a 1 kHz current across the terminals marked *I* in the preceding Figure. A Keithley Model 224 Programmable Current Source together with a Hewlett Packard Model 34683 multimeter were used to conduct the measurement. At the same time the voltage across the second set of terminals was measured and the conductivity was calculated from these parameters using Ohm's law. All measurement were conducted at ambient temperature. The following table summarizes these results.

**Table 1** Four Probe Conductivity of the Conducting Polymers

Polymer	Conductivity (S/cm)
PEDT	$2 \times 10^{-2}$
PBT	$4 \times 10^{-4}$
PHT	$5 \times 10^{-4}$
PITN	1.1

These results indicate that of the conducting polymers chosen, PITN appears to exhibit better conductivity than the other materials tested.

Impedance analysis of 0.5mm thick pellets of various materials confirmed their relative conductivities. The pellets were prepared by combining the conductive polymer with 3% polyvinylidene fluoride (PVDF) and pressing the pellets at 2000lbs. pressure in a steel mold at 120°C for 15 minutes. These results are summarized in the following Nyquist plot.

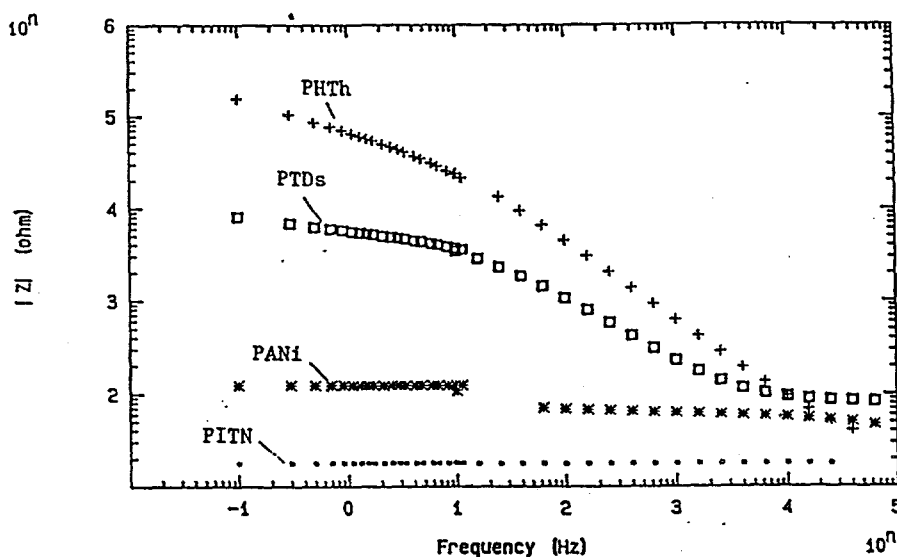


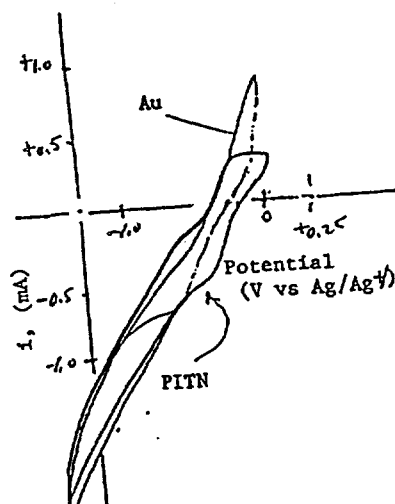
Figure 2 Nyquist Plot of Poly(isothianaphthene) (PITN)

As can be seen, the low band gap nature of PITN makes it behave like a metallic conductor with a flat impedance throughout the frequency spectrum.  $R_{dc}$  of a 0.5mm thick pellet of the doped polymer is 18  $\Omega$ , which corresponds well with the four-probe measurement of 1S/cm. This impedance behavior contrasts sharply to that of poly(3-hexylthiophene) which exhibits a declining sloped curve from low to high frequency with an  $R_{dc}$  of 3.9K  $\Omega$  for a 0.5mm thick pellet. This same behavior is noted for polyhexylthiophene.

### 2.3.3 Cyclic Voltammetry Testing

Some of the conducting polymers were subjected to cyclic voltammetry testing to ascertain the potentials of doping and undoping. PITN was one of those chosen for these tests. Following synthesis of PITN we conducted cyclic voltammetry tests of this polymer in 0.3M tetrabutyl ammonium tetrafluoroborate (TBATFB) in acetonitrile using an  $Ag/Ag^+$  reference electrode and a platinum counter electrode. A standard H-cell was used for the testing with a glass frit between the test chambers. The counter electrode was located in the same chamber as the test electrode and the reference electrode was positioned in the second chamber behind the glass frit. The PITN polymer

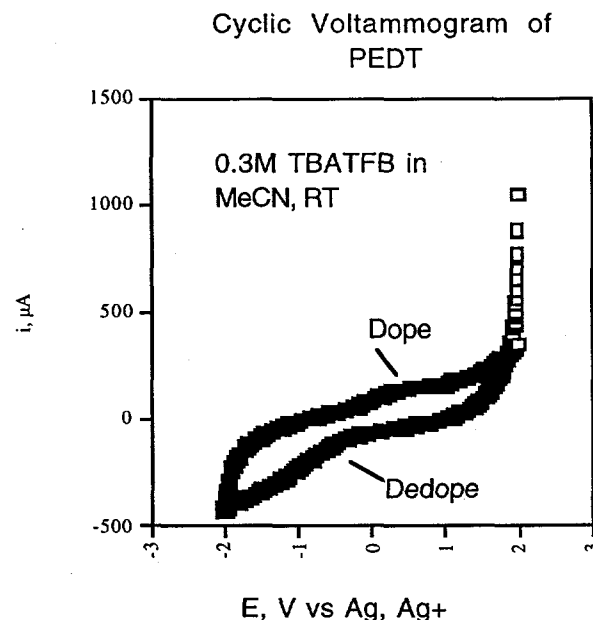
electrode was prepared by combining the polymer with 1 $\mu$ m particle size graphite powder in a 50:50 weight ratio. A pellet of this material was prepared using a steel mold and a hydraulic press. This pellet was then clipped between two pure gold strips, suspended in the electrolyte and cyclic voltammetry was performed using an Amel model 551 potentiostat and a model 567 function generator. The results of this test are shown below.



