

Supporting Information

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

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Construction of the DOE and Results

Seven variables were selected to investigate their effects on areal capacitance utilizing a Fractional Factorial Design of Experiment methodology. As mentioned in the text, the electropolymerization methods (using CV and potentiostatically) were
15 treated as two separate cases. We then constructed our design with the remaining six variables.

Utilizing a full-factorial design of experiment would require the analysis of 2^6 experimental runs for films deposited using CV polymerization, and another 2^6 experimental runs for films deposited potentiostatically; each run should then be performed in triplicate to ensure reproducibility. Given that our main purpose is to rapidly screen and identify variables of interest for further study, we have elected to perform a fractional factorial design of experiment, specifically a 2^{6-3} fractional factorial design for each
20 of the electropolymerization methods. The fractional factorial matrix utilized to conduct our analysis is shown in Table S1, with the outputs of each run denoted as well.

Table S1. Fractional Factorial Design of Experiments Matrix with Output Values^a

Run	A (# of CVs/Charge Passed)	B (Polymerization Solvent)	C (Polymerization Electrolyte)	AB (Polymerization [Electrolyte])	AC (Cycling Electrolyte)	BC (Cycling [Electrolyte])	C _{CV} (mF/cm ²)	C _{PS} (mF/cm ²)
1)	-1	-1	-1	+1	+1	+1	5.8 ± 0.5	10.9 ± 0.2
2)	+1	-1	-1	-1	-1	+1	5.3 ± 1.3	5.2 ± 2.2
3)	-1	+1	-1	-1	+1	-1	0.6 ± 0.2	1.2 ± 0.3
4)	+1	+1	-1	+1	-1	-1	3.3 ± 0.3	1.2 ± 0.3
5)	-1	-1	+1	+1	-1	-1	4.8 ± 0.6	1.7 ± 0.4
6)	+1	-1	+1	-1	+1	-1	3.5 ± 0.8	1.9 ± 0.0
7)	-1	+1	+1	-1	-1	+1	1.3 ± 0.1	9.9 ± 0.2
8)	+1	+1	+1	+1	+1	+1	11.4 ± 1.7	10.6 ± 2.0

The reported capacitance values are the average of three runs.

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In order to acquire a quantitative understanding of the effect of each of the six variables on the output, Pareto plots were generated. To quantify each variable, the output values are summed together, with the sign in front of each output determined by the combination of values unique to each variable column. For example, the effect of the # of voltammograms used during electropolymerization (column A) is determined with the following equation:

30 $(-1) \times 5.8 + (+1) \times (5.3) + (-1) \times (0.6) + (+1) \times 3.3 + (-1) \times 4.8 + (+1) \times 3.5 + (-1) \times (1.3) + (+1) \times 11.4 = 11$

The sign of the effect (in this case, +) indicates that the high value (15 cycles) is more optimal for high areal capacitance, while the magnitude of the effect (11) indicates the importance of this variable on the output.

Electropolymerization of ProDOT-Me₂

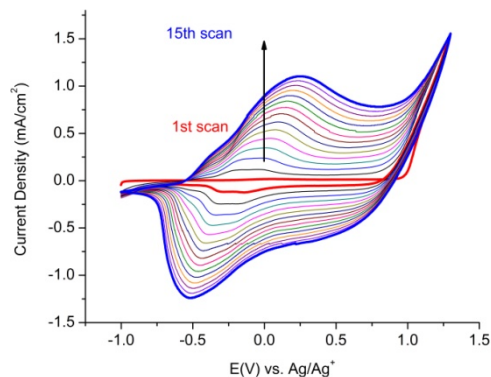
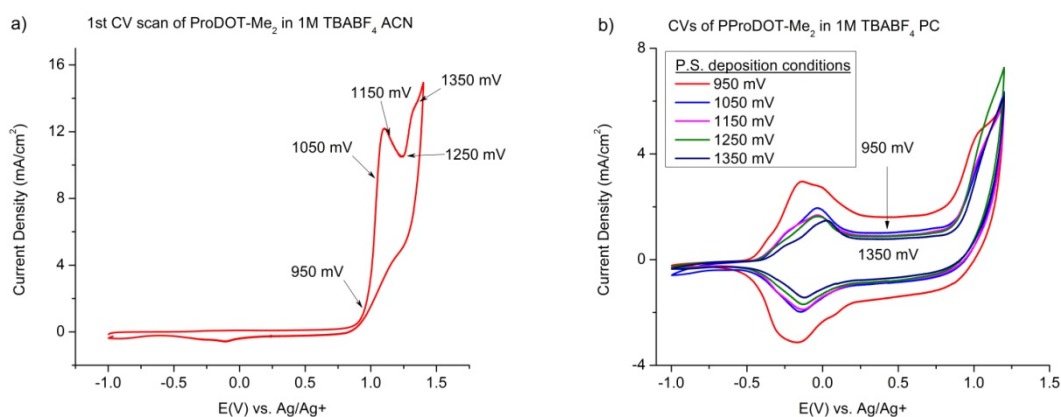


Figure S1. Representative 1st – 15th cycles of a film polymerized using run 8 conditions (polymerized using 15 scans, 1M TBABF₄ in PC).

