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Poly(3,4-ethylenedioxythiophene) as Electrode Material in Electrochemical Capacitors

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ABSTRACT

We have investigated the conjugated polymer poly(3,4-ethylenedioxythiophene) as electrode material in electrochemical supercapacitor. The conjugated polymer is prepared by chemical polymerization in the form of thin films on nonconducting plastic substrates. One film is electrochemically reduced to the neutral state, while the other is kept in the as-prepared, doped state. The films are thin immersed in a liquid organic electrolyte. In the charged state the supercapacitor cell voltage is 0.8 V and the energy density is measured to 1 to 4 Wh/kg of active electrode material, depending on the current density used during discharge. The power density (delivered energy/discharge time) also depends on the current density and at the highest current densities investigated (1 mA/cm^2) it reaches 2.5 kW/kg of active electrode material.

Introduction

Many conjugated polymers can be formed using electrochemically induced oxidation of monomers, and the material formed is usually obtained in its doped, conducting form, having positive charges distributed along the conjugated chains and anions from the supporting electrolyte inserted as charge compensating species. The films can then be switched between this doped state and the uncharged, neutral state by electrochemical means. Depending on the size of the anion inserted during the polymerization, the electrochemical switching can be accompanied by either cation or anion transport

$$P^+X^- + e^- \rightarrow P^o + X^- \text{ (electrolyte)} \quad [1a]$$

$$P^+A^- + e^- + M^+ \text{ (electrolyte)} \rightarrow P^oA^-M^+ \quad [1b]$$

Equation 1a applies for a polymer which had been polymerized in a supporting electrolyte with small anions, like ClO_4^- or BF_4^-. When the conjugated polymer is reduced, an excess of negative charge, in the form of small anions, is transported out of the film. When the film is reoxidized, the anions move back into the film. Equation 1b applies for bulky anions inserted during polymerization. In this case, reduction of the conjugated polymer gives rise to an immobilized excess of negative charge that must be compensated. This is achieved by incorporation of small cations from the electrolyte. When the film is reoxidized, these mobile cations return out into the electrolyte.

Electrochemically induced doping/undoping of conjugated polymers are being investigated for different applications, like electrochromic devices,[1-4] rechargeable batteries,[5-7] and electrochemical capacitors. Two types of electrochemical capacitors are under investigation currently: the double-layer capacitor where the charge is stored by charging of the electric double layer at the interface between a high surface area carbon electrode and the electrolyte,[8] and the redox capacitor, based on the faradaic pseudocapacitance of two-dimensional or quasi two-dimensional materials at, or within which, redox processes occur. The second type involves reactions like oxidation/reduction in microporous transition metal hydrous oxides (RuO_2,[9,10] IrO_2[11]) and oxidation/reduction reactions of conjugated polymers.[12-14] These supercapacitors are expected to work in conjunction with batteries in electrical vehicles, to provide the necessary peak-power performance, and possibly to reduce the size and enhance the life expectancy of the battery.

The conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT)[15] has been studied previously for different purposes: as a conducting surface layer for electrodeposition of copper,[16] biosensor applications,[17] and electrochromic devices[18,19] and has been shown to exhibit enhanced electrochromic switching properties and high electronic conductivity. Also, the material can be electrochemically cycled, from the doped state to the neutral state and back, even when prepared on a nonconducting substrate, indicating a high conductivity even in the undoped state. It also seems to have a higher chemical and electrochemical stability than other conjugated polymers. These observations inspired us to investigate the properties of PEDOT as an electrode material in an electrochemical capacitor.

Experimental

PEDOT was prepared in the form of films with a thickness of 7000 Å on transparency film, following the recipe proposed by de Leeuw *et al.*[16] Cyclic voltammetry was performed in 0. 1 *M* $LiClO_4$ solution in acetonitrile, using a Ag/AgCl reference electrode, a platinum counterelectrode, and the PEDOT film contacted with a small silver clamp as the working electrode. The distance from the silver clamp to the electrolyte surface was 0.5 cm and the area of the film lowered into the electrolyte was 1 cm^2.

One film was electrochemically undoped in a 0.1 *M* $LiClO_4$ acetonitrile solution by fixing the applied potential at −1.0 V *vs.* Ag/AgCl for 15 min. The other film was left in the as-prepared (doped) state. When using the two films as electrodes in a supercapacitor with the $LiClO_4$ (ACN) electrolyte, a voltage of 0.8 V could be measured between them. This was the starting configuration of the measurements presented here. The wet capacitor was characterized using cyclic voltammetry, galvanostatic discharge, and impedance spectroscopy.

