

# Towards High Power Polypyrrole/Carbon Capacitors

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## Abstract

Conducting polymers demonstrate effective capacitances of more than 100 Farads per gram, 5 orders of magnitude higher than traditional capacitors. However polymer discharge times tend to be on the order of seconds, as opposed to the milli or microseconds of conventional capacitors, so that the overall power density is still at least an order of magnitude lower. The polypyrrole devices are essentially electrolytic capacitors in which charging times appear to be limited by rates of ionic mass transport and  $RC$  charging times. Electrochemical impedance measurements suggest diffusion time constants of 33 ms in 158 nm thick polypyrrole films with volumetric capacitances of  $10^7$  F/m<sup>3</sup>. The impedance of a highly porous polypyrrole/carbon composite was measured to investigate the achievement of similarly fast response times in much thicker materials. It is shown that increasing the polypyrrole content of the film increases capacitance up to 60 F/g, but also increases the charging time constant. Analysis of the rate limiting factors suggests a method of optimizing capacitor geometry in order to maximize rates, including the prediction of device geometries that will lead to power delivery matching those of traditional capacitors.

*Keywords:* Polypyrrole; Supercapacitor; Carbon Fiber; Power Density; Impedance; Conducting Polymer

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## 1. Introduction

Capacitors [1] are fundamental electrical circuit elements that store electrical energy and assist in filtering. Commercially available ultracapacitors such as the NEC/TOKIN Supercapacitors are designed for power backup and intermittent power delivery applications. For example, NEC/TOKIN offers an electrochemical ultracapacitor with a capacitance of 1 F, a package mass of 6.7 g and a maximum DC voltage of 5.5 V (Model FC0H105ZTBR44). Peak power is 120 W/kg and the energy density is 2 kJ/kg (75 times lower than a lead acid battery). Increased power and energy densities would make a wider range of applications available for ultracapacitors, including energy recovery systems for fuel cell driven vehicles.

Polypyrrole and other conducting polymers display high volumetric and specific capacitance [2]. Polypyrrole doped with hexafluorophosphate exhibits high conductivity ( $> 40$  kS/m) and a capacitance of 100 F/g, with a time constant on the order of seconds [3,4]. How much faster can polypyrrole discharge and what is the limit on power?

The premise underlying this work is that the rate limiting factors in polypyrrole and likely also carbon nanotube-based capacitors are  $RC$  charging and the rate of ion transport within the polymer or nanotube films

themselves. These factors can be minimized either by using extremely thin films (fast mass transport), or by employing porous films with substantial electrolyte content, thereby allowing faster mass transport than is possible in solid films. Carbon fibre paper is employed to provide a porous deposition template. Polymer supercapacitors have been produced by growth in porous media [5-8]. Our contribution is the analysis of the benefits.

## 2. Experimental

Porous carbon fibre paper (CFP) (Density: 0.375 g/cm<sup>3</sup>, Thickness: 0.145 mm, AvCarb<sup>TM</sup> P50 obtained from Ballard Material Products, Inc, Lowell MA), is used as the electrode material. Two carbon fibre electrodes are separated from each other by 2mm using glass slides with  $12 \times 4$  mm<sup>2</sup> exposed to electrolyte. Electrical connections are made with the electrodes via gold wire. CFP conductivity and contact resistance are measured.

Electrodeposition of polypyrrole (PPy) in CFP is carried out in a propylene carbonate solution containing 0.06 M pyrrole and 0.05 M tetraethylammonium hexafluorophosphate (TEAP), at -30 °C at a current density of 1 A/m<sup>2</sup> [3,4], over a period of 24 hours. Impedance analysis and voltammetry are done in 0.3 M tetrabutylammonium hexa-

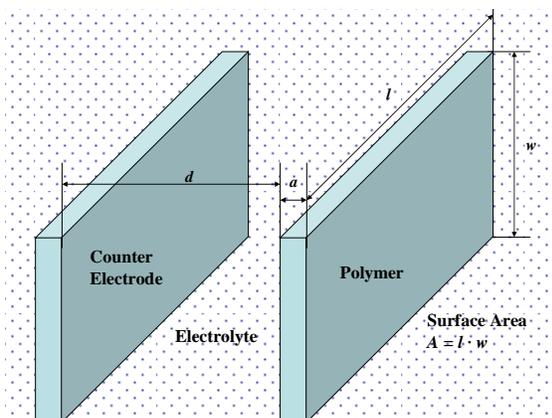


Fig 1. Dimensions of the polymer capacitor. Electrical contact to the polymer is made at intervals of length  $l$ .