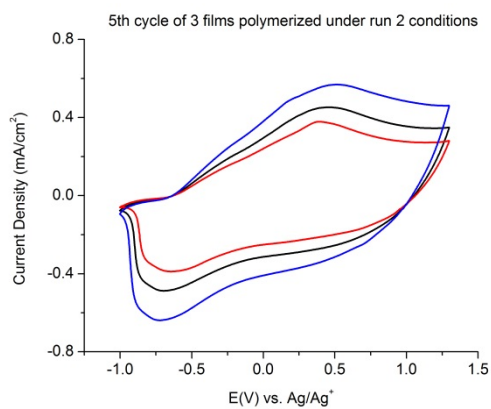
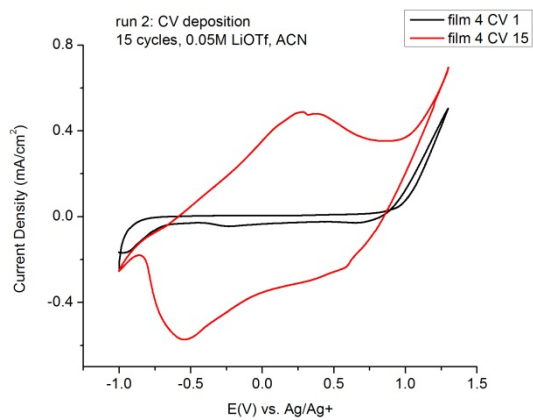
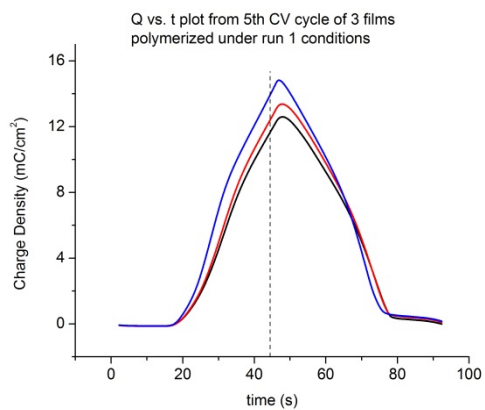
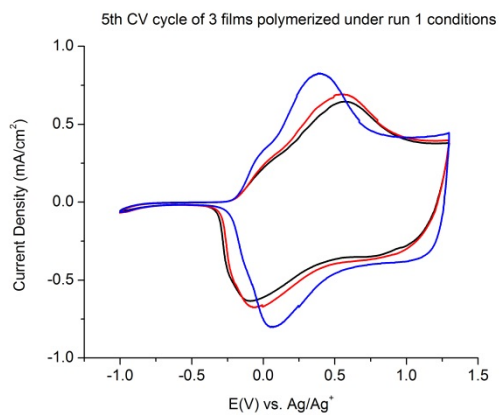
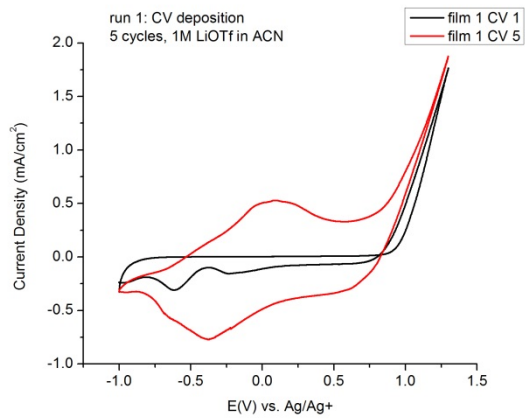