**Figure 3** Cyclic Voltammetry of Poly(isothianaphthene) (PITN)

As seen in this figure, the CV of the PITN electrode differs significantly from that of the gold control. Two distinct peaks are visible at around -500 and -600mV which indicate reversible doping of the polymer. At these potentials, it can be assumed that the PITN is p-doping. These CVs were used to qualitatively establish the doping and dedoping potentials for PITN and the results were not used to calculate the capacitance of the electrode since we did not intend to use this electrode geometry further.

We also ran a CV of the PEDT polymer the results of which are shown in Figure 4.



**Figure 4** Cyclic Voltammogram of poly(3,3-ethylenedioxythiophene) (PEDT)

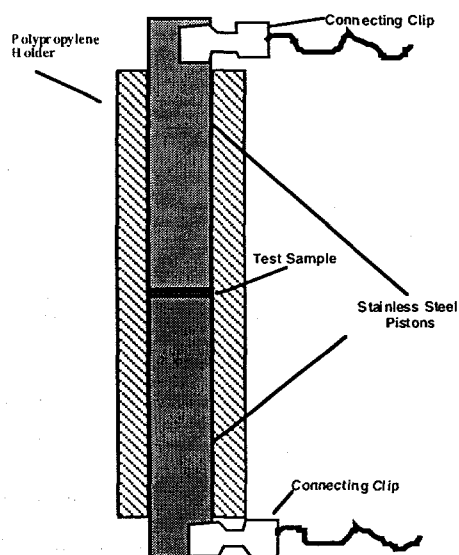
As can be seen, the p-doping and dedoping potentials of this material are somewhat similar to those of PITN, but the doping of PEDT appears to be less reversible than PITN. This observation is based on the greater asymmetry of the doping and dedoping potentials of PEDT versus PITN. As can be seen, doping appears to occur at around +300mV vs Ag/Ag<sup>+</sup>, whereas dedoping seems to happen at around -300mV vs Ag/Ag<sup>+</sup>. This would represent a 600mV window as opposed to PITN with a 100-200mV electrochemical window. One could surmise from this that the bandgap in PEDT is greater than that of PITN.

## 2.4 Capacitor Testing

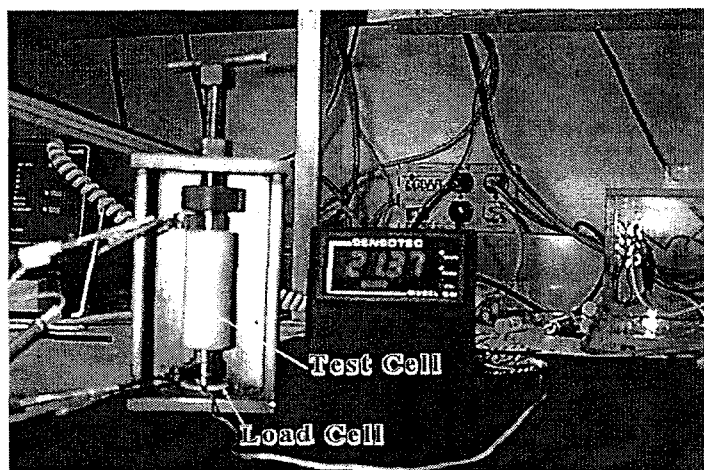
### 2.4.1 Procedures

#### 2.4.1.1 Test Apparatus

For screening purposes, we determined the energy and power characteristics of the various conducting polymers, and conducting polymer combinations using a simple two electrode cell was fabricated from polypropylene and stainless steel. This apparatus was used for the bulk of the laboratory electrochemical characterization tests. This cell contained two stainless steel piston-type electrodes fitted into a polypropylene sleeve holder. The effective surface area of the test components is 1cm<sup>2</sup>. The test cell is shown in the following figure.



**Electrochemical Test Cell**



**Test Apparatus**

Using this arrangement, the test electrodes are pressed evenly between the two blocking electrodes and the simple, one cell capacitor can be interrogated to obtain its electrochemical characteristics. For these tests, various separators were employed together with various electrolytes, both aqueous and non aprotic. Following assembly, the cell is held together by a screw pressure press fitted with a special load cell (Sensotec model 13/2443-08) and a digital readout so that each test cell is subjected to reproducible pressures. This apparatus is depicted in the photograph above.

An EG&G model 6310 electrochemical impedance analyzer together with the model 270 electrochemical software employing a chronoamperometric analysis was used for these measurements. Energy and power densities were calculated from the weight of the electrode material discounting the weight of the separator.

#### **2.4.1.2 Single Cell Capacitor Components**

##### *Substrate/Support -*

Several different conductive supports were evaluated in this effort as current collectors for the conducting polymers. The selection basis for evaluating these materials were: conductivity, relative surface area and unit weight. We chose reticulated vitreous carbon (RVC) and carbon tissue. The following table compares the properties of these two supports.



Table 2 Conductive Polymer Supports

Support	Unit weight (g/cc)	Surface Area (m <sup>2</sup> /g)	Conductivity (-cm) <sup>-1</sup>
RVC	0.049	0.07	2.1
C Tissue	0.122	0.049	0.1

The RVC is commercially available (Electrosynthesis Company, Lancaster, NY), and the carbon tissue was also obtained commercially (Optimat 203 Series, Technical Fiber products, Slat Hill, NY). The carbon tissue proved to be the most useful of the current collectors tested since its unit weight is desirable, and it lent itself well to facile activation with various conducting polymers. This particular product is a poly(acrylonitrile)-based non-woven tissue, with acrylic, phenolic, or polyester binders. It is available in a variety of units weights from 34 mg/cm<sup>2</sup> to 10 mg/cm<sup>2</sup>. Most of our work revolved around the 10mg/cm<sup>2</sup> material.

### *Clays*

Two different types of clays were evaluated as electrode supports. These were a sodium montmorillonite which is a crude clay mined in Crook County, Wyoming (SWy-1), and a calcium hectorite, also a crude clay mined in San Bernardino County, CA. Both were purchased from the Source Clay Minerals Repository (University of Missouri, Columbia, MO). The basic procedures for preparing the clay modified electrodes are described below. All references to water refer to water that was first deionized and then further purified through a reverse osmosis unit. All glassware was acid washed with 1M HNO<sub>3</sub> and water prior to use.

