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Understanding the Effects of Electrochemical Parameters on the Areal Capacitance of Electroactive Polymers

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A number of variables contribute to the electropolymerization, and the electrochemical properties, of electroactive polymers. However, few studies have attempted to acquire a unified understanding of the effects of all these variables, specifically as it relates to the capacitance of the material, as the number of
10 experiments and resources required is large. Here, the effects of seven variables on the areal capacitance of the electropolymerized dimethyl derivative of poly(3,4-propylenedioxythiophene) (PProDOT-Me₂) films are analyzed utilizing a fractional factorial design of experiments to reduce the number of experiments an order of magnitude. From this analysis, PProDOT-Me₂ films were electropolymerized from an optimal set of variables to reproducibly afford films displaying the highest capacitances observed
15 within this study. Devices were assembled from the optimized conditions, and the capacitance, energy, and power densities are reported in a framework that allows for meaningful comparison and understanding relative to commercially available supercapacitors. The supercapacitors fabricated in this study show promise towards being integrated as power sources for low-power, lightweight and flexible organic electronic devices.

1 Introduction

A number of factors are fuelling a growing interest for research in the area of electrochemical supercapacitors.¹⁻³ This motivation is spurred by the need to power a variety of modern day technologies, such as hybrid electric vehicles, portable electronic devices, and telecommunications.^{4,5} Additionally, there has been significant growth and advancement in research towards harvesting renewable energy. Many sources however, such as solar energy, do not provide a continuous and reliable energy supply. Research in energy harvesting needs to be coupled to research in energy storage for renewable energy to become a reliable and dependable source to power our everyday needs.^{3,6,7}

While, traditionally, batteries offer high energy density, and capacitors offer high power density, electrochemical supercapacitors (ESCs) bridge the gap, delivering lower energy than batteries, but at rapid charge and discharge rates to afford robust power densities.^{7,8} Of the materials that have been investigated for use as electrodes in ESCs, electroactive polymers (EAPs) possess many attractive properties, such as fast charge/discharge behavior, low cost, charge storage through Faradaic redox processes accessible throughout the bulk of the material, and electronic and structural properties that are readily tunable through structural modifications.⁹⁻¹³

Of the various ways in which EAPs can be obtained, electropolymerization offers a rapid route towards polymer films from inexpensive precursors and reagents. Additionally, a variety of morphologies and properties can be accessed by varying any one of numerous variables during electropolymerization, such as solvent, electrolyte, method of polymerization, and solution temperature, to name a few.¹⁴ Furthermore, large and intricate surfaces can be coated in this fashion, and good substrate adhesion makes it possible to deposit thick films

While work in electropolymerized EAPs for ESCs has been ongoing for quite some time, fundamental structure-property relationships are poorly understood. This understanding is complicated by the large number of variables which affect film properties. For instance, prior work has demonstrated that poly(3,4-propylenedioxythiophenes) (PProDOTs) are promising materials for use in ESCs, displaying respectable capacitance and energy densities, as well as stability over a range of temperatures and tens of thousands of cycles.¹⁵⁻¹⁷ Our group has also expanded our understanding of the potential of PProDOTs as the electrode material in ESCs and constructed modules to show the behavior of devices in parallel and in series, expanding the useable voltage range and the module current with this method.¹⁸ Recently our group has fabricated ESCs with poly(3,4-ethylenedioxythiophenes) (PEDOT) as the active material. These devices were capable of retaining >80% of the original capacitance over 400,000 cycles, and demonstrated performance comparable to commercially available supercapacitors, as well as the ability to power EAP devices.¹⁹ In spite of these promising results, electropolymerization and film cycling conditions vary from paper to paper and an understanding of how these changes impact charge storage and switching performance are unclear.

Here, we explore the structure-property relationships between

the capacitive properties of a dimethyl-substituted PProDOT (PProDOT-Me₂) and a set of seven variables that affect the electrochemical behavior of EAPs: the polymerization method, the charge passed during polymerization, the solvent, electrolyte, and electrolyte concentrations used during polymerization, and the electrolyte and electrolyte concentrations used during polymer film cycling. A systematic full-factorial evaluation of every combination of the variables investigated in this manuscript would take 128 (2⁷) experiments, if we consider only two options per variable. However, statistical tools can be employed to reduce the many experiments that come with analyzing a large number of variables, as well as to provide a more complete understanding of the results. The design, implementation, and analysis of experiments have been comprehensively detailed in the literature.^{20,21} Here, employing a fractional factorial statistical design of experiments (DOE) allowed us to dramatically streamline the initial experimental screening process while improving on cost and time efficiency. Specifically, we have optimized the areal capacitance of electropolymerized thin films while reducing the number of experiments from 128 to 16, which were then performed in triplicate to assure reproducibility. From this rapid screening stage, statistical analysis of the data allows us to determine the optimal combination of variables with minimal loss of information.

