

Supporting Information

for

Conformal Electrodeposition of Ultrathin Polymeric Films with Tunable Properties from Dual-Functional Monomers

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1. Materials

The platinum wire (diam. 0.25 mm, 99.9% trace metals basis) for the counter electrode and the chemicals 2,2-(ethylenedioxy)diethanethiol (95%), 2-allylphenol (98%), decamethylferrocene (“DMFc”, 97%), lithium perchlorate (99.99%), indium-gallium eutectic (“eGaIn”, gallium 75.5%, indium 24.5%, $\geq 99.99\%$ trace metals basis), dimethyl sulfoxide (“DMSO”, anhydrous), poly(acrylonitrile) (“PAN”, 150 kg/mol), and tetramethylammonium hydroxide pentahydrate (“TMAH”, $\geq 97\%$) were purchased from Sigma Aldrich. Tetrabutylammonium perchlorate (“TBAP”, $\geq 97.5\%$), silver perchlorate (anhydrous), Indium-Tin-Oxide (ITO) coated glass ($R_s = 70\text{-}100\ \Omega$), and acetonitrile (anhydrous) were purchased from Fisher Scientific. Lithium titanate (“LTO”, $\text{Li}_4\text{Ti}_5\text{O}_{12}$) was purchased from MTI Corporation. Triton X-100 was purchased from J.T. Baker. The silver wire for the reference electrode was supplied by Gamry Instruments. All chemicals were used without further purification.

2. Triethyleneglycol Diphenol Synthesis and Purification

The monomer denoted as triethyleneglycol diphenol (TEG-DP) for electrodeposition was obtained from the UV-initiated thiol-ene reaction between 2-allylphenol and 2,2-(ethylenedioxy) diethanethiol (TEG-DT), which were mixed at a molar ratio of 2.2:1 without solvent. In a typical synthesis, 8 mL of the liquid mixture typically was stirred in a borosilicate glass vial and exposed to 302 nm UV (8 W, 3-4 cm distance) for 48 hours. The product was then purified by column chromatography using 60 μm silica gel as the stationary phase and an acetone/hexane solvent system with increasing polarity (from 20% acetone to 60% acetone in hexane) was used as the mobile phase. The conversion of allyl groups was confirmed by proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy in deuterated chloroform on an Agilent 400 MHz VNMRS.

3. Porous Carbon Electrode and LTO-Carbon Composite Electrode Fabrication

Carbon electrodes were prepared using non-solvent induced phase inversion of a PAN solution (84 wt% in DMSO, 10.5 wt% PAN, 5.5 wt% water) cast at 200-400 μm in thickness on a DMSO-gel and immersed in DI-water, followed by cross-linking at 250 $^{\circ}\text{C}$ in air and subsequent carbonization at 750 $^{\circ}\text{C}$ for 1 hour. A wire was attached to the dense (top) side of the electrodes with silver epoxy and sealed by poly(dimethyl siloxane) (Dow Sylgard 184).

LTO-carbon composite electrodes were fabricated with the same method but using an LTO-PAN suspension. LTO dispersion was prepared by mixing LTO with a solution of Triton X-100 and DMSO. Then the dispersion and above PAN solution were mixed to form a suspension with a 2:1 mass ratio of LTO to PAN.

The resulting carbon and LTO-carbon electrodes have low-tortuosity cylindrical pores of 2-20 μm in diameter, thickness of 25~80 μm and a footprint area of 0.385 cm^2 .

4. Film Electrodeposition

The electrodeposition of TEG-DP was performed in acetonitrile at various concentrations (50 mM, 10 mM, 1 mM). The solutions contained TMAH at stoichiometric ratios to the phenol unit to form the oxidizable phenolate, as well as the supporting electrolyte TBAP at a concentration of 0.1 M. For electrodeposition, ITO-coated glass slides and a cylindrical glass cell were clamped together with an O-ring (DuPont Kalrez®), confining the deposition area to a circle of 15 mm in diameter. The deposition on porous carbon electrodes was carried out in a 4 mL glass vial. The deposition cells for both porous carbon and ITO were filled with 1 mL of monomer solution and a platinum wire counter electrode and Ag/Ag⁺ reference electrode (silver wire in 0.05 M silver perchlorate and 0.1 M TBAP solution in acetonitrile separated by a Gamry glass frit from the monomer solution) were submerged in the solution.