1. 10 g of SWy-1 was dispersed into 100mL of H<sub>2</sub>O and stirred for 48hrs. The mixture at that point became an unworkable paste, thus 100mL more H<sub>2</sub>O was added and the mixture stirred for 48hrs more.
2. A portion of the colloidal mixture from step 1 was then centrifuged at 5000rpm for 20" and the dark brown residue at the bottom of the centrifuge tubes discarded. The fine, colloidal supernatant was placed under high vacuum (1-5mm) at 22-25°C until incipient dryness was achieved.

3. 0.08gm of the freeze dried clay was placed into 10mL H<sub>2</sub>O into which the clay dispersed upon sitting at ambient temperature overnight to yield a tannish, translucent colloidal solution. The colloid from was briefly ultrasonified immediately prior to electrode coating.

Hectorite is basically a trioctahedral clay mineral of the montmorillonite group composed of hydrous silicate of magnesium and lithium and generic formula (Mg, Li)<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> that also has exchangeable Na<sup>+1</sup> and/or Ca<sup>+2</sup>. The procedure for preparing hectorite supports was basically as described for the montmorillonite, but with a couple of important changes.

Steps 1 & 2: as described above.

3. To exchange the calcium ions for sodium ions the hectorite (10g/L) was dispersed into 1M NaCl for >48hrs, the solution was centrifuged and the solids collected. The solids were then repeatedly washed with water, centrifuged and dried under vacuum to incipient dryness.

4. 0.08gm of the clay from step 4 was placed into 10mL H<sub>2</sub>O into which the clay could be colloiddally dispersed by agitation. The colloids so-formed remained stable (no settling) over the time frame of the research.

Continuous films of the clays were easily formed by deposition from an aqueous dispersion, and the thicknesses could be changed by sequential deposition and drying at ambient temperatures.

#### *Electrodes -*

The technique for preparing the electrodes preparation involved the solvent deposition detailed as follows. This technique is based on a similar technique described recently by Kuwabata et al<sup>4</sup>. Twenty five milligrams of the polyalkylthiophene was dissolved into in CHCl<sub>3</sub>, the mixture was ultrasonicated for 35 minutes, and stirred overnight to achieve dissolution. The mixture was then pipetted onto the desired support, and dried overnight under ambient conditions. Portions of the electrode were cut with a circular punch for testing.

#### *Separators -*

A number of different separators were evaluated in single cell experiments to determine which offered better electronic insulation while not impeding ionic conductivity. The following separators were tested:

**Table 3** Separators Employed in Cell Testing

Product	Manufacturer	Composition	Thickness
Cellgard (cg)	Hoechst	microporous polypropylene	0.02mm
Zitex (zt)	Norton	microporous PTFE	0.08mm
Filter paper (fp)	Whatman	cellulosic	0.18mm
Optimat (gp)	Tech Fiber Pcdts	nonwoven glass paper	0.15mm
Pellon	Frudenberg Nonwovens	Nonwoven polyethylene	0.1mm

Several analyses were conducted with these different separators and, in some cases, several layers of each separator or combinations of these separators. The abbreviations for each separator under the "Product" column heading in Table 4 are used throughout the remainder of the text. Our testing revealed that the Cellgard material was suitable for use in capacitors employing an aqueous electrolyte. However, use of Cellgard with more "active" materials such as PITN, was not possible when acetonitrile was employed as the solvent in the electrolyte. Shorting of the cell was encountered in these instances. This same problem was encountered with Norton's Zitex separator. To obtain meaningful data, early on in the program, we were forced to employ filter paper as the separator to prevent cell shorting. This proved to be a less than adequate separator material as it caused unacceptable IR losses across the cell. The solution to this problem appeared in the form of an older separator product, Pellon manufactured by Frudenberg Nonwoven (Chelmsford, Mass.). The open structure of this separator allowed us to pile up several layers (as many as five) which appeared to prevent cell shorting while at the same time did not adversely effect the IR across the cell. Pellon was the separator of choice.

#### *Electrolytes -*

Several different electrolytes were evaluated the choice of which depended on the CP in the capacitor. The nonaqueous electrolyte of choice for the best of the capacitors was 0.3-0.6M tetrabutylammonium tetrafluoroborate (TBATFB) in either propylene carbonate (PC) or acetonitrile (MeCN). All of the reagents were used as received for most of the initial testing.

## 2.4.2 Results

### 2.4.2.1 Capacitance

The capacitance of the various electrode combinations was determined using a Phillips model PM6303 RCL meter. The test cell was assembled and the series capacitance was measured prior to discharge testing of the cell. A Nichion N9608 4700 $\mu$ F electrolytic capacitor was used to calibrate the RCL meter prior to the test measurements. The results of this testing are summarized in Table 4 below:

**Table 4** Capacitance of Various Electrode Combinations

Capacitor	Capacitance mF/g Total Electrode wt.	Capacitance mF/g Active Material wt.
Nichion Capacitor	4200 $\mu$ F	-
PEDT/PEDT	3.8	10.3
PITN/PITN	7.25	14.5
PBT	3.9	17.5
PHT	0.85	1.2

The results indicate that the PITN Type I capacitor offered the highest capacity of those Type I cells tested.

### 2.4.2.2 Discharge Tests

To determine the energy and power densities of the test capacitors, we used chronopotentiometry and in some cases, chronopotentiometry combined with chronoamperometry. The EG&G Model 6310 Impedance Analyzer together with the Model 270 electrochemistry software was used for these tests. The general procedure involved charging the capacitor to 4V for up to two minutes followed by a chronoamperometric discharge at a specific current. The cell was discharged to zero volts and the energy and power densities were calculated based on the area of the discharge curve and the applied current.

Type I capacitors included PEDT, PBT, PHT, and PITN. Of the systems tested, the PITN/PEDT cell yielded the best results with calculated energy densities as high as 24Wh/kg and power densities as high as 720W/kg. The following table summarizes the better results for the various capacitors tested.