Finally, we present the results of test modules constructed using the optimal conditions predicted by the DOE. As the field of EAP supercapacitors grows, we stress the need to establish a standard set of values to report, a uniform method of evaluating these values, and the need for reproducibility to have a meaningful understanding of how EAPs measure up to other materials currently employed in supercapacitors.

2 Experimental

2.1 Materials

Electrochemical salts and solvents were purchased from Sigma Aldrich and purified as noted below. ProDOT-Me₂ was synthesized utilizing a transesterification route previously reported.²² Tetrabutylammonium tetrafluoroborate (TBABF₄) 99% was purified by recrystallization from a 1:2 ethanol:water mixture and drying in a vacuum oven at 80°C overnight. Lithium triflate (LiOTf) 99% was purified by rinsing three times with diethyl ether and drying in a vacuum oven at 150°C overnight. Propylene carbonate (sure seal, anhydrous, 99%) was used as received. Acetonitrile was distilled over calcium hydride.

2.2 Electrochemistry

Flexible gold on Kapton (Au/Kapton, 1000 Å; 1 mil Kapton/3M 966 adhesive) was purchased from Astral Technology Unlimited and cleaned by rinsing with isopropyl alcohol and drying in a vacuum oven at 80°C. A circular area 2.83 cm² served as the working electrode during electrochemical polymerization and measurements. A Ag/Ag⁺ reference electrode (10 mM AgNO₃, 0.5M TBAPF₆ or 0.5 M LiBTI in ACN) and a platinum flag counter electrode were used in the 3-electrode setup for polymerization and film cycling studies. An EG&G PAR model 273A potentiostat/galvanostat was used in conjunction with

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Corrware software to perform experiments. All solutions were purged with inert gas prior to measurements being performed.

2.3 Device fabrication and testing

PProDOT-Me₂ films were potentiostatically polymerized onto Au/Kapton using the optimized set of variables described below. Copper tape was applied to the Au/Kapton to serve as a contact. The PProDOT-Me₂ film serving as the anode was held at 1.3 V while the PProDOT-Me₂ film serving as the cathode was held at -1 V. Two drops of gel electrolyte (0.5 M TBAPF₆, 6 % w/w PMMA in PC) were placed on each film and the two halves were pressed together with a separator paper (5 μm AN50 polypropylene filter paper, Millipore) sandwiched in between to prevent shorting. The device was finally encapsulated with a Wilson Jones laminator, LP35HS, in a 3 mil laminated pouch.

The ESCs were tested by first cycling the device via cyclic voltammetry (CV) between -1.0 and 1.3 V for 5 cycles to break in the system. The device was then discharged potentiostatically, holding the device at 0 V for 60 s. The device was held at 0 mA for 10 seconds before galvanostatically charging until the voltage across the device was approximately 1 V. The device was again held at 0 mA for 10 seconds before galvanostatically discharging until the device voltage was approximately 0 V. Finally, the device was held at 0 mA for 10 seconds. From these measurements, total charge passed during charging could be readily calculated. Dividing this by the voltage range and the electrode area gives the areal capacitance of the devices.

3 Results and discussion

3.1 Experimental design

When trying to assess the effects of a large number of variables on an output, a typical approach is to change the value of one variable until a desired outcome is observed. Then, this variable is fixed, and a second variable is tuned, and so on. This one variable at a time (OVAT) approach, however, relies on trial and error for optimization. OVAT also does not consider all possible combinations of variables, and at best relates which set of conditions, only out of the ones tested, is optimal. Additionally, quantifying the effects of each variable is not possible. Finally, the OVAT methodology does not consider the possibility that variables are capable of interacting with one another to influence the outcome. The benefit of reducing the number of runs with an OVAT approach is severely offset by the incomplete understanding of the system that is acquired.

In this work, a fractional factorial DOE is employed to preserve the reduced number of runs of an OVAT design while overcoming its deficiencies and affording a more thorough

understanding of our system. While factorial designs have been widely and effectively implemented, and the construction and analysis of fractional DOEs have been thoroughly described,^{20, 21} there are few examples of its usage in the literature.²³⁻²⁵ To the best of our knowledge there has only been one instance of applying a fractional DOE towards evaluating the capacitive properties of an electropolymerized conjugated polymer film.²³ We therefore begin by briefly describing the concepts of the DOE.