fluorophosphate (TBAP) in acetonitrile using a Solartron SI 1260/1287. A 158 nm film of PPy is also electrodeposited under the same conditions, but onto a gold substrate. Measurements on this PPy film were performed in 0.05 M TBAP in propylene carbonate.

### 3. Device Analysis

Two fundamental processes are assumed to determine the capacitor charging time, namely  $RC$  charging and ionic mass transport within the capacitor [3, 4]. The  $RC$  limits result from the combination of the device capacitance and the resistances of the electrolyte,  $R_e$ , of the contacts,  $R_c$ , and of the polymer, carbon or composite material itself,  $R_p$ . Given an electrode area  $l \times w$ , thickness,  $a$ , capacitance per unit volume,  $C_V$ , and a spacing between the electrodes of  $d$ , as depicted in Fig 1, the charging time constant due to the combination of the volumetric capacitance, the finite electrolyte resistivity,  $\sigma_e$ , and the contact resistance, is:

$$\tau_{RCV} = (R_e + R_c) \cdot C_V \cdot \frac{(l \cdot w \cdot a)}{2} = \frac{d \cdot a}{2 \cdot \sigma_e} \cdot C_V + R_c \cdot C_V \cdot l \cdot w \cdot a. \quad (1)$$

The two electrodes are assumed to have equal capacitances.

Finite polymer/carbon/composite conductivity,  $\sigma_p$ , leads to a voltage drop along the electrodes, thereby slowing charging. The resulting time constant is:

$$\tau_{RCVP} = R_p \cdot C_V \cdot (l \cdot w \cdot a) = \frac{l^2}{\sigma_p} \cdot C_V. \quad (2)$$

A third time constant results from the electrolyte resistance in the pores of the material, and is expressed:

$$\tau_{REVP} = \frac{a^2}{\sigma_e \cdot \gamma} \cdot C_V, \quad (3)$$

where  $\gamma$  represents the area fraction of the pores, and can also account for the tortuous paths taken by ions in the pores. If the number of ions in the pores is insufficient to balance charge in the polymer then rates of diffusion into the pores will also need to be considered. Furthermore if the polymer layers are sufficiently thick then ion and electron transport into them will limit charging rate.

We now assume that the capacitance observed at any given frequency depends on the depth to which ions and, in porous films, electric fields, can penetrate into the electrodes. On times scales at which mass transport within the electrodes limits charging the apparent volumetric capacitance will be lower than the capacitance observed at longer times. In cases where  $RC$  charging is dominant, mass transport limits are estimated using a model in which capacitance is allowed to vary with frequency.

Such an  $RC$  limited case is modeled using a resistance,  $R_s$ , in series with resistor,  $R_p$  and capacitor,  $C$  in parallel.  $R_s$  represents the sum of the contact and solution resistances.  $C$  results from the charge stored in the polymer/electrolyte or carbon/electrolyte double layers and within the polymer volume.  $R_p$  represents leakage.  $R_s$ ,  $R_p$ , and  $C$  are calculated by least squares fitting to impedance data. A second fit is then done in which the capacitance,  $C$ , is allowed to vary as a function of frequency. The frequency dependence of the model capacitance is then used to estimate the time constant for mass transport within the electrode.