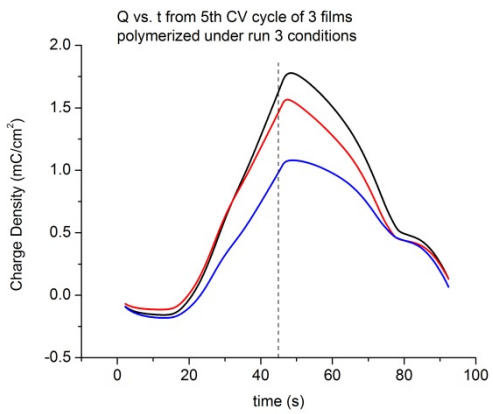
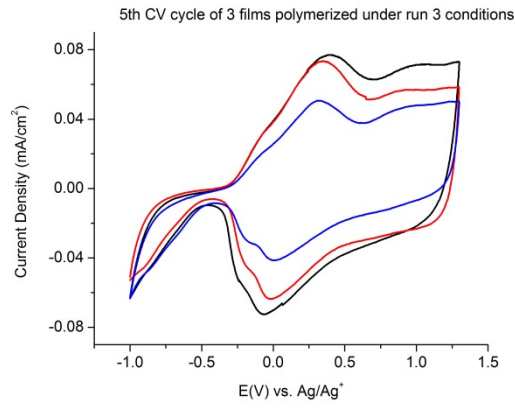
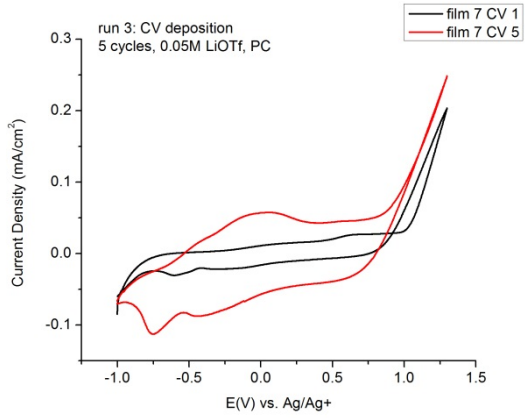
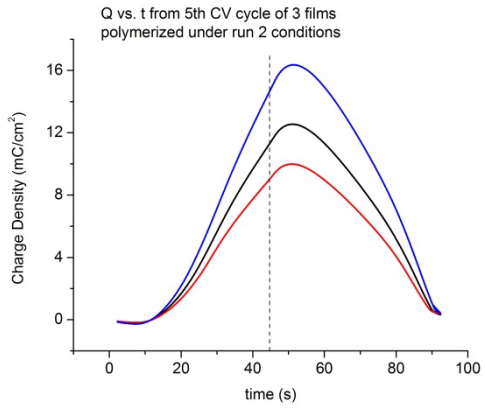
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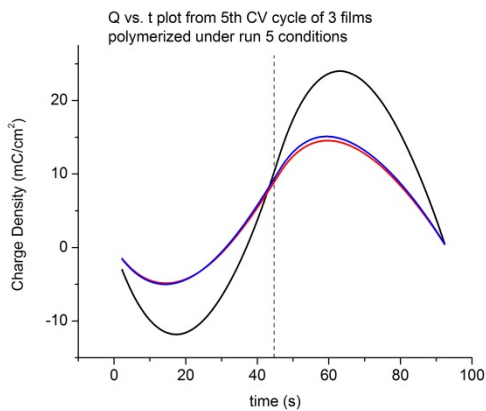
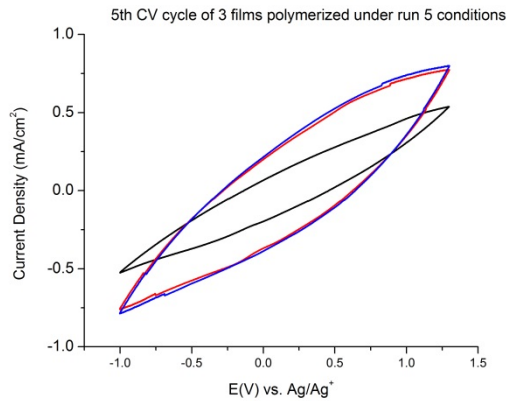
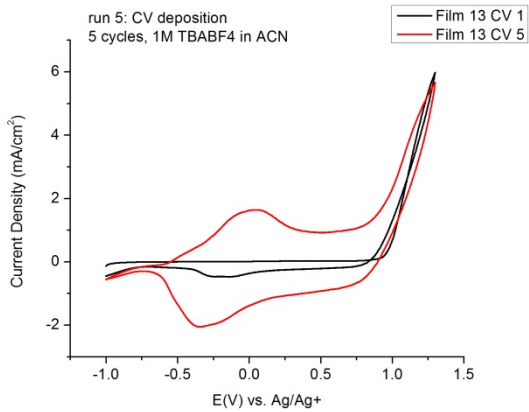
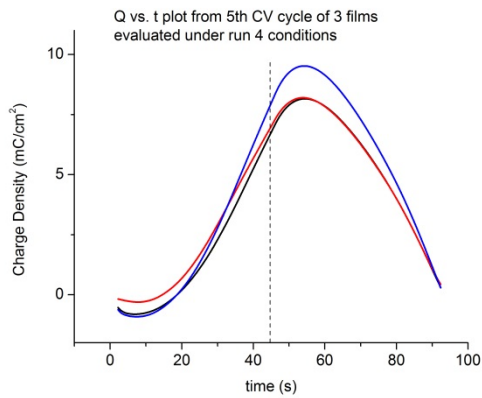
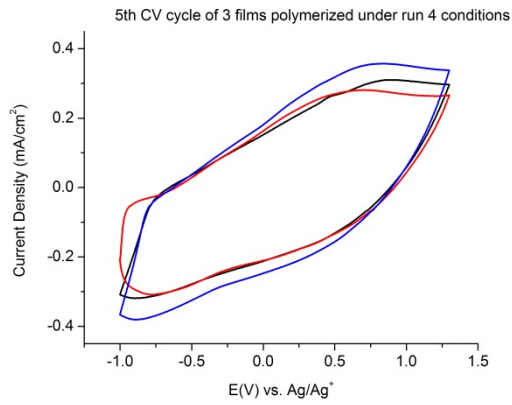
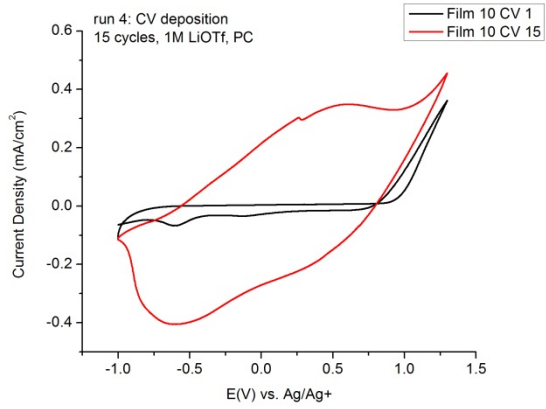
Figure S2. a) 1st scan of a ProDOT-Me₂ monomer solution. The various potentials noted are those at which potentiostatic deposition was carried out to determine the optimum potential for potentiostatic deposition; b) scans of the polymer film after potentiostatic deposition at various potentials. From this, it is observed that the current density is highest from films deposited at 0.95 V.

