LA-SUB--94-16

**Final Report for Contract Research on
Electrochemical Capacitors Based on Conducting Polymers**

January 15, 1992 - August 31, 1992

**Dr. John P. Ferraris
Department of Chemistry
The University of Texas at Dallas**

**John P. Ferraris
Professor of Chemistry
October 22, 1992**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

28

Final Report for Contract Research on Electrochemical Capacitors Based on Conducting Polymers

Conducting polymers (CPs) have attracted attention as potentially useful materials for electrochemical capacitors due to their high energy storage capacity and their comparatively low cost. During the course of this research we explored a number of poly(heteroaromatic) systems, in conjunction with several non-aqueous electrolytes, that could be used as active materials in electrochemical capacitors. We identified a new configuration for such capacitors based on p- and n-dopable polymers and prepared a number of such materials. A new electrolyte, **TMATFMS**, which facilitates n-doping in these polymers was also synthesized and tested. A patent disclosure on these discoveries has been filed with Mr. Ray Wilson of LANL.

Conducting Polymers as Energy Storage Devices

Electrochemical (super)capacitors differ from more traditional systems in that the distance over which charge is stored is on the order of Angstroms and are thus potentially capable of producing very large capacitances. Two charge storage mechanisms pertain in these systems: surface and bulk. The first is exemplified by supercapacitors based on high surface area C in aqueous acid media wherein the intrinsic limitations of double layer (dl) capacitance (tens of $\mu\text{F cm}^{-2}$) are partially offset by the high surface area ($> 10^3 \text{ m}^2 \text{ g}^{-1}$). This technology is relatively inexpensive and fairly well developed. Still, supercapacitors based on C/aqueous electrolytes are limited to $< 5 \text{ Wh kg}^{-1}$, which is inadequate for electric vehicle (EV) applications.

The second mechanism, illustrated by the electrosorption of cations onto the surface of ruthenium and iridium oxides, provides much greater intrinsic capacitance than dl charging and greater ultimate energy densities ($10\text{-}50 \text{ Wh kg}^{-1}$). The cost of these active materials, however, is prohibitive for the large scale devices needed in EV applications.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Conducting polymers are a class of materials that are comparatively inexpensive and can be electrochemically doped to high levels thus combining the benefits of the two systems described above. Most CPs are readily p-dopable and some (polypyrrole [PPy], polyaniline [PANI]) are stable in aqueous media. Symmetrical capacitors based on p-dopable CPs (Type I, described in the patent disclosure) are limited in their energy density in that only a fraction of the stored charge is recoverable. The charged capacitor starts at some initial voltage and discharges until both electrodes are at the same potential according to:

Hence only about 1/2 of the total possible charge that can be stored on each electrode is recoverable. Since the energy stored by the capacitor depends on potential ($E = \int V dQ$), the use of aqueous solvent further constrains the energy density of such capacitors due to the limited (ca 1V) potential window for this solvent. Increasing this range is highly desirable and two avenues are open. First, expand the solvent/electrolyte's potential window by going to non-aqueous systems. Second, construct asymmetric devices by using different p-dopable CPs for the cathode and anode which display their redox behavior over different potential ranges (Type II). For example, PPy could be used for one electrode and polythiophene (PT), which oxidizes at higher potentials, for the other. Since the charge/discharge curves are displaced relative to each other, the potential window of the capacitor is widened and more of the stored charge on each electrode can be extracted.

This benefit can be further increased by constructing the capacitor with p- and n-dopable electrode materials. Here the charge/discharge curves are completely separated and, depending on the materials chosen, the potential

range can be increased to over 3 V. (Type III) The capacitor may be symmetrical (i.e., the same polymer is used for both cathode and anode) or asymmetrical, in which different polymers are selected to optimize the performance of each electrode. Although there are many p-dopable CPs, those which can undergo reversible n-doping are rare, mostly being limited to polyacetylene (PA), polyphenylene (PP) and PT and its derivatives. Stability and fabrication considerations suggested PT derivatives as likely candidates. An example of a symmetrical system based on PT is:

For CPs to be useful in EV charge storage applications, they must exhibit reversible, rapid and stable cycling, and have high energy and power densities. As stated above, energy densities may be increased by widening the capacitor's potential window. This requires the use of aprotic non-aqueous solvents, electrolyte salts stable to a wide voltage range and, probably p- and n-dopable materials. The total energy of the device depends on the amount of material present, hence thick polymer deposits may be needed. Reversibility and speed of the device are dependent on the conductivity of the polymer, the supporting electrolyte and the kinetics of counterion migration into an out of the film upon cycling. Thus the morphology of the film must be considered. Dense materials can impede ion transport. Thick mats of globular polymer may possess high resistance contacts between particles. Substituents that severely disrupt the planarity of the polymer backbone will reduce the electronic conductivity. Electrolyte salts with large lattice energies [usually combinations of small (hard) cations with small (hard) anions] will be strongly ion-paired and will have reduced conductivities. However, very large cations or anions will be slow to enter the polymer matrix upon doping/dedoping.