**Table 5 Energy and Power Outputs of Various Capacitors**

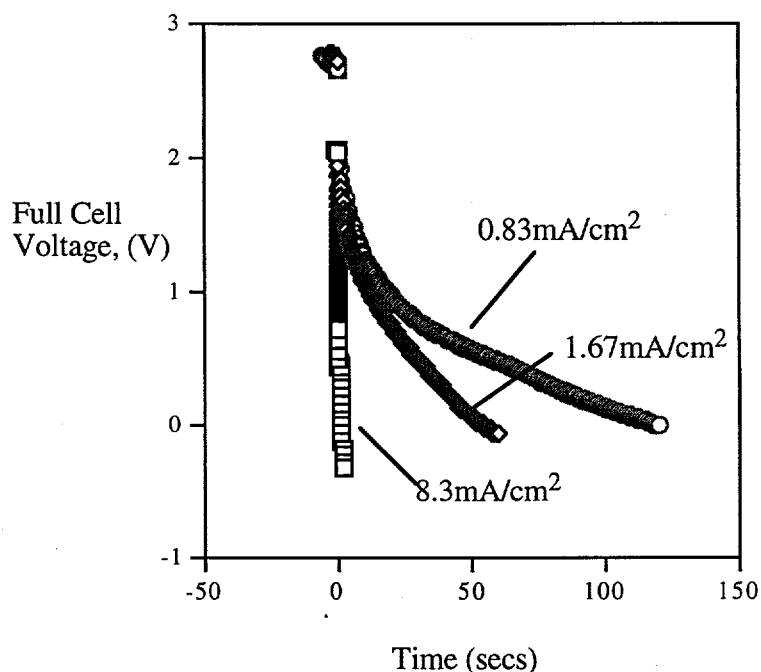
Capacitor	Discharge (mA/cm <sup>2</sup> )	Energy Density (Wh/kg)	Power Density (W/kg)
PBT	1.27	1.38 (6.3)*	621 (2836)*
PHT	1.27	1.2 (1.7)*	216 (306)*
PEDT/PEDT	1.67	2.7	666
PITN/PITN	1.67	2.8	169
PITN/PEDT	1.00	24	720

\*based on the weight of CP on the electrode

The energy and power densities were calculated based on the total weight of the electrode materials and did not take into account the weight of the separator or electrolyte.

The results for the materials are interesting, particularly the Type II capacitor PITN/PEDT. In one experiment, we were able to demonstrate an energy density of 24Wh/kg. However, we found this combination to be susceptible to degradation upon cycling and most of our later experiments resulted in energy densities of around 5 to 7Wh/kg. The Type I PITN cell was also somewhat interesting, but not much more energetic than the Type I PEDT cell.

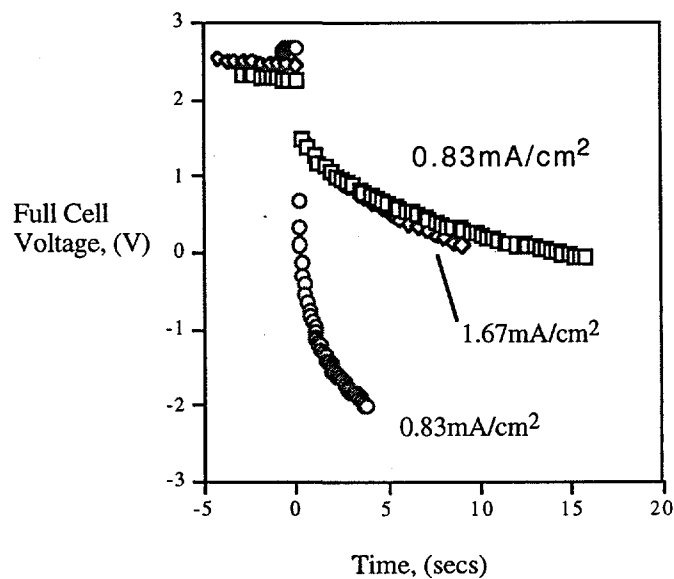
The following plots are composite discharge curves for various Type I capacitors. The first is for the PITN Type I cell.



**Figure 6** Discharge Curves for the Type I PITN cell, 0.6M TBATFB, Pellon

As can be seen, as the current density increases, the discharge time decreases dramatically. The discharge at  $0.83 \text{ mA/cm}^2$  is interesting in that the shape of the curve is quite flat after 50 seconds of discharge; almost "battery-like". This is more like Type II discharge behavior as described by Rudge et al<sup>5</sup> and was accentuated when we combined PEDT with PITN. Unfortunately, this combination was apparently not very stable. We observed this peculiar shape for PITN throughout our testing. This deserves more work, since battery-like discharge at a constant voltage is a worthwhile goal for the "ideal" electrochemical capacitor.

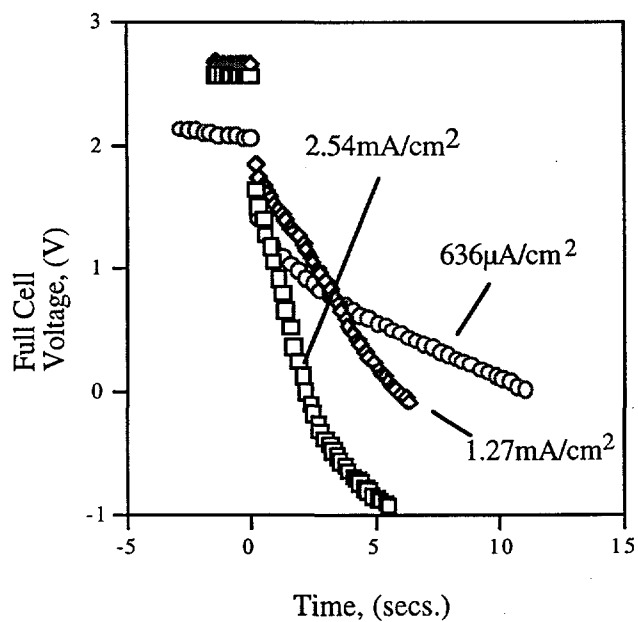
The discharge curve for the Type I PEDT cell is included below.