In a factorial DOE, each variable, qualitative or quantitative, is typically probed at two arbitrary extremes (formally, "levels", denoted as a high (+) and a low (-) level (e.g. if the variable is concentration, then a high concentration and a low concentration are selected as the two levels). While more levels can be examined, this leads to a rapid escalation in the number of experiments. By performing experimental runs consistently using two levels rather than a random range of variables (as typified in an OVAT), the effect of each variable on the output, as well as the interactions between variables, can be quantifiably examined.

In a full factorial DOE, all possible combinations of variables are examined. When the number of variables is large, however, this can lead to an impractical number of experiments. To reduce time and resources, select fractions of the full factorial DOE can be carefully chosen and performed. It should be noted, however, that the individual experiments do not provide meaningful information; it is only when they are analyzed collectively that conclusions can be drawn. In addition, it must be stressed that the reduction of experiments occurs at the expense of understanding how variables interact with one another and how these interactions weigh on the output. To afford a thorough understanding of a system, the effects of each variable determined needs to be deconvoluted from possible variable interactions that contribute to the same observed effects. The initial set of experiments, then, serves to screen the many variables to identify those with the largest effect on the output, and the combination which optimizes the output. An understanding of the effects of the individual variables and their interactions can be achieved using a small number of additional experiments.

We have selected seven variables, listed in Table 1, which influence the electrochemical properties of electropolymerized films. These variables are the electrochemical deposition method and the electrochemical conditions that define how thick a film is deposited, the electropolymerization solvent, electrolyte and electrolyte concentrations, and finally the electrolyte and electrolyte concentrations used in the solvent to cycle the polymer film. A full factorial DOE investigating these 7 variables at 2 levels per variable would have required 2⁷ or 128 experiments. The fractional factorial employed however reduces this number to 16 experiments, which are detailed in Table S1. An important

Table 1 List of electrochemical experimental variables employed and their levels.

	Experimental Variables	Low Level (-)	High Level (+)
A	Polymerization Method: CV, potentiostatic	5 cycles (CV), 130 mC/cm ² (potentiostatic)	15 cycles (CV), 650 mC/cm ² (potentiostatic)
B	Electropolymerization Solvent	ACN ($\epsilon = 37.5$)	PC ($\epsilon = 64.9$)
C	Electropolymerization Electrolyte	LiOTf (larger anion radius)	TBABF ₄ (smaller anion radius)
D	[Electropolymerization Electrolyte]	0.05 M	1 M
E	Film Cycling Electrolyte	LiOTf (larger anion radius)	TBABF ₄ (smaller anion radius)
F	[Film Cycling Electrolyte]	0.05 M	1 M

consequence of reducing the number of runs is that it permits us to perform experiments in triplicate, which would have been unwieldy otherwise. This in turn allows us to assess the reproducibility of the experiments, which will be critical when analyzing the results of the fractional factorial DOE and to ensure that the analysis is meaningful.

The method of electropolymerization stands out among the variables investigated, as deposition using CV or potentiostatic deposition operate under fundamentally different mechanisms of polymer deposition. The film quality and performance is not necessarily superior using one method or the other. We have therefore designed a fractional factorial set of experiments centered around films polymerized by CV, and a set of experiments centered around potentiostatically polymerized films.

The high and low values for each variable were determined as follows. The extreme values chosen for the electropolymerization limits – specifically the number of CV cycles, and the amount of charge passed during potentiostatic deposition – provided a range of relatively thin and relatively thick films. The electropolymerization solvents investigated reflect two solvents of differing dielectric constants commonly employed in the electropolymerization of heterocycles. The electrolytes reflect systems with varying anionic volumes, where triflate has a volume that is almost twice that of tetrafluoroborate. Finally, the high and low electrolyte concentrations represent extremes when compared to values commonly found in the literature.