### 4. Results and Discussion

#### 4.1 Polypyrrole thin film results

Figure 2 is a Nyquist Plot obtained using a 158 nm thick polypyrrole film. The capacitive behaviour becomes apparent at frequencies below 7 Hz. Analysis of the time constants indicates that it is the electrolyte resistance combined with the volumetric capacitance that limits the rate of response. An estimate of the frequency dependence of capacitance, shown in Figure 2, indicates that it reaches  $1/\sqrt{2}$  of its low frequency value at 5 Hz (33 ms time constant), suggesting that mass transport in the PPy is occurring much faster than the  $RC$  charging time. The specific capacitance is just over 100 F/g. If the series resistance is dramatically reduced (e.g. by reducing the

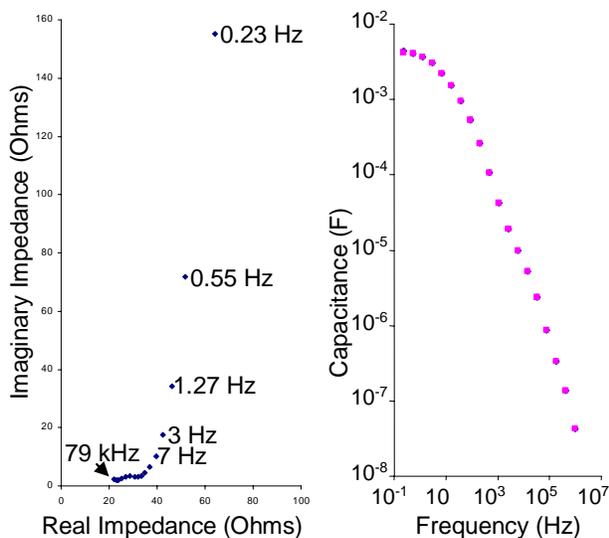


Fig. 2: Impedance and estimated capacitance of a 158 nm thick polypyrrole film.

spacing between electrodes) and no other factor limited rate, then the mass transport would restrict peak power to approximately 750 kW/kg (electrode mass only), with an average power of 324 kW/kg. The power estimate assumes discharge across a resistor equal in magnitude to the internal resistance, and charging to 1 V. The power density will not be as high in real devices as electrolyte and counter electrode masses need to be accounted for. However, the estimated power is 30 times higher than is reported for a competitive ultracapacitor technology and far in excess of the < 1 kW/kg of lead acid batteries [9]. The energy density is 50 kJ/kg, about 1/3<sup>rd</sup> that of a lead acid battery.

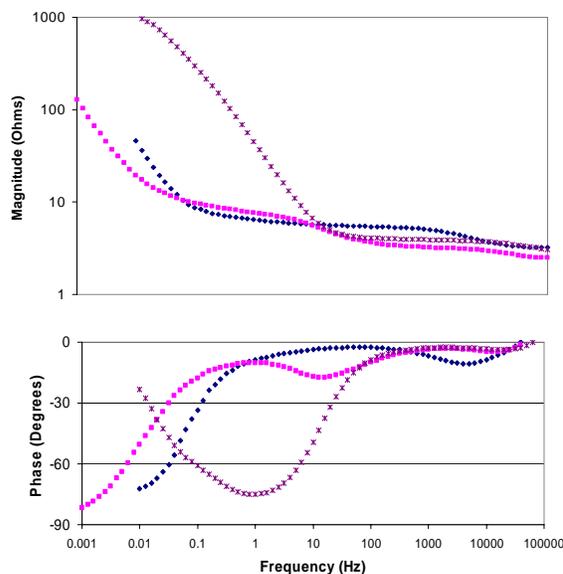


Fig. 3. Measured Magnitude of Impedance and Phase vs. Frequency. The x's represent the impedance of the carbon fibre paper alone, the diamonds the impedance after 6 hours of polypyrrole deposition and the squares 24 hours of deposition.

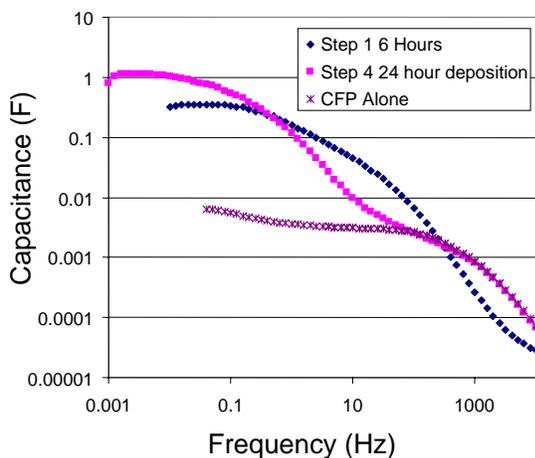


Fig. 4. Capacitance of the polymer/carbon fibre paper composite.