All electrochemical experiments were performed on a Gamry Reference 600+ potentiostat. Cyclic voltammetry (CV) on porous carbon was performed on the 50 mM TEG diphenol monomer solution between -1 V and +1 V vs. Ag/Ag⁺ at 50mV/s for 6 separate cycles. Chronoamperometry (CA) on ITO was conducted on all monomer solutions at 7 different potentials (-0.5 V, -0.3 V, -0.1 V, +0.1 V, +0.3 V, +0.5 V, +0.7 V vs. Ag/Ag⁺) for a duration of 20 minutes. Before and after each deposition, CVs of 0.001 M decamethylferrocene in 0.1 M TBAP solution in acetonitrile were utilized to evaluate the surface passivation, sweeping between -0.85 and -0.05 V vs. Ag/Ag⁺ for 3 cycles at 50 mV/s. The resulting poly(TEG-diphenol) (or simply pTEG-DP) coated substrates were cleaned with acetonitrile, and dried at room temperature in an ambient atmosphere.

Exploration of the water effect on the film property was conducted in solutions with a composition of 25 mM TEG-DP, 50 mM triethylamine (TEA, anhydrous), 0.1 M TBAP and 5 water concentrations (0 M, 0.125 M, 0.25 M, 0.375 M, and 0.5 M). Films were deposited on ITO at 0.2 V vs. Ag/Ag⁺ for 20 min. Post-deposition CA for the anhydrous (0 M water) group was then carried out in 0.025 M triethylamine and 0.1 M TBAP solution applying 0.2 V vs. Ag/Ag⁺ for 5 minutes.

The electrochemical quartz crystal microbalance (E-QCM) measurement was performed on the QSense Electrochemistry module on a Biolin Scientific E4 QCM-D where an ITO coated quartz crystal with a resonance frequency of 5 MHz, a silver wire, and a platinum foil were assembled as working electrode, quasi reference electrode (QRE), and counter electrode, respectively. Change of mass of 50 mM TEG-DP monomer solution during the CV sweeping from 0 to 1.4 V vs. Ag QRE was recorded using Q Sense E4 Quartz Crystal Microbalance.

5. Film Characterization

Film thickness and roughness measurements were carried out on an Asylum Research MFP-3D Infinity Atomic Force Microscope (AFM) using alternating contact mode with a $20 \times 20 \mu\text{m}^2$ and $500 \times 500 \text{ nm}^2$ field of view, respectively. Scanning electron microscopy (SEM) of the films was performed on a Zeiss Supra 55 SEM with an electron beam accelerating voltage of 3 kV using an in-lens or secondary electron detector. Two-electrode electrochemical impedance spectroscopy (EIS) measurements were performed on a Gamry Reference 600+ potentiostat using a gallium-indium eutectic drop sandwiched between the pTEG-DP coated (working electrode) and a bare ITO-coated glass slide (counter and reference electrode) separated by a 1 mm silicone rubber spacer resulting in a contact area of $0.785\text{-}3.14 \text{ mm}^2$. EIS measurements were taken around the open circuit potential with a signal amplitude of 10 mV over the frequency range of [0.05 Hz, 5 MHz]. The same ‘sandwich’ setup was used in dielectric breakdown measurements but a linearly increasing potential was applied at a scan rate of 50 mV/s until the current increased dramatically and deviates from the ohmic behavior.

6. Battery test

Pulse potentiostatic deposition was employed on porous carbon lithium titanate (LTO) composite electrodes where a 5-second potentiostatic voltage at +0.1 V (vs. Ag/Ag⁺) was applied followed by a 10-second rest for monomer replenishing and equilibrating in the 3D structure and the process was repeated for 240 cycles to reach a total deposition time of 20 minutes. Then the coated electrode was wetted with an excess of 1 M lithium hexafluorophosphate (LiPF₆) in EC:DMC 50/50 v/v electrolyte and assembled with a polypropylene separator and a lithium metal anode. The obtained coin cell was charged and discharged at 9.1 mA/g (0.05 C, C-rate is calculated based on the theoretical LTO capacity, 175 mAh/g) on an MTI Battery Analyzer.