3.2 Electrochemical polymerization of ProDOT-Me₂

Films were deposited from a 25 mM ProDOT-Me₂ electrolyte solution using the conditions established in the experimental design, polymerizing either by cycling from -1.0 to +1.3 V vs. Ag/Ag⁺ as previously reported and shown in Figure S1, or using a fixed potential of +0.95 V vs. Ag/Ag⁺. The monomer concentration was chosen to afford a rapid polymerization rate while conserving the amount of starting material consumed. The optimal potentiostatic deposition potential was determined by electropolymerizing at 0.95, 1.05, 1.15, 1.25, and 1.35 V, as shown in Figure S2a. The amount of polymer deposited was kept constant by passing 150 mC/cm² across a platinum button electrode. The film was then rinsed and cycled in monomer-free electrolyte solution from -1.0 to +1.3 V for 5 cycles. The general

shape of all the voltammograms were identical as shown in Figure S2b, however the largest capacitances were observed for films potentiostatically deposited at +0.95 V. This potential was therefore chosen as the deposition potential.

3.3 Assessment of areal capacitance

In the conjugated polymer ESC literature, a variety of capacitances are reported, most commonly mass capacitance and areal capacitance. Given that the masses of electropolymerized films on surfaces of several square centimeters are typically on the order of less than a tenth of a milligram to milligrams, measurements of film masses can be unreliable, especially without being certain that electrolyte and solvent have been fully removed. Area, however, can be consistently reproduced using electrode cells that confine the electrode area in contact with electrolyte solution. Throughout this work, areal capacitance was utilized to optimize electrochemical conditions.

In an ideal ESC, the charge accumulates linearly (current is constant) as a function of increasing voltage during charging/discharging. This gives rise to a rectangular shaped current vs. voltage plot. When assessing the supercapacitive properties of an EAP film, the cyclic voltammogram of the film should therefore ideally display a current response that is independent of voltage. In practice, the redox chemistry present often leads to the observation of current peaks. Measuring the amount of charge passed during the charging/discharging of a polymer film from its neutral to its oxidized state, and dividing this value by the voltage window, affords the average capacitance. Finally, normalizing to the area of the film gives the areal capacitance.

3.4 Statistical analysis of experimental results

From the fractional factorial DOE performed, the mean effects of the variables shown in Table 1 on the areal capacitance of the resulting polymer film have been determined quantitatively, as summarized using the Pareto plots in Figure 1. Pareto plots provide two pieces of information about a variable's effect: the magnitude of the bar indicates how large an effect that variable has on the output; the sign of the bar indicates whether a low level or high level are predicted to afford large areal capacitances. Each mean effect is the result of adding the contributions of the effect

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of the individual variable plus select second and third order interactions defined by our particular experimental design. For the sake of simplicity, we assume that the effect of the higher order interactions is negligible compared to the effect of the main variable (i.e. no interaction model).

3.5 Effects of electropolymerization method

Polymerizing using CV or a constant potential occur through different mechanisms, which has implications on the electronic properties of the subsequent films. When polymerizing by CV, the potential is swept repeatedly, with polymer deposition occurring during anodic sweeping and polymer neutralization occurring during cathodic sweeping. Therefore, polymerization is repeatedly initiated and terminated. In contrast, during potentiostatic polymerization, the voltage is held constant, and the growing film is constantly in its charged state. Additionally, when polymerizing ProDOT-Me₂ using CV, relatively high potentials of 1.3 V were required to drive polymerization, while potentiostatic polymerization occurred at 0.95 V. Finally, when polymerizing using CV, counterions actively intercalate and exit the growing film during each scan. In contrast, during potentiostatic polymerization counterions are continuously incorporated throughout the film to stabilize the charged state. Both the different potential windows and polymerization mechanisms are expected to give rise to polymer films with unique morphologies, electronic properties, and areal capacitances.

The Pareto plots in Figure 1 indicate that the effects of electrochemical variables on areal capacitance are different for films polymerized potentiostatically or by CV. This supports our decision to consider the two electropolymerization methods separately. Focusing on Figure 1b, we note in particular that for potentiostatically polymerized films, variables affecting the polymerization conditions have a relatively small effect on capacitance, with the electrolyte concentration in the polymer cycling solution having the greatest effect by far. In contrast, for films polymerized by CV, as seen in Figure 1a, variables associated with both electropolymerization and polymer cycling affect the capacitance to a large degree.

3.6 Effects of electropolymerization limits

The relationship between electropolymerization limits and areal capacitance differs between films polymerized potentiostatically or using CV. For the latter, the number of cycles has a large effect on the capacitance, with the capacitance optimized through a greater number of cycles, leading to the electrodeposition of more material. In contrast, the areal capacitance of potentiostatically polymerized films is optimized when less charge is passed during film formation, leading to the electrodeposition of less material.