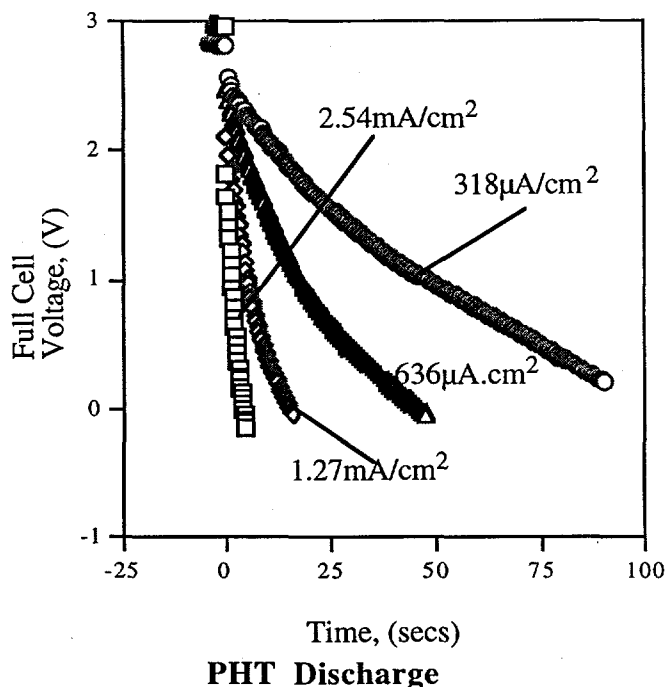
**Figure 11 PEDT Type I Discharge**

As can be seen from this plot, this system pales by comparison with the PITN cell. The discharge behavior is typical Type I, exponential voltage decay.

Polyhexylthiophene (PHT) and polybutylthiophene (PBT) were tested next in the type I configuration. The results of these tests are shown below.



**PBT Discharge**



As can be seen, these materials offered slightly better discharge performance than PEDT, but were not quite as good as PITN. The active material loadings of these two capacitors were significantly different which accounts for the seemingly improved performance of the PHT over the PBT. In reality, the loading of conducting polymer in the case of PHT was eight times greater than that of the PBT. The difference in energy density and power density of these two material is quite striking when the discharge results are normalized as depicted in Table 5. As can be seen, based on the weight of active material, PBT is quite energetic offering the second highest energy density and the highest power density of the materials tested. Obviously solvent deposition of this material onto carbon tissue is not the optimum method of applying it to a conductive support. More efficient techniques are needed to increase the loading of PBT on the active support and thereby increase the energy and power densities of the resulting Type I capacitor.

The following results are for the better Type II cells.

The optimum results for a Type II capacitor were with PEDT/PITN with PITN as the working electrode. PEDT was solvent deposited from hexafluoroisopropanol onto carbon tissue and PITN was deposited onto the carbon tissue using the PHT technique. TBATFB (1M) in MeCN was the electrolyte and two pieces of Pellon sandwiched between it served as the separator. Under these conditions, this cell yielded a one-time output of 24Wh/kg and a power density of 720W/kg. The following figure is the discharge curve for this test.



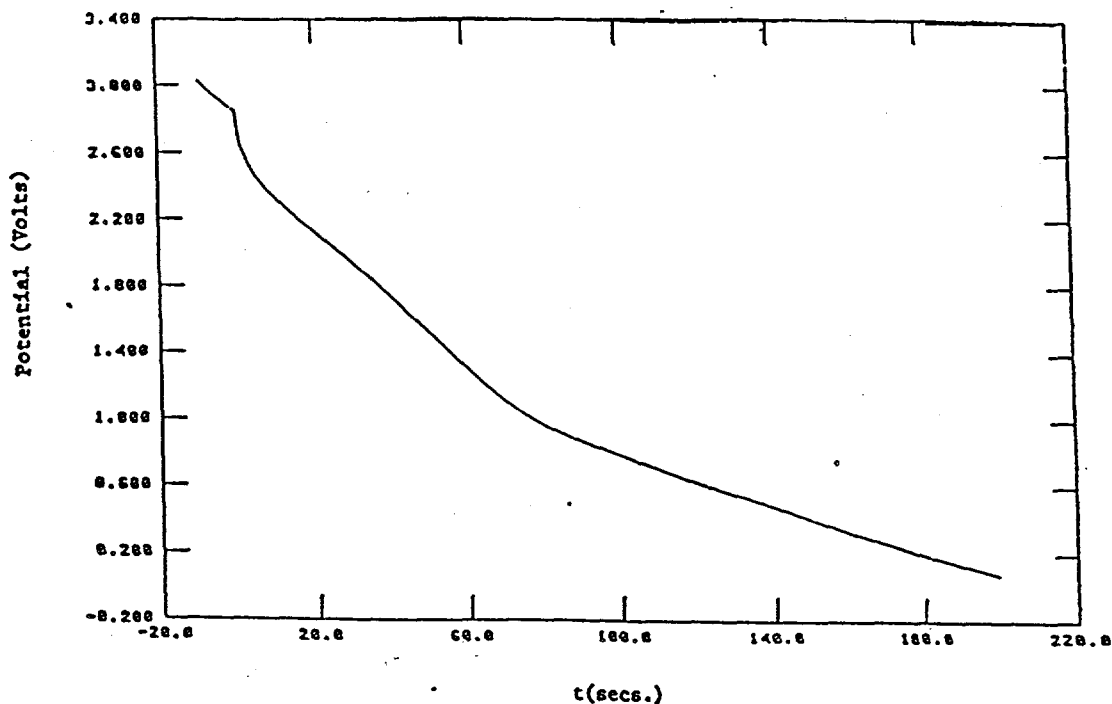
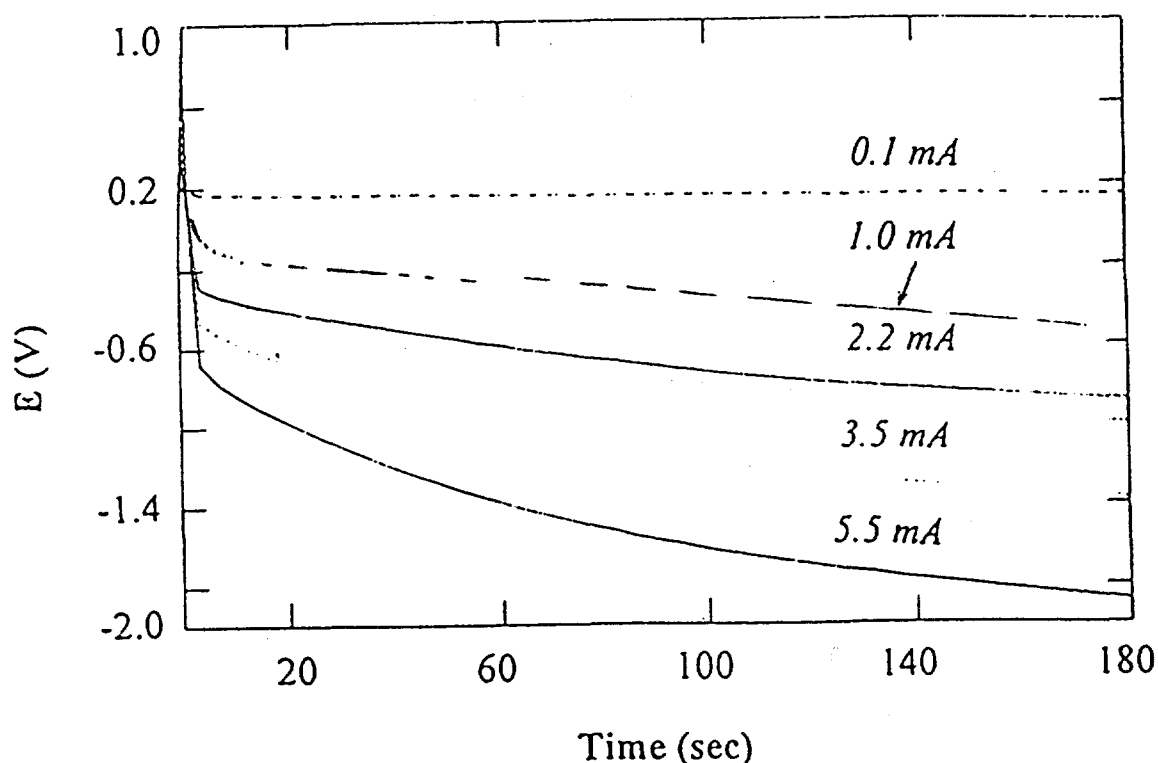