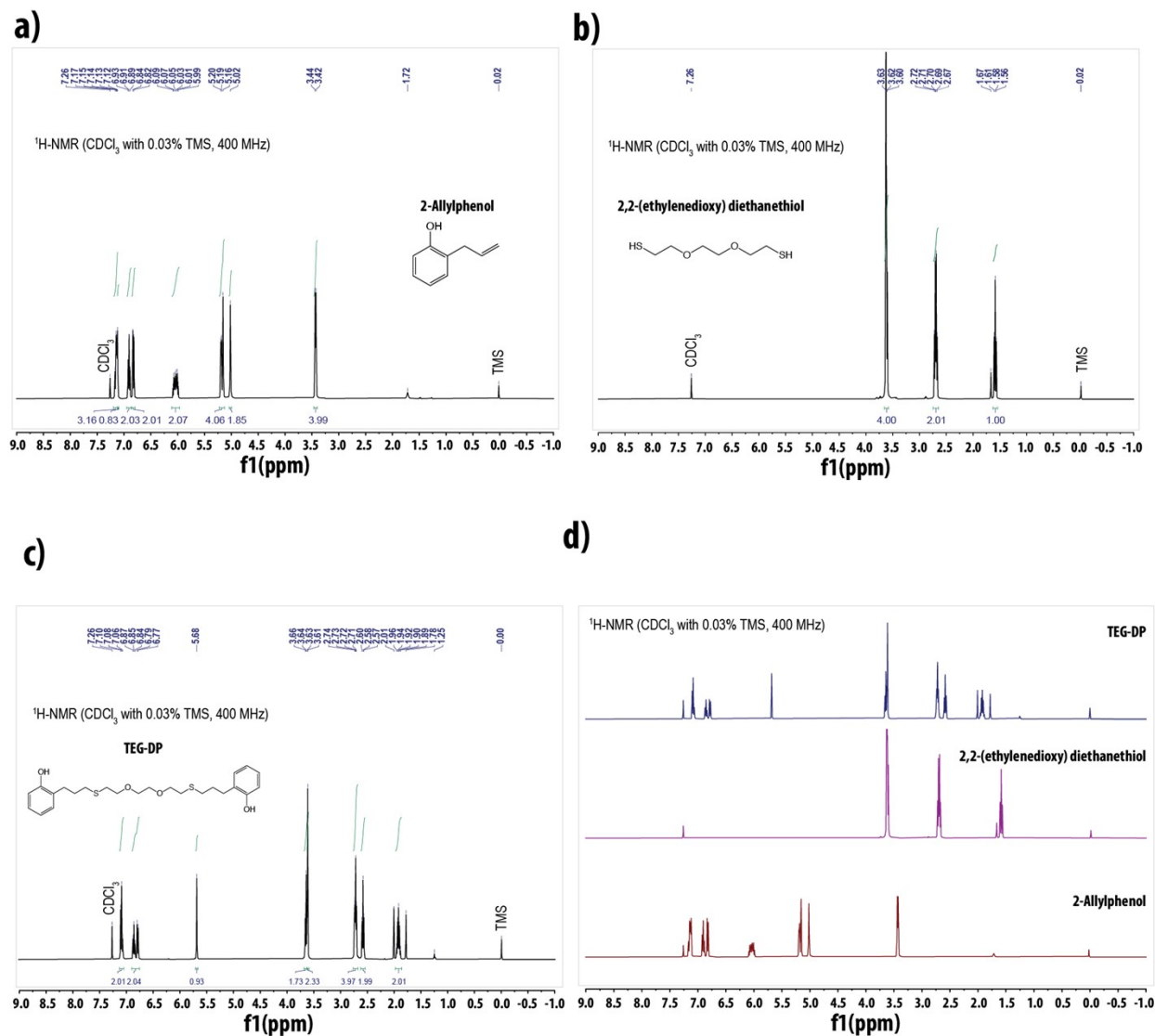


Figure S1. ¹H-NMR spectra and chemical structure of (a) 2-allylphenol, (b) 2,2-(ethylenedioxy) diethanethiol, and (c) TEG-DP. (d) Overlaid ¹H-NMR spectra of TEG-DP, 2-Allylphenol and 2,2-(ethylenedioxy) diethanethiol.