The electrochemical measurements were performed using a universal electrochemical system (Autolab, EchoChemie) and for the impedance analysis we used an HP 4192 impedance analyzer. For evaluation of the impedance results we used Equivalent Circuit software (B. A. Boukamp).[20]

Results and Discussion

We used cyclic voltammetry to detect electrochemical activity of the films. The cyclic voltammogram of a PEDOT film in 0.1 *M* $LiClO_4$ in acetonitrile (Fig. 1) has a shape we recognize from work on other polythiophenes and polypyrrole. It shows a large non-faradaic, residual current at the end of the anodic wave, associated with a charging of a pseudo-capacitance due to internal double layers of the material. The value of this capacitance can be calculated as the ratio between the residual current and the sweep rate of 6 $mF/cm^2 \approx 100\ F/cm^3$. This value is comparable to earlier reported values for polypyrrole.[21]

Some groups have reported earlier that n-doping should be possible in PEDOT, and preliminary experiments in our lab show that it is, but only at low temperatures. Since it is beneficial for the capacity of the capacitor to use a polymer that may be both p- and n-doped,[14] voltammetry was performed at room temperature down to −3.5 V *vs.* Ag/AgCl, but no reduction wave was found. This means that the symmetrical capacitor is built with one PEDOT electrode in the doped state, and the other in the neutral state. It has been reported from studies of capacitors with polypyrrole as electrode material, that the low conductivity of the neutral state causes too high an internal resistance, and that a configuration with one highly doped electrode and one lightly doped electrode gives a better performance.[12] PEDOT, however, has exceptionally good switching capability in the neutral state, even on a nonconducting substrate, so we see no problems with using the full range of doping, from the highly doped down to the neutral state.

Figure 2 shows the results of cyclic voltammetry of a wet PEDOT/PEDOT supercapacitor. The response is rate dependent,

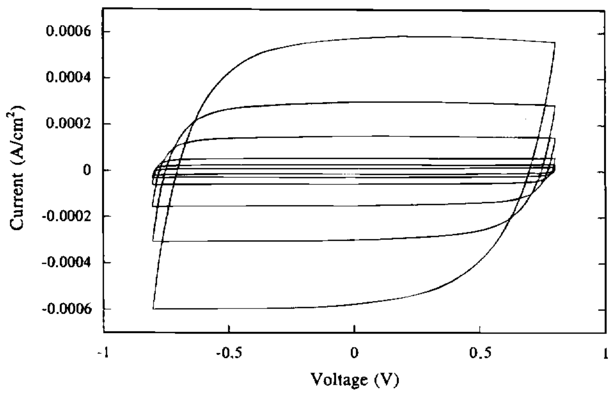


Fig. 2. Cyclic voltammetry at different sweep rates of a PEDOT/PEDOT supercapacitor with $LiClO_4$ (ACN) electrolyte. Sweep rates: 5, 10, 20, 50, 100, and 200 mV/s.

as expected, and even at rather high sweep rates the curves approach the ideal rectangular shape. If we plot the capacitive current as a function of sweep rate, we obtain a linear relationship, giving a redox capacitance of 3 mF/cm^2, almost independent of sweep rate.

To better analyze the difference between the neutral and the doped state regarding charge-transfer and electrical resistance, impedance spectroscopy was used and the results were evaluated using a modified Randles equivalent circuit.[22] The impedance of a PEDOT/PEDOT supercapacitor in the charged state ($\Delta V = 0.8$ V) and in the uncharged state ($\Delta V = 0$ V). The high-frequency region is usually considered to reflect the bulk properties of the electrolyte, but in this case this part also includes the resistance of the polymer electrodes. The intercept with the real axis corresponds to the total bulk resistance, and we can see in Fig. 3 that the charged capacitor has a slightly higher internal resistance, due to the lower electrical conductivity of the film that is in the neutral state. The medium frequency region shows the impedance response of the charge-transfer between the electrode and the electrolyte. In this case, the semicircle obtained has a very small radius (close-up in Fig. 3), showing a value of the charge-transfer resistance of a few ohms, in both the charged and the uncharged state. At low frequencies, the impedance is usually determined by the diffusion of ions in the polymer film, giving a linear behavior with a frequency independent phase angle of $\pi/4$. This region cannot be observed in our measurements, but the impedance approaches a pure capacitive response with a phase angle of $\pi/2$ directly. This capacitance is the same capacitance we discussed when interpreting the cyclic