Figure 12 Type II PITN/PEDT Cell 0.6M TBATFB in MeCN, Cellgard

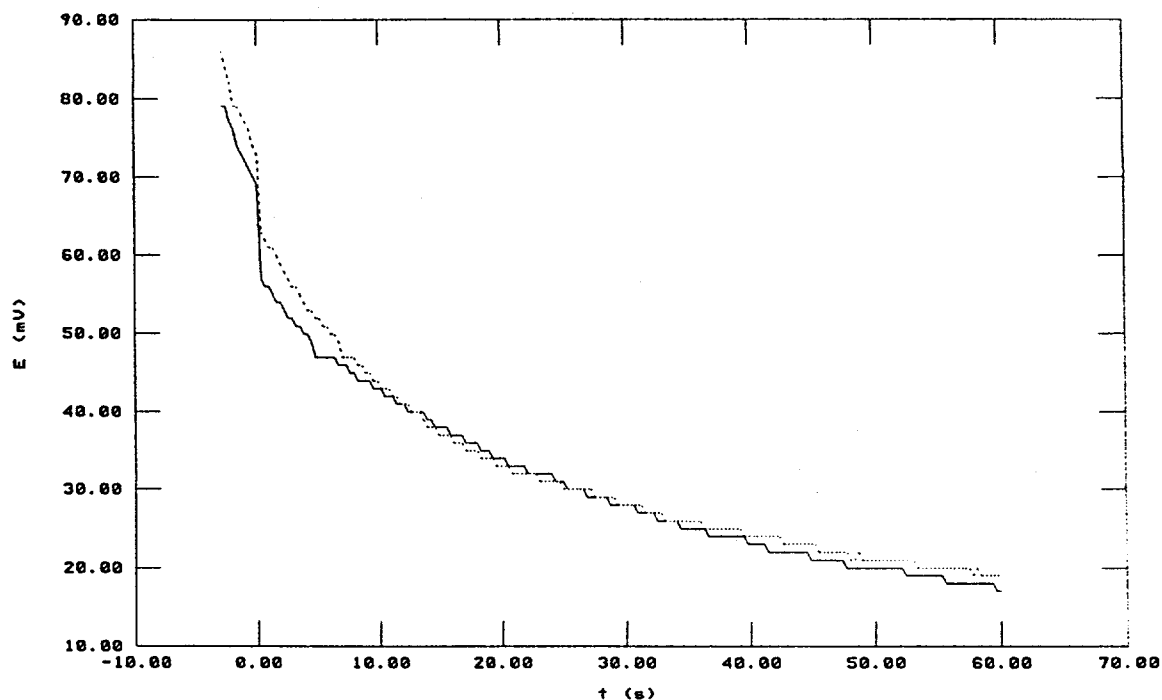
As can be seen, the discharge curve for this cell yielded a very desirable result in that the starting voltage was quite high (3V) and the curve was not flatter than the standard exponential decay observed with most ultracapacitors. In this cell the PITN was the anode on charging. This discharge curve was the best obtained with this Type II system, but we were unable to repeat this result and this discharge occurred only once with this cell. We suspected that one of the conducting polymers was decomposing as a result of the charge cycle (4V for 2 mins) which led to decreased performance with successive cycling. As a result we reverted back to the PITN Type I system which appeared to be more stable. We also studied a polyaniline/PEDT Type II system, and a representative discharge curve is shown below.