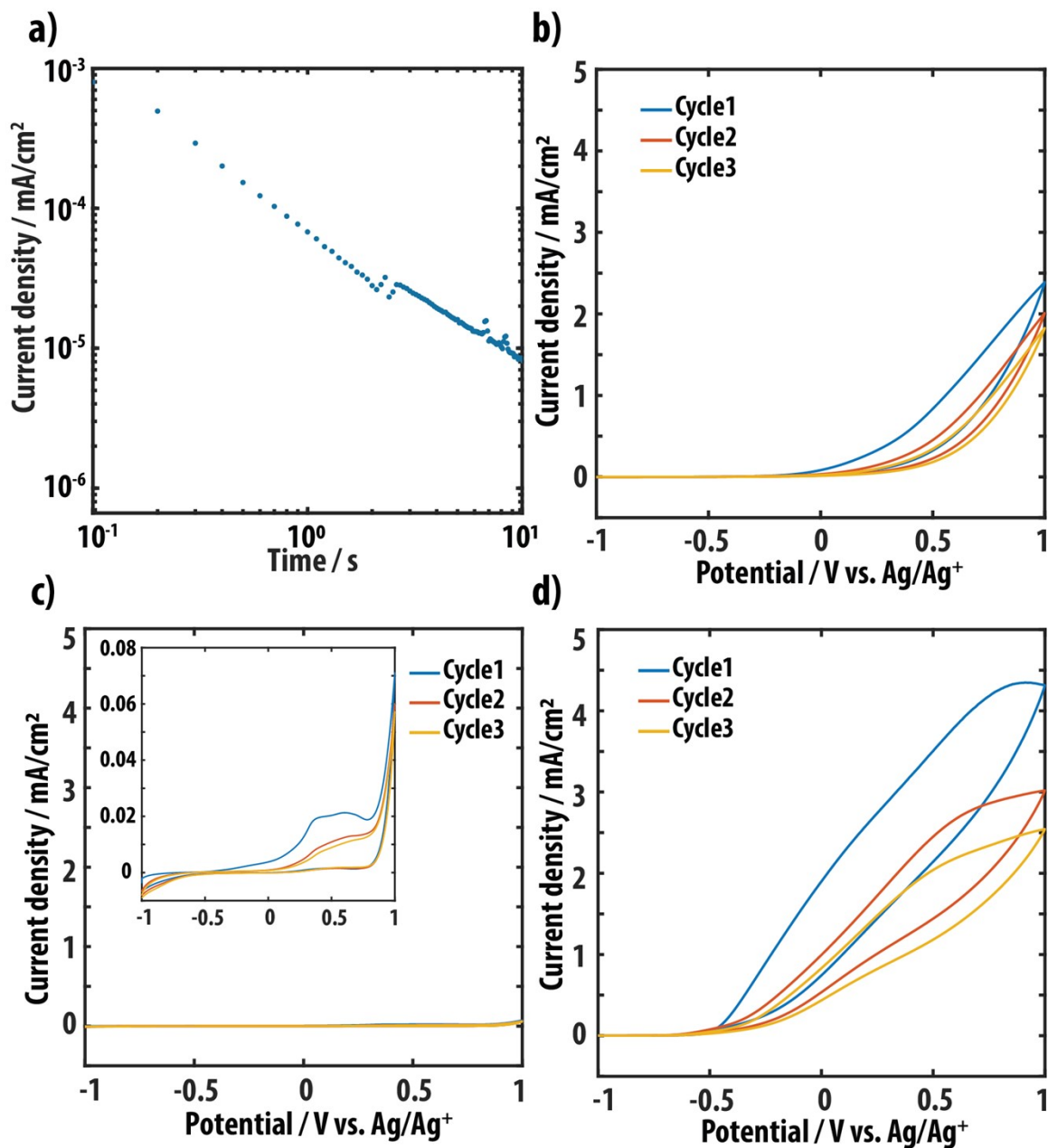


Figure S2. (a) Chronoamperometry of 100 mM TBAP solution at +0.7 V vs. Ag/Ag⁺. Cyclic voltammetry of acetonitrile-based solutions containing (b) 100 mM TMAH·5H₂O and 100 mM TBAP, (c) 50 mM 2,2-(ethylenedioxy) diethanethiol and 100 mM TBAP, and (d) 50 mM 2,2-(ethylenedioxy) diethanethiol, 100 mM TMAH·5H₂O and 100 mM TBAP.

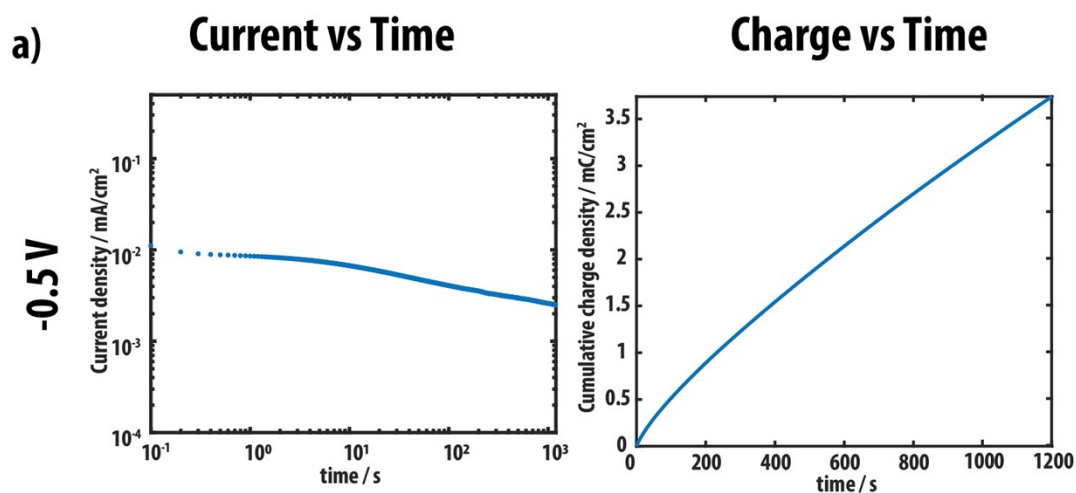


Figure S3a. Chronoamperometry and cumulative charge of 50 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = -0.5 \text{ V}$ vs. Ag/Ag^+ which is categorized as regime 1.