Choice of polymer:

Thin films of PT have been reported to reversibly p- and n-dope using tetraalkylammonium based electrolytes. We have confirmed this. Our results

show that while the ability to p-dope is not significantly reduced upon going to thicker films, n-doping is severely compromised for films $> 1\mu\text{m}$ thick. [Using tetrabutylammonium hexafluorophosphate (TBAPF₆), PT, when deposited with a growth charge of 7.2 C cm^{-2} , lost its ability to n-dedope.] Another report shows that poly(3-phenylthiophene) [P3PT, Figure 1] also p- and n-dopes and has a smaller energy gap than PT (1.74 eV vs 2.1 eV).

Figure 1

We synthesized 3PT, electropolymerized it onto C paper electrodes, and examined the polymer's p- and n-doping characteristics as a function of thickness using tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN). A typical cyclic voltammogram for this polymer is given in Figure 2. Since we were interested in the amount of charge that could be extracted from the material our goal was to maximize the areas marked p-dedoping and n-dedoping and have them as nearly equal as possible.

Figure 2. Cyclic Voltammogram of P3PT

The **P3PT** system retained its n-dopability to greater thicknesses than did **PT** but the n/p dedoping ratio still dropped to ca 25% for films grown at 7.2 C cm^{-2} . (Figure 3) When films of **P3PT** were grown to the same nominal thickness (i.e., to the same total growth charge of 3.6 C cm^{-2} , i.e., a thickness that meets the DOE requirement for energy density) but at different current densities, the n/p dedoping ratio was essentially constant at about 40% (Figure 4).

Figure 3

Figure 4

One of the as yet unanswered questions regarding the suitability of CPs in supercapacitors is their long term stability. The wide potential window accessed in Type III devices places constraints on the nature and purity of solvent and electrolyte. The reactivity of the n-doped polymers at high negative potentials to water and adventitious electrophiles can be particularly troublesome and shifting the potential window toward more positive values (while maintaining its width) is desirable. To this end, the monomer 3-(4-fluorophenyl)thiophene (3FPT, Fig. 1) was synthesized, electrochemically polymerized onto C paper. It was hoped that the electron withdrawing F would shift oxidation and reduction waves anodically. The amount of polymer deposited was linearly related to the growth charge (Figure 5).

Figure 5

The n/p dedoping ratio determined as a function of growth charge (i.e., thickness) for **P3FPT** cycled in 1.0M TEABF₄/AN is displayed in Figure 6. This ratio starts at >100 % for the thinnest (< 1μm) films and decreases to *ca* 60% for the thickest (> 1μm) films. It is about 72% for films grown at 3.6 C cm⁻². This is a significant improvement over **P3PT** and it is important to determine whether the effect is steric, electrical [*via* field(I) or resonance(M)] or some combination so that better performing materials can be designed. The covalent radius of F is not much greater than H so it is unlikely that the effect is steric. On the other hand, even though F is more electron withdrawing than H and hence possesses a negative field effect (-I), it is mildly electron donating by resonance (+M). In such cases (-I, +M), it is difficult to predict which contribution, if any, dominates.

Figure 6

Other monomers were prepared and surveyed to help elucidate the relative contributions. These were **3TT**, whose CH_3 substituent is weakly electron donating (+I, +M) but presents a greater steric demand than -H or -F; **3TFM** whose CF_3 substituent is strongly -I with steric requirements comparable to CH_3 ; **3tB** which is weakly (+I) but sterically demanding. The monomer **3NT** was prepared to increase the steric demands of the aryl group. One measure of a substituent's electron donating or withdrawing ability is its Hammett σ constant which sums up the total electrical effects of that group attached to a benzene ring. The substituents on the phenyl group in the above monomers are in the *para* position making σ_{para} constants most appropriate.

Table 1 gives the onset potentials for monomers and the peak doping and dedoping potentials for oxidation and reduction of the corresponding polymers.