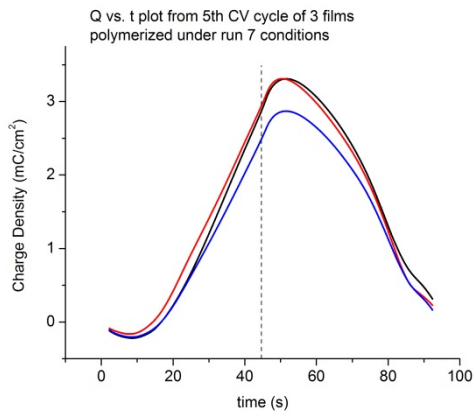
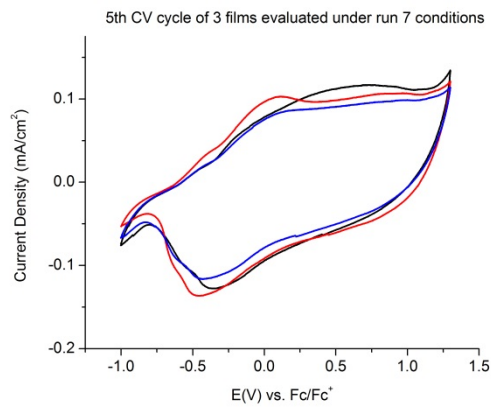
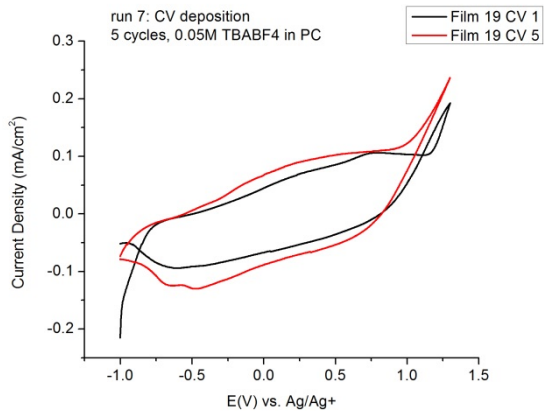
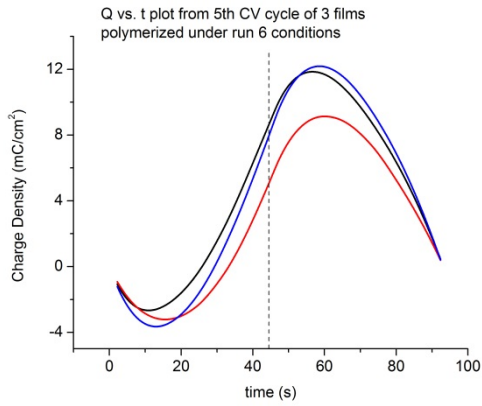
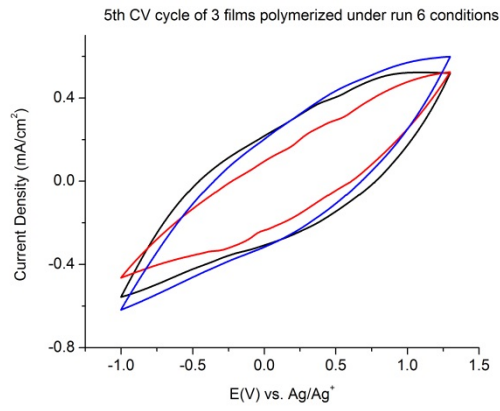
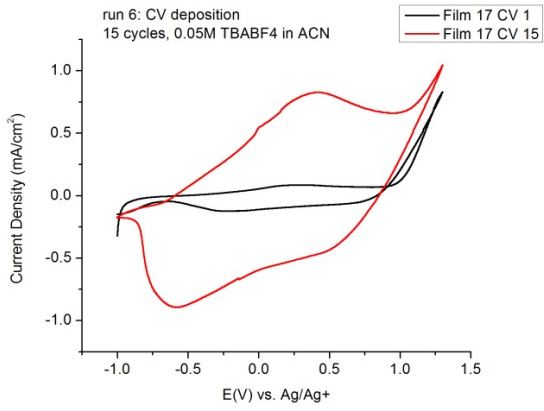
Electrochemistry of PProDOT-Me₂ Polymerization Using CV Evaluated Using Runs 1-8 Conditions