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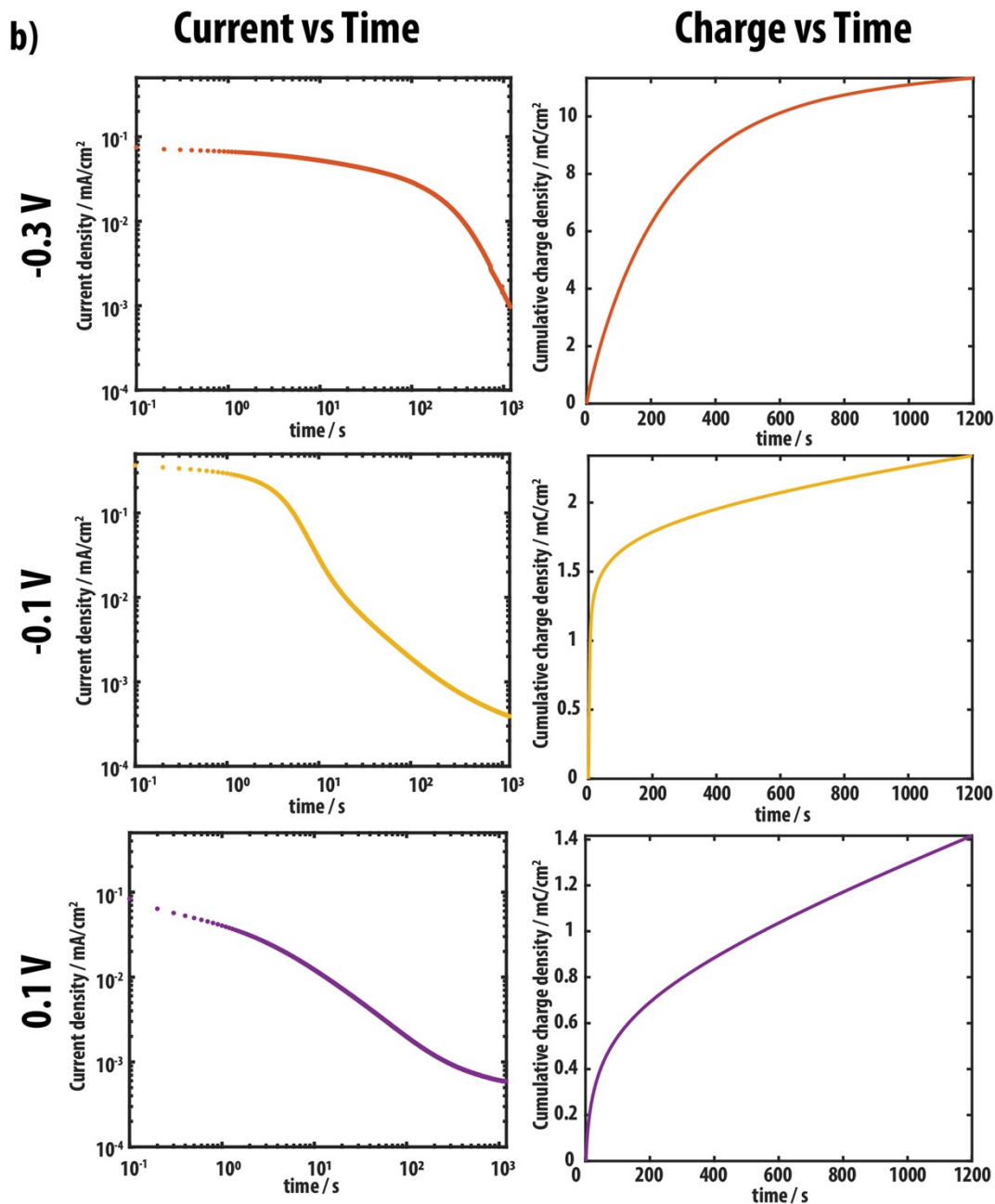


Figure S3b. Chronoamperometry and cumulative charge of 50 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = -0.3$ V, -0.1 V and $+0.1$ V vs. Ag/Ag^+ which are categorized as regime 2.