The effect of the charge passed, however, is relatively insignificant. The electropolymerization limits also affect the oxidation potential of the resulting polymers. Considering films polymerized by CV, those deposited over 15 cycles afford films with onsets of oxidation lower than films electropolymerized from 5 cycles, as seen in Figure S3. For the former, this increases the potential window where the films are electroactive, giving rise to higher areal capacitances. For potentiostatically polymerized films, the onset of polymer oxidation is similar regardless of the amount of charge passed during polymerization. An increase in the charge passed during polymerization leads instead to thicker films, which impedes the rate of ion diffusion through the bulk of the film. This is reflected in the resistive voltammograms of films potentiostatically polymerized from high levels of charge passed, as seen in Figure S4.

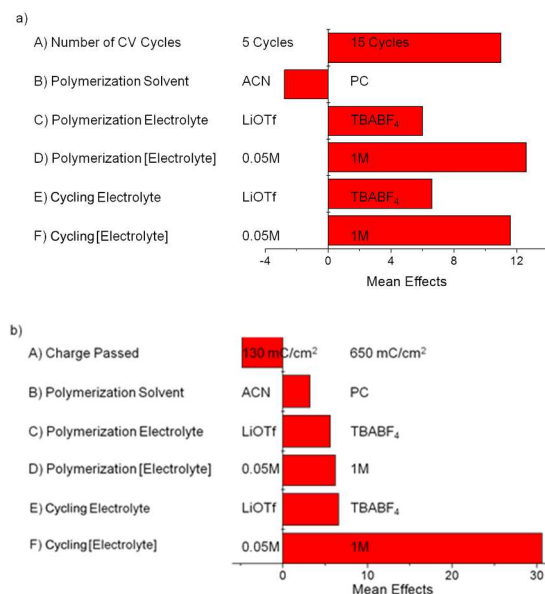


Fig. 1 Pareto plots showing the optimal levels of each variable and the magnitude of their effects as derived from the DOE for PProDOT-Me₂ films polymerized by a) CV, and b) potentiostatically.

3.7 Effect of electropolymerization solvent

Of the variables tested, the choice of polymerization solvent was found to have the smallest effect on the areal capacitance. Large effects of solvent on morphology and electronic properties have been observed in other conjugated systems such as polypyrroles and polythiophenes.^{26, 27} Work on 3,4-ethylenedioxythiophene has observed that films polymerized from PC lead to smooth, ordered morphologies, while films polymerized from ACN lead to more disordered and roughened morphologies.²⁸ The results here

therefore suggest that the variations in polymer film morphology arising from using different electropolymerization solvents are not large enough to strongly affect the areal capacitance of the film.

3.8 Effects of electropolymerization electrolyte and concentration

The electrolyte species and concentration have a far more pronounced effect on the areal capacitance of films polymerized by CV compared with potentiostatically polymerized films. This can be attributed to their different electropolymerization mechanisms. During repeated cycling between neutral and oxidized states, the diffusion of ions into and out of the film repeatedly swell and shrink the growing polymer network. This in turn has been shown to give rise to a more disordered and open polymer matrix depending on the nature of the electrolyte.²⁹ For both cases, the electrolyte concentration is shown to have the largest effect of the variables considered, while the identity of the electrolyte has a relatively small effect. The concentration affects the kinetics of electropolymerization, which in turn impacts the morphology of the electropolymerized films.

While there is much precedent that electrolyte plays a large role in the electropolymerization of many conjugated systems,^{27, 30, 31} previous work on the effects of the electrolyte, solvent and electropolymerization mechanism on the morphology of PEDOT films displayed a similar trend to our results. In that study, the identity of the electrolyte also had little effect on the film morphology. Instead, the electropolymerization mechanism was also observed to have a large effect on morphology.²⁸

3.9 Effects of cycling electrolyte and concentration

For both potentiostatically polymerized films and films polymerized by CV, the cycling electrolyte concentration has a large effect on the areal capacitance of the film, while the role of the electrolyte identity has a larger effect on films polymerized by CV. These trends may reflect how readily the film charges and discharges to its full potential. For the polymer film to be more fully charged, higher counterion concentrations are required to stabilize the oxidized state of the polymer, leading to the strong dependency on electrolyte concentration. The rate at which the counterions can diffuse through the film also depends on the electrolyte identity. The smaller BF_4^- anion is likely more capable of rapid diffusion through the polymer film.