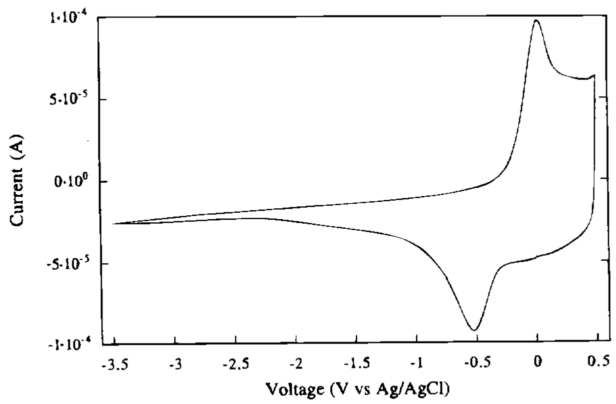


Fig. 1. Cyclic voltammogram of a PEDOT film on transparency film in 0.1 *M* $LiClO_4$ (ACN). Sweep rate 10 mV/s. Ag/AgCl as reference electrode and platinum foil as counter-electrode.

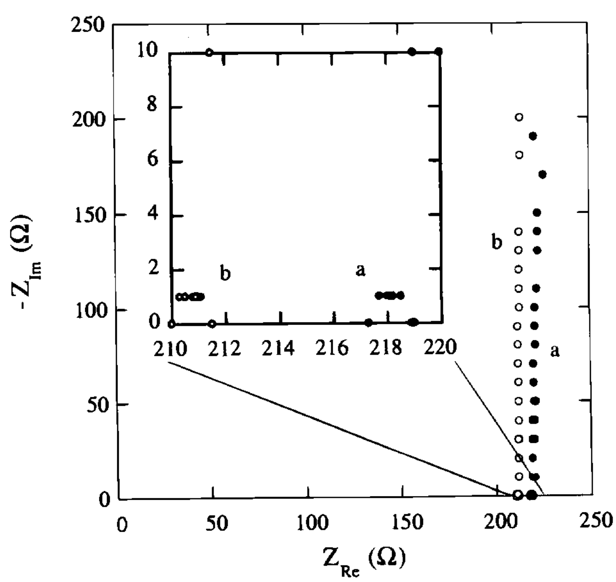


Fig. 3. Impedance spectroscopy of a PEDOT/PEDOT supercapacitor in $LiClO_4$ (ACN) electrolyte; (a) uncharged state, $\Delta V = 0$ V and (b) charged state, $\Delta V = 0.8$ V.

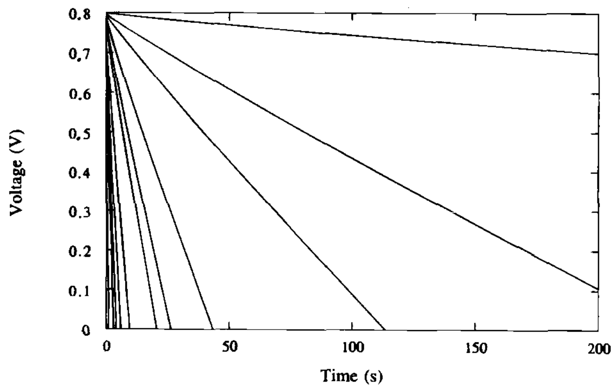


Fig. 4. Galvanostatic discharge curves for a wet PEDOT/PEDOT supercapacitor using different current densities. The total charge drawn from the capacitor is ~2 mC, varying slightly with the current density. This charge corresponds to a doping level of ~20%. Current densities 1 to 1000 μA/cm².

voltammetry, and the value estimated from the impedance measurements using an Equivalent Circuit simulation software (3 mF/cm²) agrees with the value obtained from cyclic voltammetry.

Figure 4 shows the galvanostatic discharge curves for different current densities for the wet PEDOT/PEDOT supercapacitor. The IR-drop is small and the discharge curves are close to linear, showing that the capacitance is almost constant. From the discharge behavior, values of charge density (Fig. 5a), energy density (Fig. 5b), and power density (Fig. 5c) were calculated per unit mass of capacitor active material, considering both electrodes for different current densities. Both the amount of extracted charge and energy decreases with increasing current density. This is explained by an increased internal polarization at higher current densities. The average delivered power, calculated by dividing the delivered energy with the discharge time, increases with increasing current density, as expected.