X	σ_{para}	$E_{\text{mon onset, a}}$	$E_{\text{peak p-dope}}$	$E_{\text{peak p-dedope}}$	$E_{\text{peak n-dope}}$	$E_{\text{peak n-dedope}}$
CH ₃	-0.17	0.93	0.69	0.62	-2.12	-1.90
C(CH ₃) ₃	---	0.93	0.73	0.63	-2.12	-1.94
H	0.00	0.97	0.72	0.64	-2.00	-1.89
F	0.06	0.95	0.72	0.63	-2.04	-1.90
CF ₃	0.54	0.95	0.95	0.74	-1.94	-1.87

In general the trends are as expected with electron donating substituents ($\sigma < 0$) shifting the peak p- and n-doping values toward less positive potentials and electron withdrawing groups ($\sigma > 0$) shifting them to more positive potentials, although the potential shifts are not great. Furthermore, there appears to be little substituent effect on the monomer onset potential. This is most likely due to the symmetry of the highest occupied molecular orbital for these monomers which places a node between the phenyl and thiophene rings thus decreasing the latters' sensitivity to substituents.

The dihedral angle (θ) between the phenyl group and the thiophene is also an important consideration since communication *via* resonance scales approximately as $\cos(\theta)$ dropping off considerably for $\theta > 40^\circ$. Molecular mechanics calculations (PCModel, Chem 3D+) give $\theta = 27^\circ$ for the monomers, thus allowing communication from the substituents. Sterically demanding groups at the *para* position should not affect this dihedral angle in the monomer. However, it could be significantly altered in the polymer where solid state effects may force the rings out of coplanarity to a much greater degree. Clearly more work needs to be done with these and other derivatives to differentiate between electrical and steric effects. The above results, notwithstanding, sterically

demanding groups may increase the interchain packing distance, thus facilitating counterion transport into and out of a more open structure.

For **P3NT**, n - dedoping was essentially nonexistent, despite the presence of n-doping. This result suggests one possible mechanism for charge trapping in these polymers. The naphthyl group is known to readily form radical anions and may serve as a trap for negative charge during the n-doping process. As the polymer is reduced, the backbone becomes negatively charged (and conducting) and cations move into the matrix. Electron transfer may then occur to the naphthyl group which is probably not coplanar with the backbone. (MM2 calculations show that it is 51° out of coplanarity with the thiophene in the monomer). Upon n-dedoping, the backbone becomes insulating thus preventing back electron transfer. When the polymer chain starts to conduct again at positive potentials (p-doping), the charge trapped on the naphthyl group can be released. This validity of mechanism for charge trapping will be explored via EQCM experiments.

The best n/p dedoping ratios were obtained from **P3FPT** but these were still <100% for usefully thick films. Since none of the polymers displayed any difficulty in p-doping upon thickening, efforts were directed toward increasing the n/p dedoping ratio for thicker films. Early on it was observed that large cations (TBA) were less effective for n - doping than smaller ones (TEA) and experiments were conducted using tetramethylammonium salts (BF₄, PF₆). Unfortunately the small size of the cation and anion resulted in strong crystal forces which limited the solubility to ~ 0.1M and hence lowered the electrolyte's conductivity. Even so, the n-doping efficiency was clearly better using the smaller cation. A review of the literature revealed that the trifluoromethanesulfonates of TBA and TEA were known and these had high solubilities (and conductivities) in acetonitrile. The TMA salt was not reported. Synthesis of this salt followed a straightforward neutralization of tetramethylammonium hydroxide with trifluoromethane sulfonic acid and removal of the water. Recrystallization from acetone or acetone-hexane gave analytically pure **TMATFMS** as a white solid, m.p. 383-384 C. [Analysis: Calc (obsd): C: 26.91 (26.87), H: 5.42 (5.13); N: 6.28 (6.17); F: 25.53 (24.10); S: 14.3 (14.55)] More importantly, this salt could be dissolved to 1.0M in acetonitrile. Conductivity measurements were made as a function of concentration and are plotted in Figure 7.

When P3FPT was cycled in this electrolyte (1.0M/AN) the n/p dedoping ratio was 100% and remained essentially unchanged as a function of thickness! This was a significant finding in that it will simplify device fabrication since now *equal* amounts of polymer can be deposited on the cathode and anode and equal amounts of charge can theoretically be injected and extracted from each.

Figure 7

Some of the areas that need to be addressed in future research efforts are:

- 1.) Determination of the mechanism of charge trapping so that it can be eliminated or minimized.
- 2.) Enhancement of dopability *via* changes in polymeric molecular structure and morphology.
- 3.) Optimization of doping/dedoping rates for power density.
- 4.) Optimization of long term cyclability.
- 5.) Design and synthesis of solution processible CPs.