3.10 Polymer films from optimized conditions

Having established an optimized set of electrochemical variables from the DOE, PProDOT-Me₂ films were prepared using these new sets of conditions. Films polymerized by CV were prepared from a 1 M TBABF₄ solution in ACN using 15 CVs and cycled in a 1 M TBABF₄ solution in PC; potentiostatically polymerized films were prepared by passing 130 mC/cm² to polymerize the film in a 1 M TBABF₄ solution in PC and cycled in a 1 M TBABF₄ solution in PC. In Figure 2 and Table 2, the areal capacitances of films polymerized by CV using the optimized set of variables are shown, ranging from 14.2 to 20.7 mF/cm². When compared to the areal capacitances from the runs in Figure S5, the optimized capacitance is higher, as expected. Potentiostatically deposited films, shown in Figure 3 and Table 2, led to films with optimized capacitances of 10.8 mF/cm², comparable to

capacitances from run 8 in Figure S6. These similarities in capacitances are nevertheless consistent with the calculations of the DOE. The conditions used in run 8 and the optimized conditions differ only in the amount of charge passed during polymerization. The effect of this variable is calculated to be small, and as a result, it is expected that the areal capacitances from both sets of conditions are identical within error.

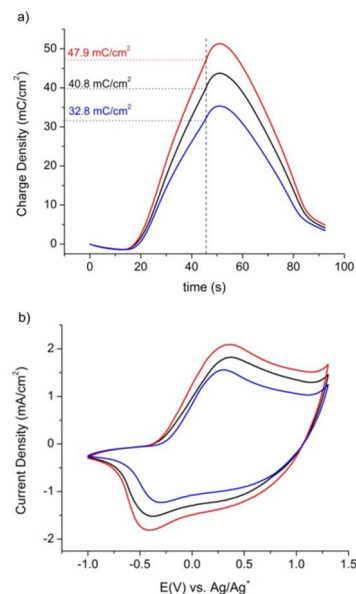


Fig. 2 a) Charge passed in PProDOT-Me₂ films polymerized by CV and cycled using DOE predicted optimal conditions (polymerization: 15 cycles, ACN, 1 M TBABF₄; film cycling: 1 M TBABF₄ in PC); b) charge-discharge cycles of a PProDOT-Me₂ film at 50 mV/s using the same conditions as in part a.

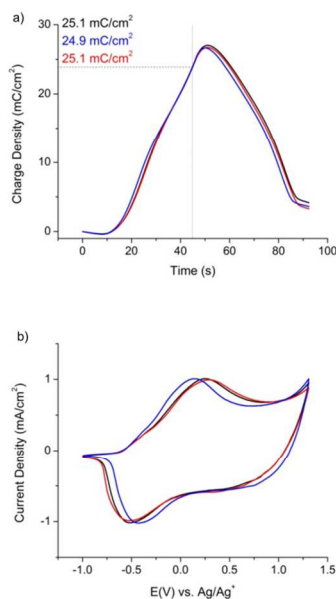


Fig. 3 a) Charge passed in potentiostatically polymerized PProDOT-Me₂ films and cycled using DOE predicted optimal conditions (polymerization: 130 mC/cm², PC, 1 M TBABF₄; film cycling: 1 M TBABF₄ in PC); b) Charge-discharge cycles of PProDOT-Me₂ at 50 mV/s using the same conditions as in part a.

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Table 2 Areal capacitances and theoretical capacitances from DOE-derived optimized conditions^a

Polymerization Method	Capacitance (mF/cm ²)	Theoretical Capacitance at		
		0.25 e ⁻ /ring (mF/cm ²)	0.33 e ⁻ /ring (mF/cm ²)	0.50 e ⁻ /ring (mF/cm ²)
CV	17.6	14.8	19.7	29.6
CV	20.7	15.8	21.1	31.6
CV	14.2	10.5	14.0	21.1
CV avg	17.5 ± 3.25	Estimated doping level = 32%		
PS	10.9	10.9	14.6	21.9
PS	10.9	6.9	9.2	13.8
PS	10.8	9.0	10.8	16.2
PS avg	10.8 ± 0.05	Estimated doping level = 31%		

(a) Theoretical capacitances were determined by calculating the number of repeat monomer units based on the film weight, and the total charge based on the capacitance, and calculating the total charge per number of monomer units

Figures 2 and 3 also illustrate differences in the reproducibility of the film's electrochemical properties as a function of the electropolymerization method. The three traces in each figure show the results collected from three separate films polymerized and evaluated under the same conditions. In Figure 2a, films polymerized by CV give rise to a noticeable range in the amount of charge passed during cycling. In Figure 2b variations in the peak values and the onsets of oxidation, as well as variations in the current densities, are observed across the three films. In contrast, as seen in Figure 3a, potentiostatically polymerized films gave rise to nearly identical amounts of charge passed during cycling. In Figure 3b, the CVs of the three films display the same onsets of oxidation and current densities, with only slight variation in the peak values. These results demonstrate that the films polymerized using optimized potentiostatic polymerization conditions give rise to higher reproducibility with regards to their electrochemical properties.