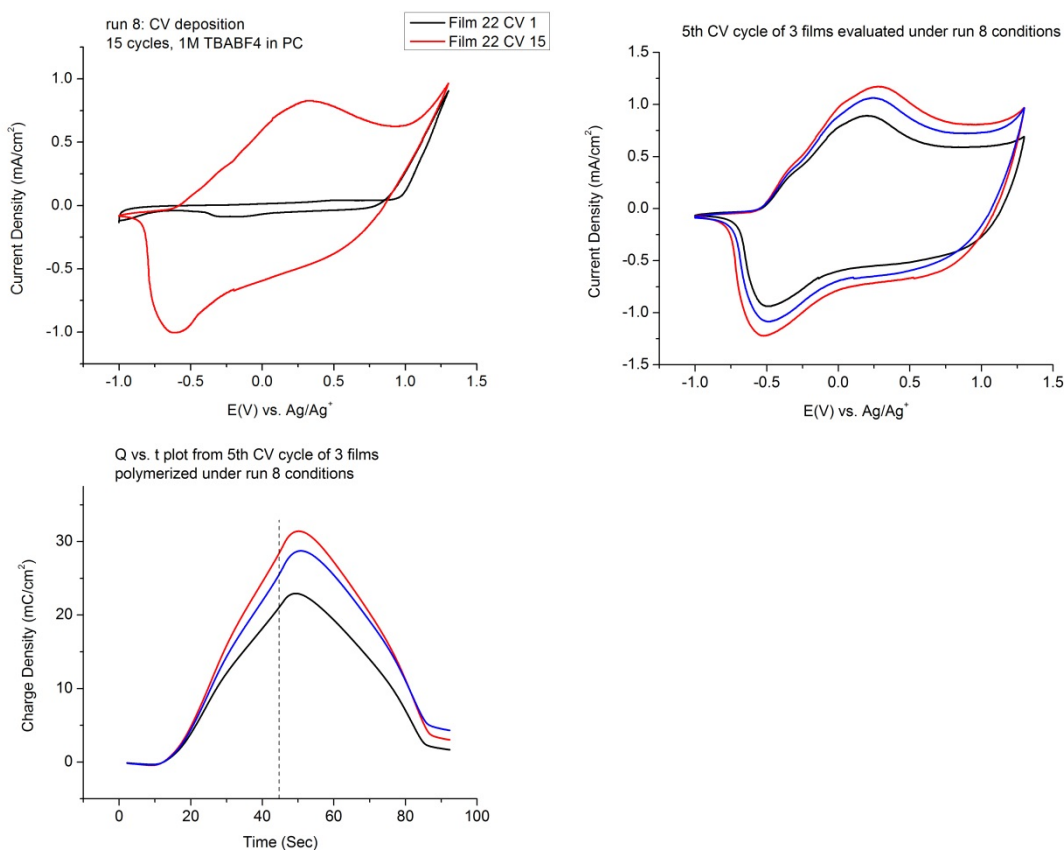
10 Each of the 8 runs provided unique conditions for electropolymerization and polymer film switching. In Figure S4, the polymer film scans and Q vs t plots demonstrate the switching behavior. Each run was performed in triplicate and the results overlaid to demonstrate the reproducibility of each run. The electropolymerization cycles are shown for only one of the three triplicates for the sake of clarity, where the contrast between the first and last cycles provides a qualitative understanding of the electropolymerization process.