**Figure 13** PANi/PEDT Discharge 1M TBATFB in EC/PC (30:70)

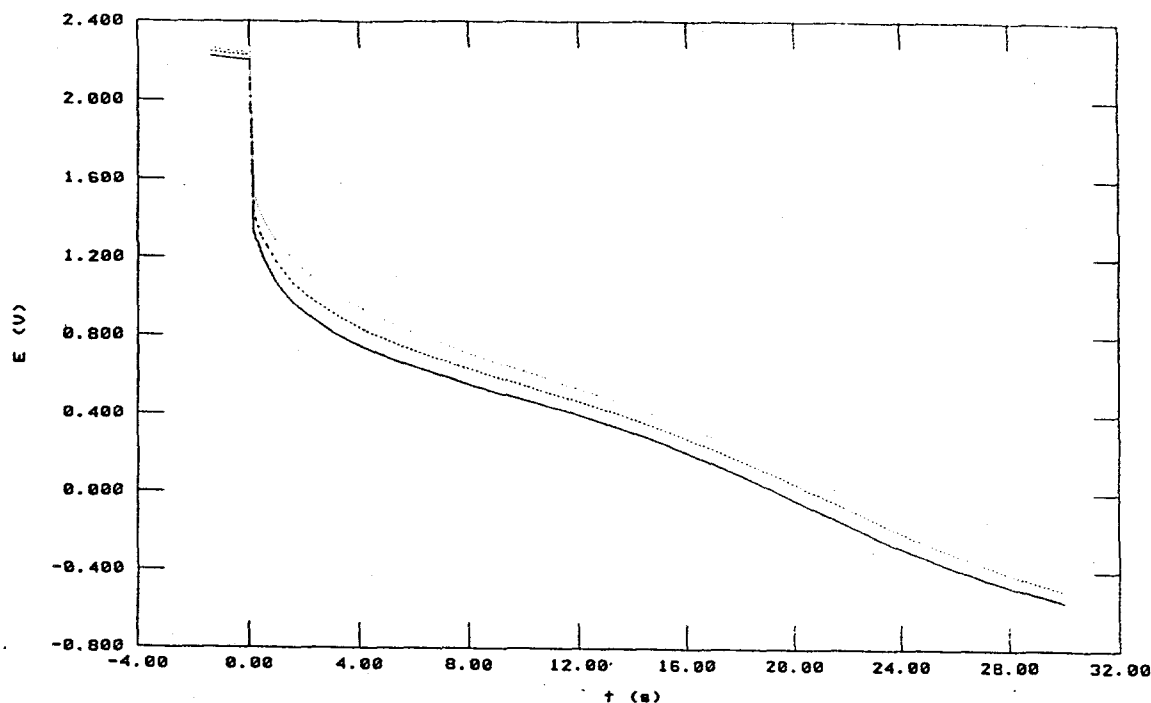
It can be noted from this charge/discharge composite, the PANi/PEDT Type II capacitor did not perform nearly as well as the PITN Type I cell. With the PANi/PEDT cell, the voltage has diminished to nearly zero after 20 seconds of discharge. The PITN cell, on the other hand, maintains voltage for nearly a minute.

In addition to examining carbon tissue as the electrode support and various materials as separators, we also solvent deposited several conducting polymer directly onto clay supports which served as the separator. The procedure for this is detailed in section 2.4.1.2. The clay itself can be used directly as a separator electrolyte, because it has cations associated with the structure. However, the pure clay will not support very high current discharges as demonstrated below. We discharged a PITN Type I cell using pure montmorillonite as the separator. The SWy-1 clay made superior films, and were studied preferentially.



**Figure 14** Discharge of PITN Type I with Pure Montmorillonite as Separator

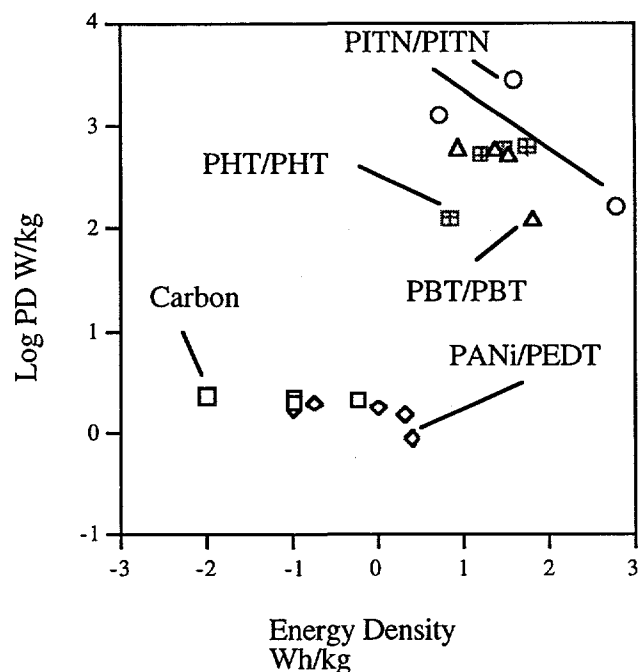
Note that the discharge is long-lived, but does not result in a very high energy density ( $<0.1 \text{ Wh/kg}$ ). In addition, the conducting polymer did not charge to a useful voltage, probably due to the ohmic losses across the clay. Adding TBATFB in MeCN between pieces of clay, onto which was solvent deposited a polyhexylthiophene, improves the performance of a Type I cell. In this case the weight of active material on the clay was around  $50 \mu\text{g/cm}^2$ . We stacked two cells of this material together with the liquid electrolyte in between and discharged at  $250 \mu\text{A}$ . The results are shown below.



**Figure 15** Polyhexylthiophene on Montmorillonite with 0.6M TBATFB in MeCN as electrolyte

By contrast, adding a good electrolyte to the mix greatly improves the picture as evidenced by the ability of the conducting polymer to attain a high voltage on charging, and the length of discharge at a reasonable current density of around  $360\mu\text{A}/\text{cm}^2$ . The clay provides good electrical insulation while supporting ionic transfer of the electrolyte. As can be seen, with successive cycles, the performance of the system does not greatly degrade. This cell yielded an energy density of around  $27\text{Wh}/\text{kg}$  based on active material. This would appear to be a useful approach for preparing capacitor electrodes in the future.

Following discharge tests, we compared the energy and power densities of the various systems tested. A composite Rangone plot is included below.