SEM images in Figure 4 display porous morphologies both for films polymerized potentiostatically and by CV. The images also support the more disordered and irregular nature of the films polymerized using CV. In Figure 4a acquired at lower magnification, the film surface looks uneven, characterized by the presence of irregularly shaped nodular features varying in size from one to tens of microns long. The roughness of the film is also characterized by the large variations in brightness, brought on by charging effects from less conducting regions of the film.

In contrast, images of potentiostatically polymerized films shown in Figures 4c and 4d appear more ordered and smoother. Charging effects are also less pronounced, which can be related to the improved ordering giving rise to more conducting films. At lower magnification in Figure 4c, features are small and more regular in size; this evenness persists at higher magnifications in Figure 4d. The reproducibility of the electrochemical properties of the two types of films, discussed with regards to Figures 2 and 3, is reflected on the microscopic level in the SEM images, which show greater disorder and irregularity in films polymerized by CV compared with the evenness of potentiostatically polymerized films.

Doping levels of the optimized systems were estimated in order to assess the electroactivity of the film. This calculation was performed by determining the number of polymer repeat units present in a film, the amount of charge passed during oxidation of the film, and then calculating the fraction of charges per repeat unit. This then also assumes that the capacitance in conjugated polymers arises predominantly from Faradaic processes.³² In Table 2, the doping levels of the films were found to be comparable and independent of the polymerization method, with a charge stored over every three ProDOT-Me₂ units. These doping levels are among the highest observed in 3,4-polyalkylenedioxythiophene systems,³³⁻³⁵ and higher than previously reported PProDOT-Me₂ doping levels.³⁶ This indicates that the fractional factorial DOE employed provides an efficient

route towards optimized polymer films, which are electroactive throughout the bulk of the material. The film capacitances achieved in our optimized systems therefore provide an understanding of the full potential that PProDOT-Me₂ films can achieve. As we move towards considerations of device performance, the lack of film-to-film reproducibility in polymer films deposited using CV leads to poor charge balance and unreliable device outputs. We therefore moved forward in this work with potentiostatically polymerized films in our device modules.

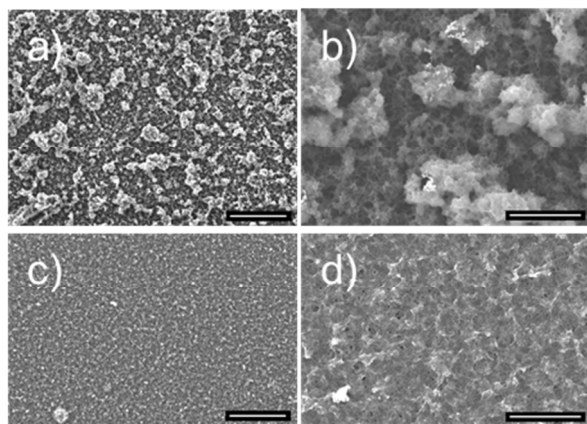


Fig. 4 a) & b) SEM images of PProDOT-Me₂ films electropolymerized using CV and cycled using optimized conditions. c) & d) SEM images of PProDOT-Me₂ films potentiostatically electropolymerized and cycled using optimized conditions. Scale bars are 20 microns (a & c) and 5 microns (b & d) in length.

3.11 PProDOT-Me₂ devices

Type 1 ESC devices – consisting of the same p-dopable EAP on both electrodes – were constructed as shown in the schematic of Figure 5. The optimized conditions determined from Figure 1b were used, with the films polymerized using 130 mC/cm² from a 1 M TBABF₄ in PC solution and cycled in a 1 M TBABF₄ in PC solution. In the construction of the device, PMMA was added to the electrolyte solution to formulate a gel electrolyte, as it proved easier to handle. The device is assembled in its charged state with one polymer film in its fully oxidized state and the other film in its fully neutralized state. When the device is then fully discharged, each film attains a partially charged state. After assembly, devices were cycled over their full potential range of electroactivity for 10 CV cycles to break in the device.