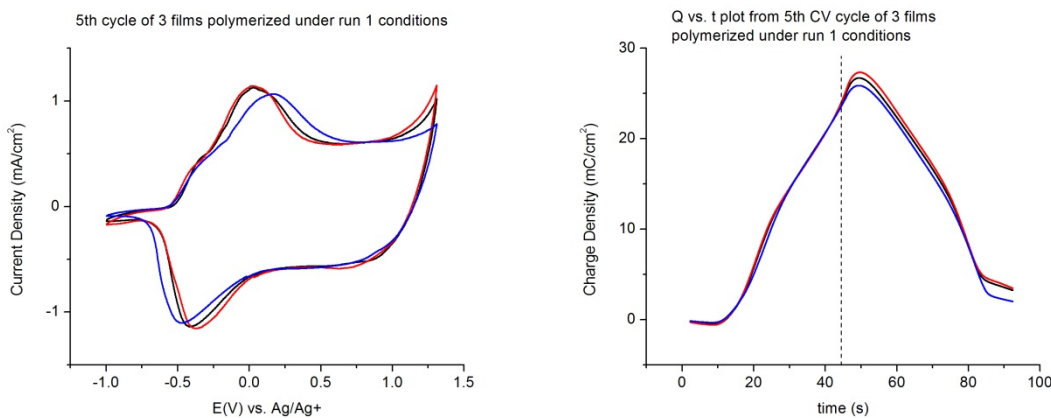


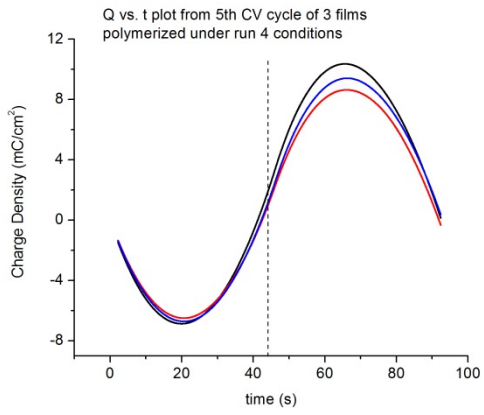
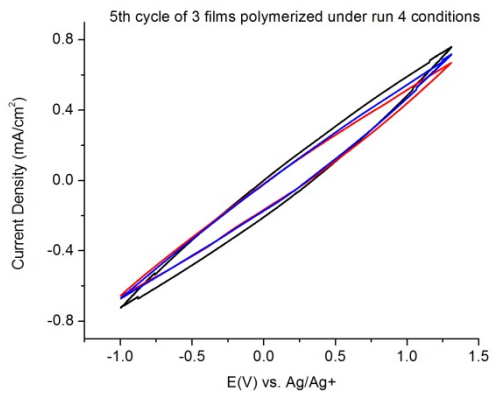
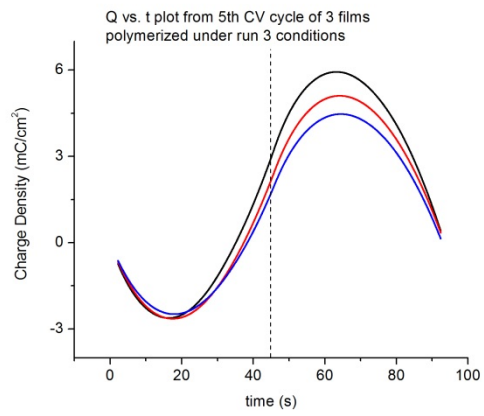
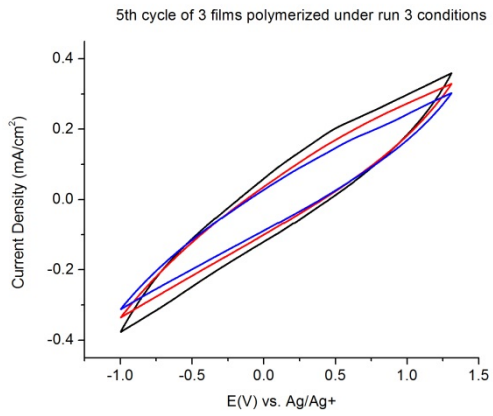
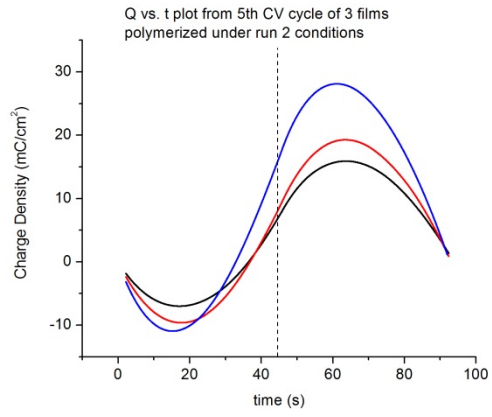
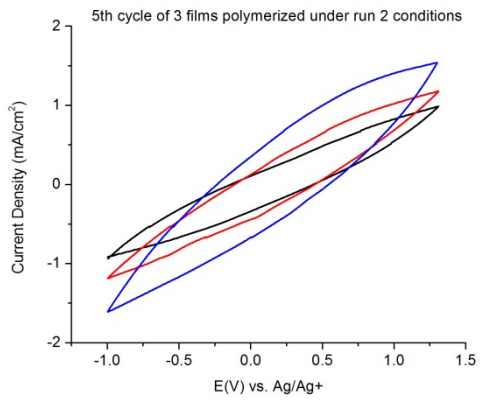