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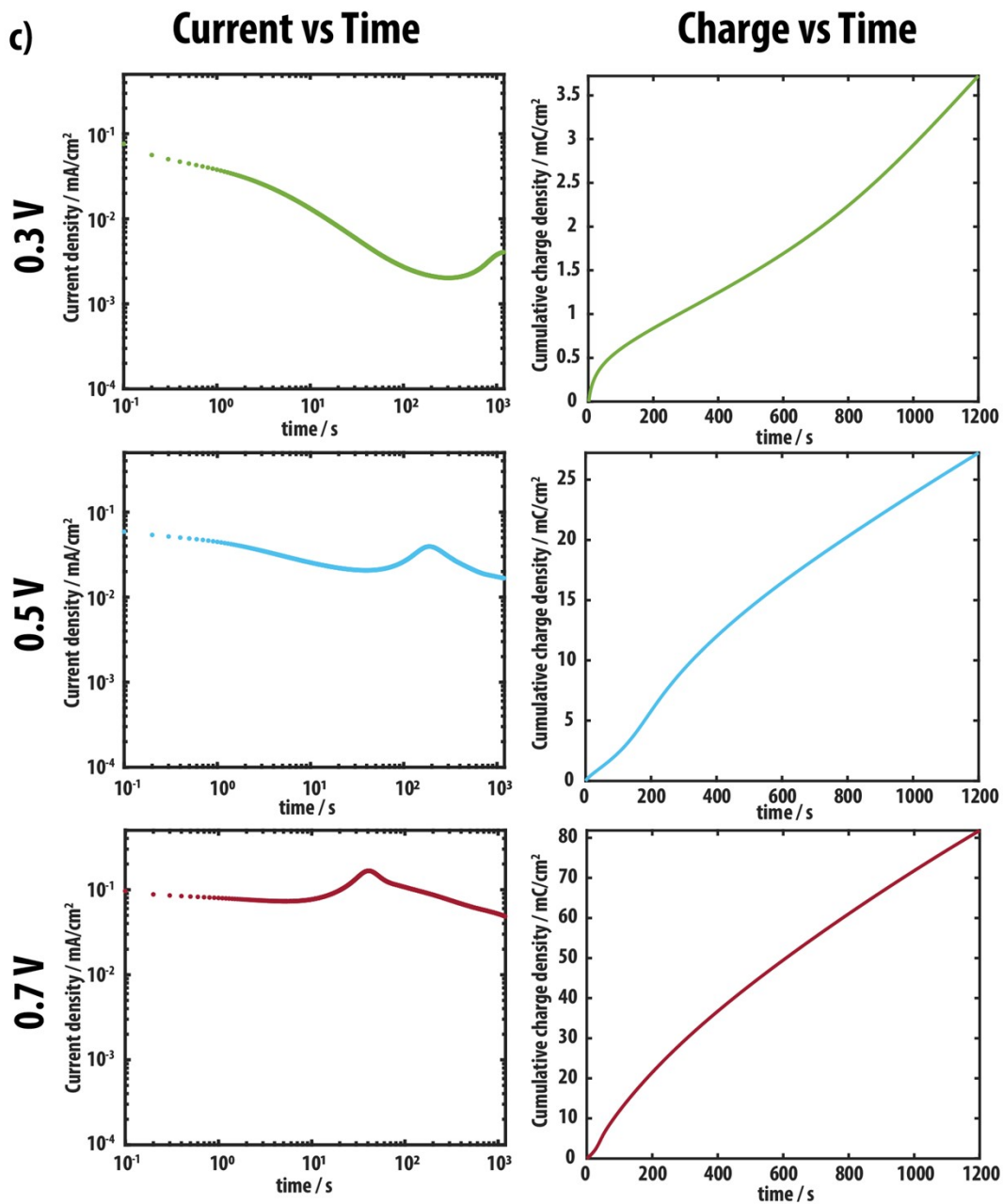


Figure S3c. Chronoamperometry and cumulative charge of 50 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = +0.3$ V, $+0.5$ V and $+0.7$ V vs. Ag/Ag⁺ which are categorized as regime 3.