What needs to be done in order to achieve these power densities? Based on electrolyte conductivity, the spacing between electrodes would have to be reduced to several micrometers to achieve the desired rates. However, even at several micrometers the volume of electrolyte far exceeds

the volume of the electrodes, which are 158 nm thick. To obtain high power and energy densities the spacing should be reduced to <158nm, a challenge to fabricate & assemble.

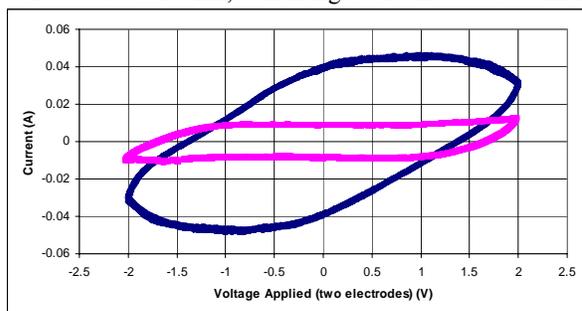


Fig. 5. Cyclic voltammogram at 10 mV/s and 50 mV/s scan rates after 24 h of polypyrrole deposition in carbon fibre paper.

#### 4.2 Polypyrrole in Carbon Fibre Paper

Porous electrodes offer the possibility of increasing power without the need for ultrathin electrodes and separators. These are created by growing polymer within a porous electrode, in this case carbon fibre paper. The impedance plots in Figure 3 show a general increase in capacitance as electrodeposition time is increased, and an accompanying reduction in frequency response. Table 1 summarizes the impedance response, showing the fit parameters and the capacitor time constants. The measured time constants range from 13 ms to 13 s, and are approximately in inverse proportion to the capacitance. The estimated capacitance saturates in value with continued deposition. In fact after 18 hours of deposition the apparent capacitance decreases. This decrease is the result of a substantial evaporation in the solvent before and during the measurement.

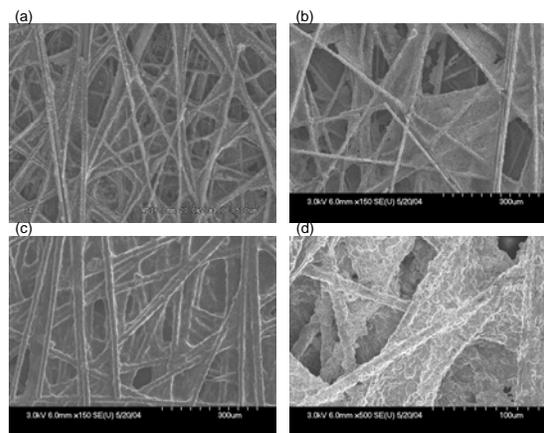


Fig. 6: SEM images of carbon fibre paper (a) uncoated, (b) coated for 2.5 hours, (c) coated for 16 hours, (d) close-up of (c).

Figure 4 shows the estimated capacitance as a function of frequency. The time constants suggested by the capacitance plots are 0.8 ms for the bare CFP, 0.4 s after 6 h, and 5 s following 24 h of deposition. For reasons that are unclear, both the 12 and 18 hour depositions had very high leakage (low  $R_p$ ) with the phase never reaching 45°.

Cyclic voltammograms (CV) generated after 24 h of deposition are shown in Figure 5. The rounded appearance indicates charging time, while the flat response seen in the slow scan shows a capacitive response between  $\pm 1.25$  V.

Electron micrographs of the initial carbon fibre electrode and following 2.5 h and 16 h of deposition are presented in Figure 6. The carbon fibres are approximately 8  $\mu\text{m}$  in diameter. Polypyrrole coats the fibres, and is between fibres. The film remains porous even following 16 hours of deposition, but the porosity appears to be reduced. Electrodeposition is found to occur throughout the film.

## 5. Discussion and Conclusions

What are the rate limiting factors, and what might be done in order to substantially increase speed? Estimates of a number of potentially rate limiting time constants are presented in Table 2.  $\tau_{MC}$  is the time constant associated the frequency dependence of capacitance, as estimated from data in Figure 4.  $\tau_M$  is measured, as given in Table 1.