U.S. Department of Energy (DOE) has set up some goals for electric vehicle power supercapacitors.[23] For practical applications, the high energy density goal (>15 Wh/kg) must be achieved while enabling discharge of the capacitor at a power density of at least 1.5 kW/kg. In addition, cycle life (greater than 100,000 cycles) and cost (less than $1/Wh) goals must be met. Table I shows the data of the PEDOT/PEDOT supercapacitor, calculated per weight of active electrode, and the goals. The power density is calculated as the energy density divided by the discharge time and we have estimated the density of PEDOT as 1.5 g/cm³. We observe that the power density at high current densities of the PEDOT/PEDOT supercapacitor is very high, even compared to supercapacitors with a polymer that can be both n- and p-doped as electrode material.[13,14] To achieve a higher energy density, we must increase the cell voltage, either by combining PEDOT with another material having suitable electrochemical properties or modifying PEDOT to stabilize the n-doped state even at room temperature.

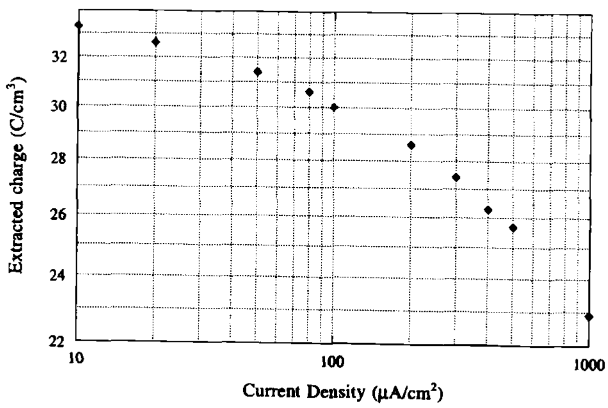
Table I. Comparison of the PEDOT/PEDOT supercapacitor with the goals set up by U.S. Department of Energy.

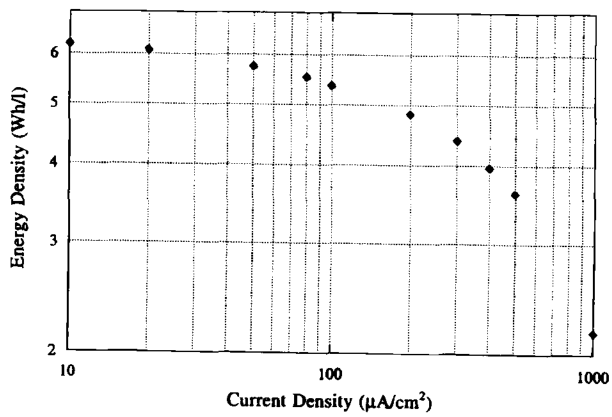
	Voltage (V)	Energy density (Wh/kg)	Power density (W/kg)
DOE goals	—	15	1500
PEDOT/PEDOT	0.8	1 to 4 (High CD to low CD)	35 to 2500 (low CD to high CD)

CD = current density.
All values for the PEDOT/PEDOT capacitor calculated per unit weight of active electrode material.

Conclusion

We have shown that poly(3,4-ethylenedioxythiophene) is an attractive material for use as electrode material in electrochemical supercapacitors due to its fast kinetics and good electrochemical stability. The supercapacitor studied in this work, comprising two PEDOT electrodes and a liquid electrolyte ($LiClO_4$ dissolved in acetonitrile) and not optimized in any way, encourages us to continue the work on polymer supercapacitors; results for a PEDOT capacitor with a solid polymer electrolyte is under way. It would be interesting to replace, or coat, one PEDOT electrode with another





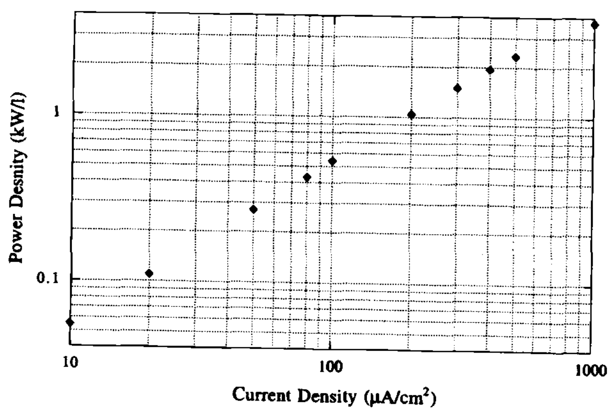


Fig. 5. (a, top left) Extracted charge, (b, above) energy, and (c, left) power per unit volume of active electrode material as a function of current density used during discharge.

conjugated polymer having suitable electrochemical properties to increase the cell voltage of the device and increase the energy density.