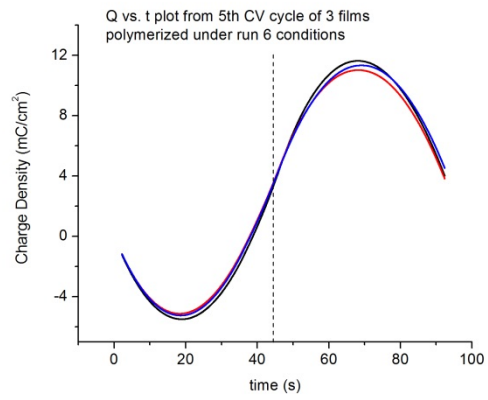
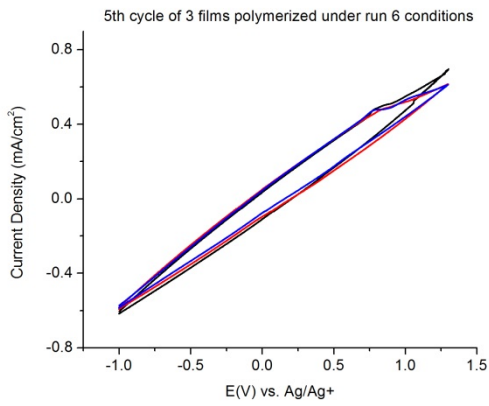
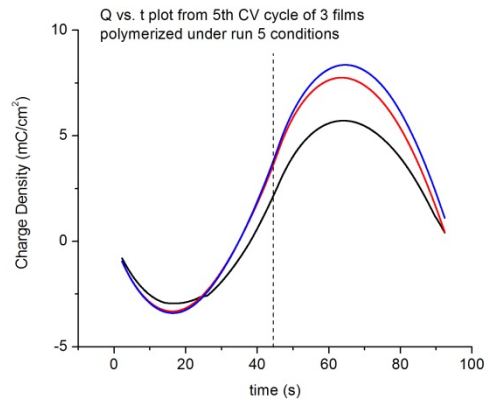
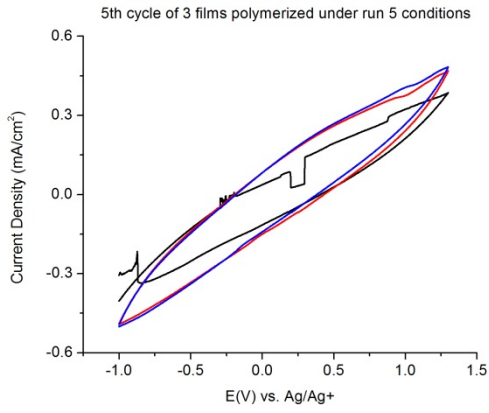
5 **Figure S3.** The electrochemical behavior of ProDOT-Me₂ electropolymerization using CV, as well as the behavior of the corresponding polymer films, evaluated under the conditions of the 8 runs. The electropolymerization scans show the behavior of one film, while the polymer electrochemistry shows the overlaid results of three films performed in triplicate for each run.

Electrochemistry of Potentiostatically Deposited PProDOT-Me₂ Evaluated Using Runs 1-8 Conditions

Each of the 8 runs provided unique conditions for electropolymerization and polymer film switching. In Figure S5, the polymer film scans and Q vs t plots demonstrate the switching behavior. Each run was performed in triplicate and the results overlaid to demonstrate the reproducibility of each run. The electropolymerization is not shown.