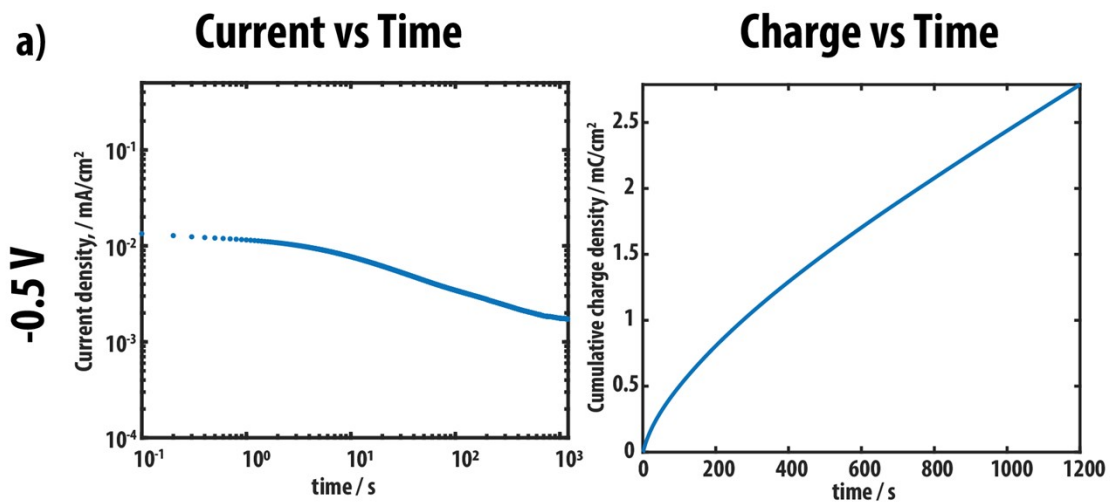


Figure S4a. Chronoamperometry and cumulative charge of 10 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = -0.5 \text{ V}$ vs. Ag/Ag^+ which is categorized as regime 1.

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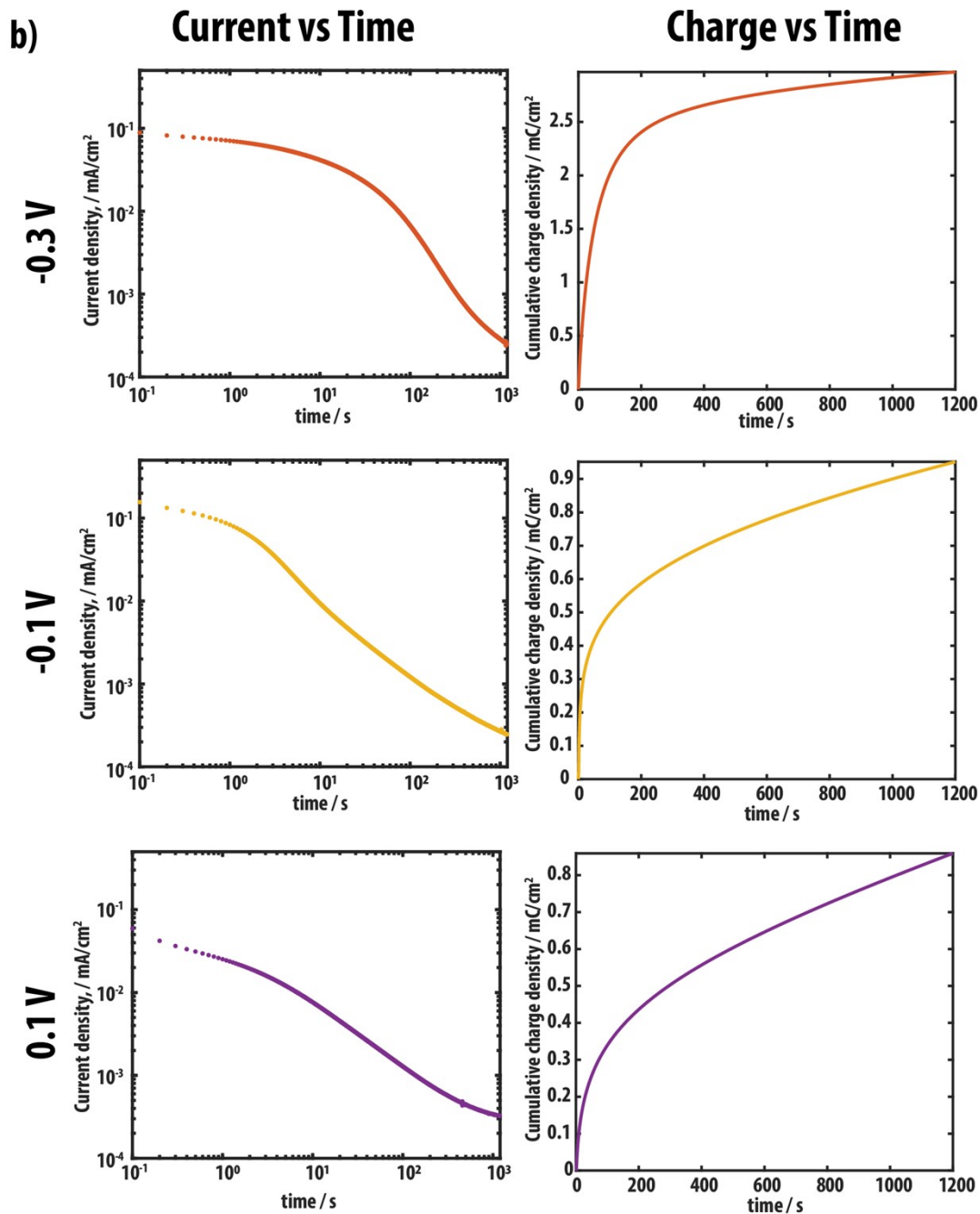


Figure S4b. Chronoamperometry and cumulative charge of 10 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = -0.3$ V, -0.1 V and $+0.1$ V vs. Ag/Ag^+ which are categorized as regime 2.