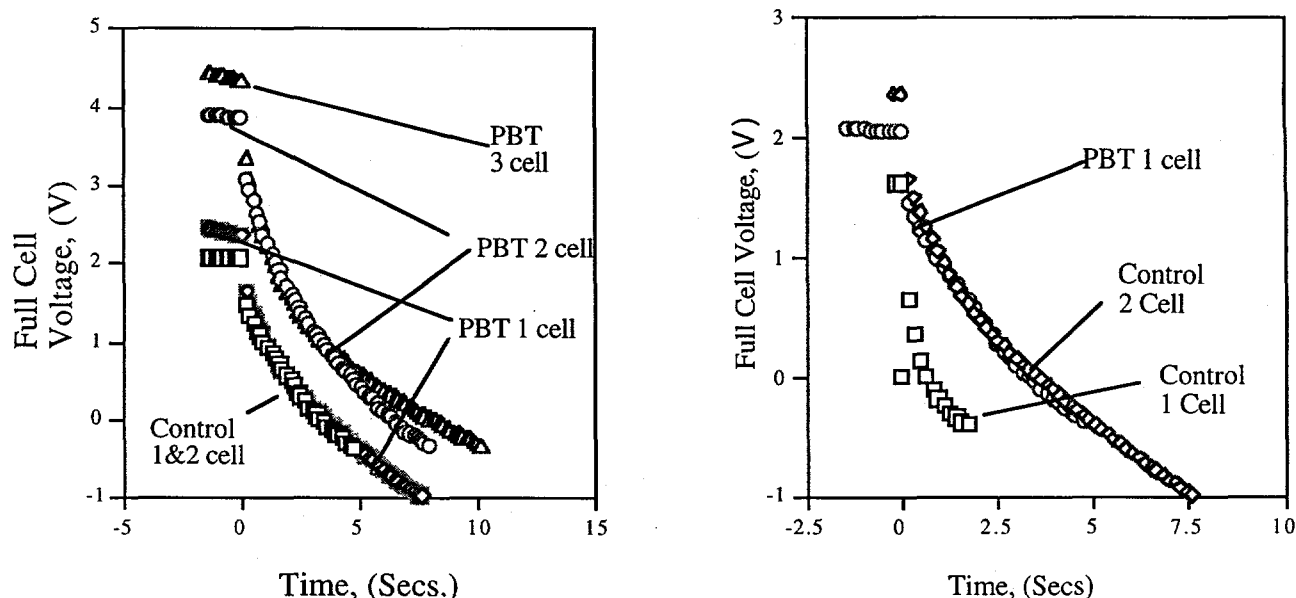


**Figure 16** Composite Rangone Plot

This plot confirms that the PITN Type I capacitor is superior to all others tested in this program. Interestingly, the PBT Type I was a close second and with PHT the third best of the group. All of these Type I systems performed far better than a comparable carbon capacitor which was very close in performance to a Type II Polyaniline/PEDT cell.

#### 2.4.2.3 Capacitor Results.

To demonstrate how these systems would perform in a capacitor design, we constructed several bipolar (stacked) capacitors of up to three cells and discharged them at a set current. The cells were charged galvanostatically to set voltages of up to 9V. A control consisting of plain carbon tissue was run to compare its performance to that of the conducting polymer capacitors. PBT was chosen as the conducting polymer for this aspect of the program. Stainless steel foil was used to ionically insulate the cells while providing electrical contact between the cells in the stack. Filter paper soaked in 0.6M TBATFB in MeCN was used as the separator. The capacitors were discharged at 1.7mA/cm<sup>2</sup>. The results of these tests are shown below.



**Figure 15** Capacitor Discharge Tests

As these results indicate, as we increased the number of cells in the test capacitor, the output voltage increased steadily from 2.5V to 4.8V while the current output did not keep pace. This is to be expected in a multi-cell stacked configuration. Interestingly, increasing the number of cells in the control capacitor did not dramatically improve its output voltage. It would appear that the doping phenomenon of the conducting polymer greatly improves both the current and voltage output of the capacitor. The initial prototype cell consisted of a stainless steel cell housing with 17mg/cm<sup>2</sup> carbon paper (Technical Fiber Products, Slate Hill, NY), a filter paper separator (Whatman #4) and 1.0M TBATFB in MeCN electrolyte. This initial effort at fabricating a device will allow us to obtain initial discharge curves for the control material. Although this is a useful test device, the weight of the solid foil current collector and the cell housing were far too high to allow for meaningful energy densities to be achieved. We intend to use lighter materials for fabricating the actual working devices.

We plan to coat the carbon paper with PITN and PEDT and construct a similar capacitor and compare the results with the control cell. We expect considerable improvement, but we need to find a lighter cell housing, lighter separator and lighter current collector. We expect to try expanded metal foils as a current collector and have obtained samples of Exmet foils for testing.

### 3.0 Conclusions and Recommendations

This program has successfully demonstrated the potential for conducting polymer electrochemical supercapacitors; however, much work remains before these devices can be commercialized. More specifically both Type I and Type II capacitors were constructed using clays as supports, and polyalkylthiophenes as the conductive electrodes. Also a polyisothionaphthalene based polymer showed promise. Multicell capacitors were also constructed, and successfully tested.

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D. Naegele in "*Electronic Properties of Conjugated Polymers III*" eds. H. Kuzmany *et al.*, Springer-Verlag, Berlin, pp. 428-431, **1989**.

<sup>1</sup>. A. Rudge, J. Davey, J. Raistrick, S. Gottesfeld and J.P. Ferraris, *J. Power Sources* **47**, 89, (1994).

<sup>2</sup>. S. Gottesfeld *et al.*, Proceed. Electrochem. Soc. Meeting, Oct., 1995, Chicago, IL.

<sup>3</sup>. von Asselt, R.; Hoogmartens, I.; Vanderzande, D.; Gelan, J.; Froehling, P.E.; Assuems, M.; Aagaard, O. and Schellekens, R., *Synthetic Metals*, **74**, 65-70, (1995).

<sup>4</sup>. Kuwabata, S.; Tsumara, N.; Goda, S-i. Martin, C. and Yoneyama, H.; *J. Electrochem. Soc.*, **145**, (5), 1415-1420, (1998).

<sup>5</sup>. Rudge, A.; Davey, J.; Raistrick, I, and Gottesfeld, J. *Power Sources*, **47**, 89-107, (1994).