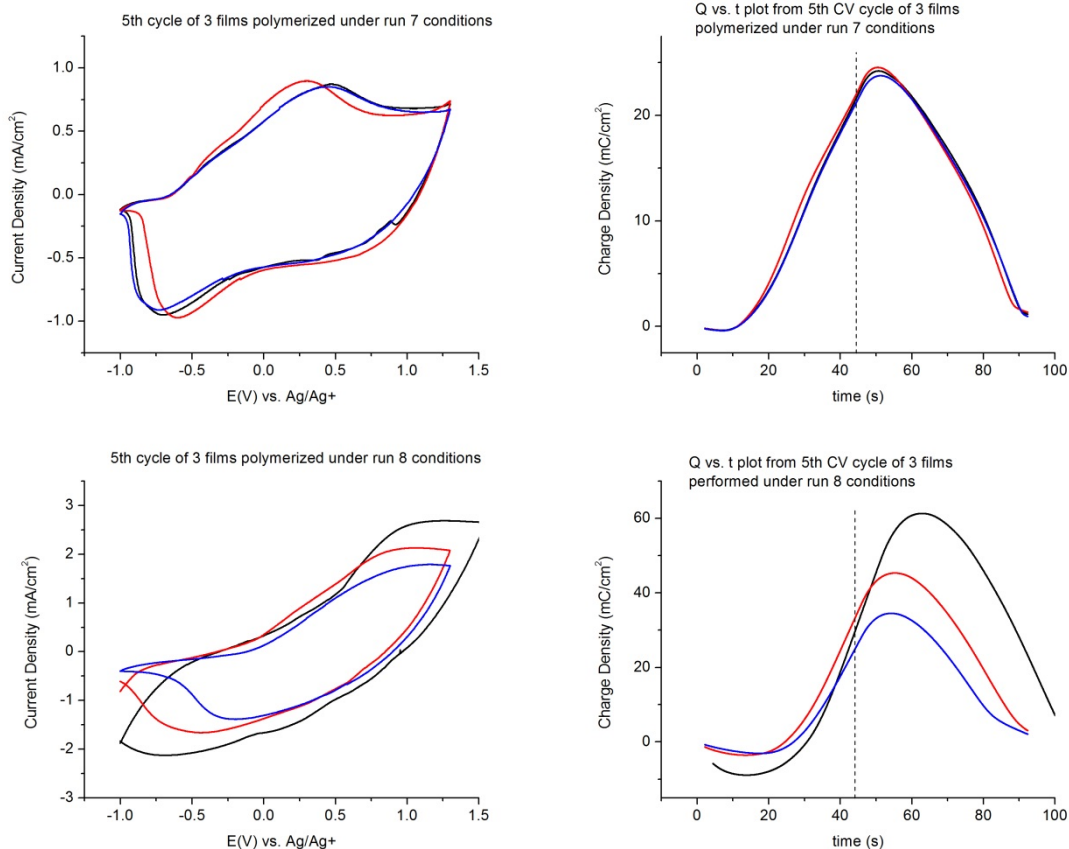


Figure S4. The electrochemical behavior of PProDOT-Me₂ films deposited potentiostatically, evaluated under the conditions of the 8 runs. The polymer electrochemistry shows the overlaid results of three films performed in triplicate for each run.

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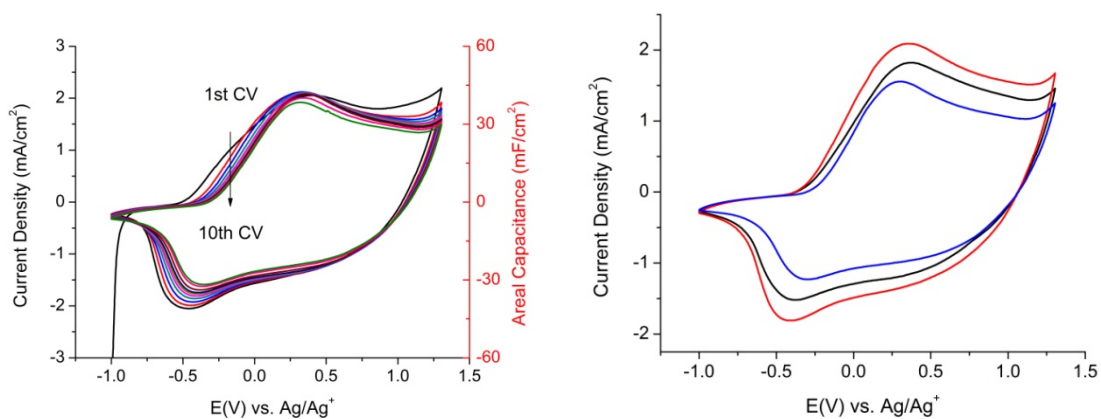


Figure S5. (a) 1st – 10th scans of a PProDOT-Me₂ film electropolymerized polymerized using CV and switched using optimized areal capacitance conditions; (b) 10th cycle of three films evaluated under optimized areal capacitance conditions to demonstrate reproducibility.

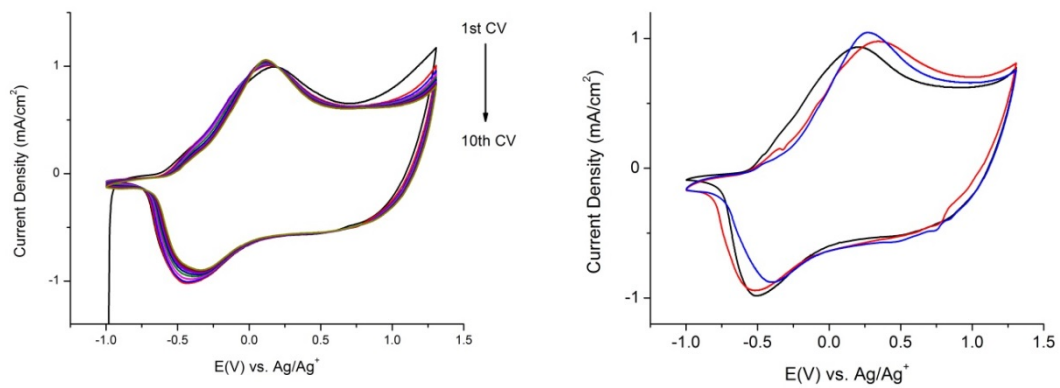


Figure S6. (a) 1st – 10th scan of a PProDOT-Me₂ film electropolymerized potentiostatically and switched using optimized areal capacitance conditions; (b) 10th cycle of three films evaluated under optimized areal capacitance conditions to demonstrate reproducibility.