Devices were then assessed using a galvanostatic charging and discharging procedure described in the experimental section. Such a testing procedure simulates supercapacitor performance during operation, and a representative plot is shown in Figure 6. Three devices were constructed and attained reproducible capacitances on average of 6.5 ± 0.1 mF/cm² (i.e. ~18 mF), values on the order of some commercially available ESCs.³⁷ Our PProDOT-Me₂ ESCs have the advantage of being constructed from materials that can be readily integrated into lightweight and flexible devices. The results from these optimized systems demonstrate the efficacy of employing a fractional factorial DOE when designing experimental conditions to achieve films optimized for performance and reproducibility.

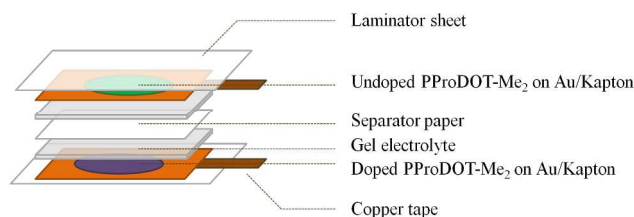


Fig. 5 Schematic of Type-I supercapacitor devices.

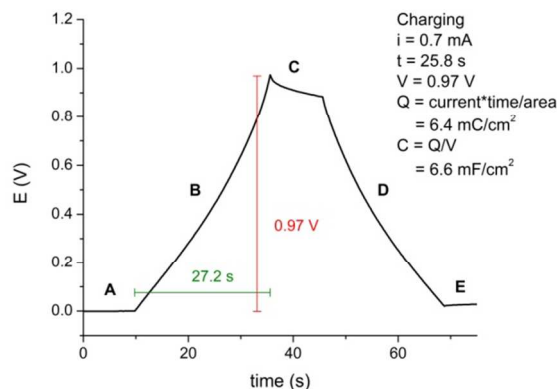


Fig. 6 The electrochemical potential vs. time behavior of a device during testing is shown. The steps of the procedure are indicated on the graph and are as follows – 0. Device discharged (potentiostatic hold at 0 V for 60 s); A. galvanostatic holding at 0 mA for 10 seconds; B. galvanostatic charge until device charged ~1 V; C. galvanostatic holding at 0 mA for 10 seconds; D. galvanostatic discharge until device discharged ~1 V; E. galvanostatic holding at 0 mA for 10 seconds.

4 Conclusions

In prior work, PProDOTs have been identified as promising materials for use in electrochemical supercapacitors. Here, we have utilized a fractional factorial design of experiments to rapidly screen a number of variables and elucidate the effects of each variable and the combination that would achieve optimized areal capacitances. The doping levels of the optimized films were among the highest observed for this system, and the subsequent supercapacitive properties derived from these films reflect the full potential of the material. This work provides a framework around which further experiments can logically proceed to fine-tune the variables determined to have a large effect on areal capacitance.

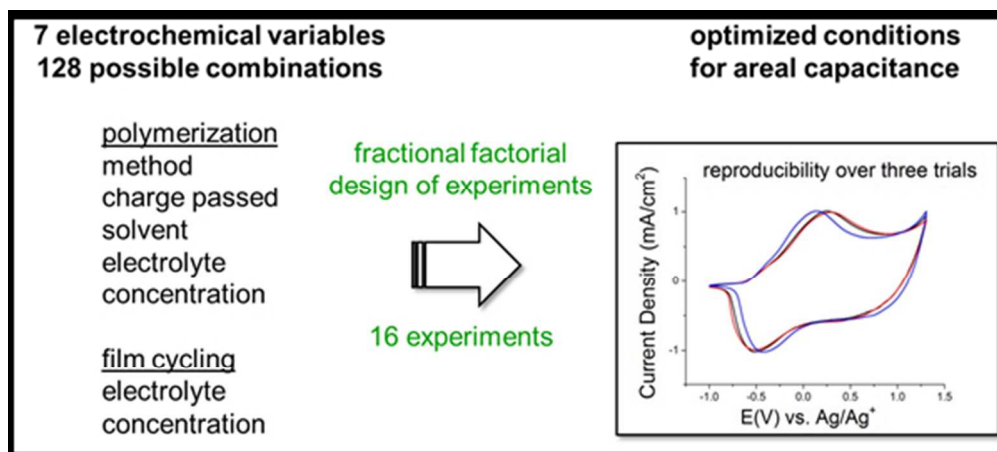
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Notes and references

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101x45mm (150 x 150 DPI)