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Cathodic Behavior of Alkali Manganese Oxides from Permanganate

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ABSTRACT

The reaction of potassium, sodium, and lithium permanganate in water at 170°C leads directly to potassium, sodium, and lithium manganese dioxides, $A_yMnO \cdot nH_2O$, with a $R\bar{3}m$ rhombohedral structure. These crystalline layered structures after dehydration readily and reversibly react with lithium through an intercalation mechanism. The capacity for lithium is a function of the alkali ion present, and the larger potassium ion maintains the capacity best. For lithium there is a tendency to convert to the spinel structure which leads to loss of capacity.

Introduction

Manganese oxides are of particular interest as battery cathodes because they readily intercalate lithium into their structures and manganese is low cost relative to the commercially available $LiCoO_2$. However, only 0.5 lithium can be cycled per manganese atom in the spinel $LiMn_2O_4$ so that their energy densities are no higher[1] than that of $LiCoO_2$ or $LiTiS_2$. Hence, extensive research is currently underway to find promising candidates for cathode materials in lithium secondary batteries, and a manganese oxide that behaved like the layered $LiCoCO_2$ would be a prime candidate for this application because of its high free-energy of reaction with lithium and relatively low cost.

We have been studying hydrothermal methods as a new approach to form cathode active oxides. Hydrothermal synthesis has been shown to be a powerful technique in the synthesis of novel compounds.[2] This technique has been used recently to form new metal oxides, such as manganese oxides,[3,5] vanadium oxides,[6-8] molybdenum oxides,[9] and mixed metal oxides.[10] To maximize the free-energy of lithium intercalation, it is desirable to have the manganese in as high an oxidation state as possible; thus, the permanganate ion is the preferred starting point. The effectiveness of using potassium permanganate as the starting reagent to prepare layered manganese oxides, such as the Ranciete form, has been reported.[11,12] Feng *et al.*[5] reported the formation of manganese rich dioxide, $Na_{0.40}Mn_{2.15}O_2 \cdot 0.6H_2O$ by the hydrothermal treatment of γ-MnO_2 with NaOH.

* Electrochemical Society Active Member.

Recently, we synthesized layered sodium and potassium manganese oxides, with the TiS_2 structure, by the mild hydrothermal decomposition of their permanganates.[3,4] We here report the successful formation of a layered lithium manganate, and the electrochemical behavior of all three oxides in lithium cells.

Experimental

The lithium manganese dioxide was synthesized by the hydrothermal decomposition of lithium permanganate, following the method used for potassium and sodium manganese oxides.[3,4] The lithium permanganate, $LiMnO_4$, was prepared by titrating a 0.3 *M* solution of $HMnO_4$ with LiOH until the pH reached 9. The $HMnO_4$ was synthesized by passing a 0.3 *M* $KMnO_4$ solution through a column containing proton-charged cationic ion exchanger. The pH of the $LiMnO_4$ solution so formed was adjusted to about 5.2 with nitric acid, which helps drive the reaction to completion,[4] and reacted hydrothermally for 3.5 days at 160°C in a Teflon lined Parr reactor. The resulting brown lithium manganese oxide was filtered, and dried at 45°C in air for use. The pH of the solution after reaction was alkaline, pH 12 to 13. The direct hydrothermal reaction of $HMnO_4$ at 160°C led to MnO_2 instead of the desired layered $H_xMnO_2 \cdot nH_2O$.

X-ray powder diffraction was performed using Cu K_α radiation on a Scintag θ-θ diffractometer. The thermogravimetric analysis (TGA) data was obtained on a Perkin-Elmer Model TGA 7, and the chemical analysis was obtained on an ARL Spectrospan-7 DCP atomic emission spectrometer. Electrochemical studies were conducted in lithum cells using $LiAsF_6$ in propylene carbonate (PC):(dimethyl-