Table 1. Summary of successive polypyrrole depositions in CFP.

Sample	$R_S$ ( $\Omega$ ) $\pm 10\%$	$R_P$ ( $\Omega$ ) $\pm 20\%$	C (F/g) $\pm 10\%$	$\tau_M$ , Time Constant (s)
No PPY	4	925	0.5	0.013
6 h PPY	5	125	33	2.5
12 h PPY	3	9	60	-
18 h PPY	2	2	45	-
24 h PPY	5	260	60	13

The time constant associated with the electrolyte and contact resistances,  $\tau_{RCV}$ , clearly needs to be reduced in order to achieve higher power. Contact resistance can be virtually eliminated by metal coating the electrodes. The electrolyte resistance can be decreased by reducing the spacing between electrodes. In order to allow a 100 Hz bandwidth (1.6 ms time constant) the spacing would need to be just under 1  $\mu\text{m}$  at maximum capacitance. If thinner electrodes are used the spacing between electrodes could be increased (e.g. for a 15  $\mu\text{m}$  thick electrode, 10  $\mu\text{m}$  spacing).

Table 2. Measured and calculated time constants for CFP/PPy electrodes.

	$\tau_M$ (s)	$\tau_{RCV}$ (s)	$\tau_{RCVP}$ (s)	$\tau_{RCEP}$ (s)	$\tau_{MC}$ (s)
Carbon Fibre	0.013	0.01	0.0007	0.003	0.0008
6 h PPY	2.5	2	0.05	0.2	0.4
24 h PPY	13	4	0.1	0.3	6

Finite conductivity of the electrode,  $\tau_{RCVP}$ , and of the electrolyte within the electrodes,  $\tau_{RCEP}$ , do not limit rate. If a 100 Hz bandwidth is desired for the highest capacitance, however, the spacing between electrical contacts with the electrode would need to be reduced to approximately 1 mm or less, and the electrode thickness would need to be  $\leq 15$   $\mu\text{m}$  in order for these factors not to be limiting.

After 24 h,  $\tau_M$  is more than double any of the other time constants, suggesting that some rate limiting factors have not been accounted for. Pores may have been filled in or reduced significantly constricted after sustained deposition, reducing charging time.

The time constant derived from the capacitance,  $\tau_{MC}$ , is dominated by a number of factors, including the resistance of the electrolyte within the polymer, as given by  $\tau_{RCEP}$ , the

resistance of the electrode,  $\tau_{RCVP}$ , and transport of ions into the polymer itself. The response after 6h suggests that the electrolyte resistance in the pores is the limiting factor. This rate limit is easily dealt with by reducing the electrode thickness. The 6 s measured capacitance rise time in the 24h sample is not accounted for by any of the estimated time constants. There are a number of factors that have not been considered that could be limiting rate including the speed of ion transport within the polymer layers, and the fact that the electrolyte concentration in the pores may be insufficient to balance polymer charge. Figure 6d shows nodular structures characteristic of electrodeposited polymer. The image suggests that the polymer thickness is in excess of 10  $\mu\text{m}$  in some places. At such thicknesses time constants on the order of seconds are expected [3,4].

A key aim in the development of ultracapacitors is to minimize charge and discharge times. The analysis has proposed a number of time constants that limit rate. By employing appropriate device geometries these time constants can be dramatically reduced. Reduction of the thickness of the carbon fibre paper to 15  $\mu\text{m}$  and of the inter electrode spacing to 10  $\mu\text{m}$ , for example, is expected to enable a 100 Hz bandwidth. Although this analysis provides a guide as to how to increase rate via changes in geometry, it is an extrapolation and does not account for factors such as speed of ion insertion into the polymer and the effects of pore occlusion by deposited polymer. These factors can be modelled providing the micro and nanostructure of the electrodes are known.

It is demonstrated that the capacitance of carbon paper sheets is increased by the incorporation of electrodeposited polypyrrole, reaching up to 60 F/g of dry electrode. The increase in capacitance is associated with a decrease in frequency response, with the time constant dropping as low as 13 s. Nevertheless, analysis of the rate limiting factors suggests that it is possible to dramatically improve rate by reducing electrode thickness and electrode spacing.

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