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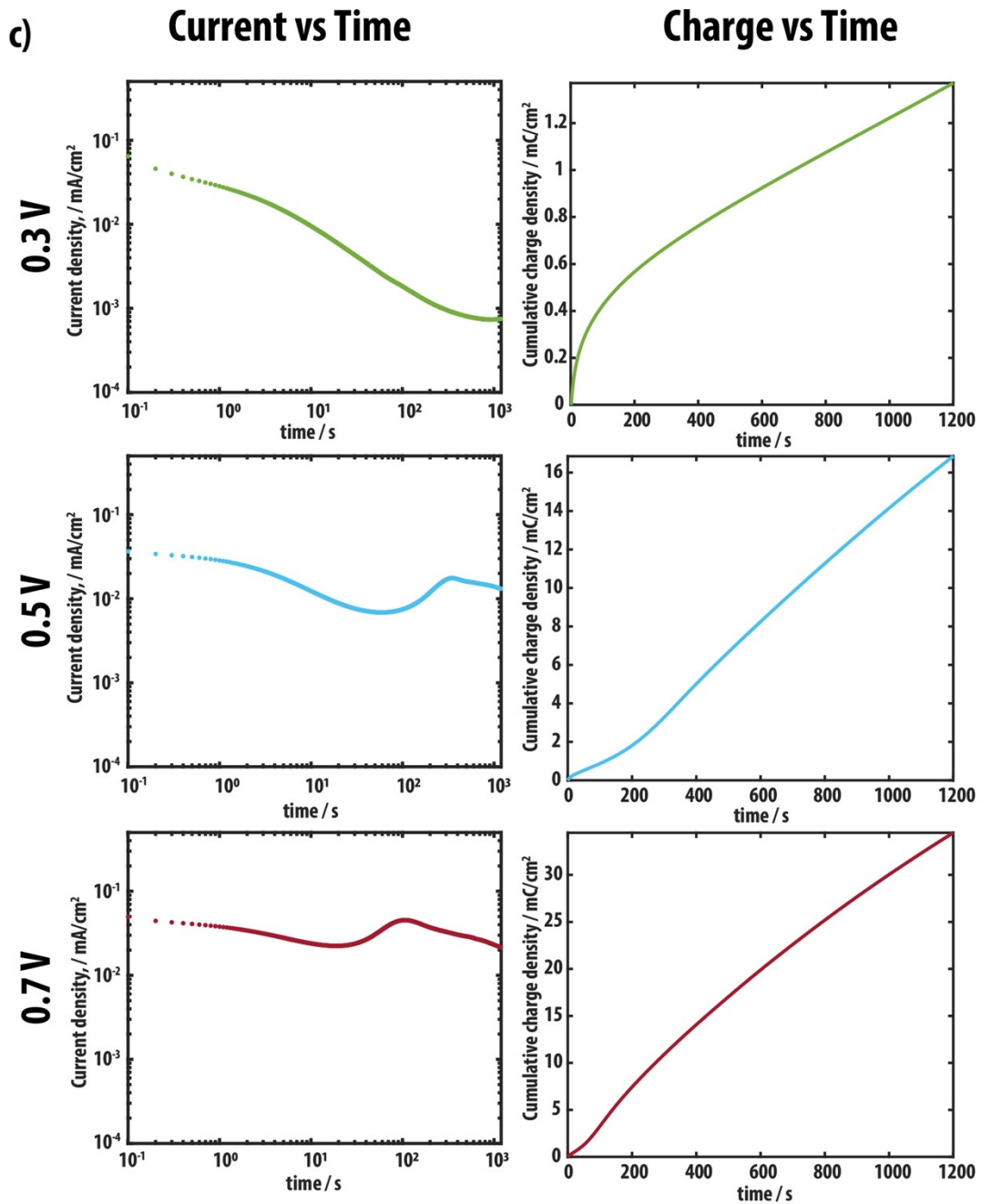


Figure S4c. Chronoamperometry and cumulative charge of 10 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = +0.3$ V, +0.5 V and +0.7 V vs. Ag/Ag⁺ which are categorized as regime 3.

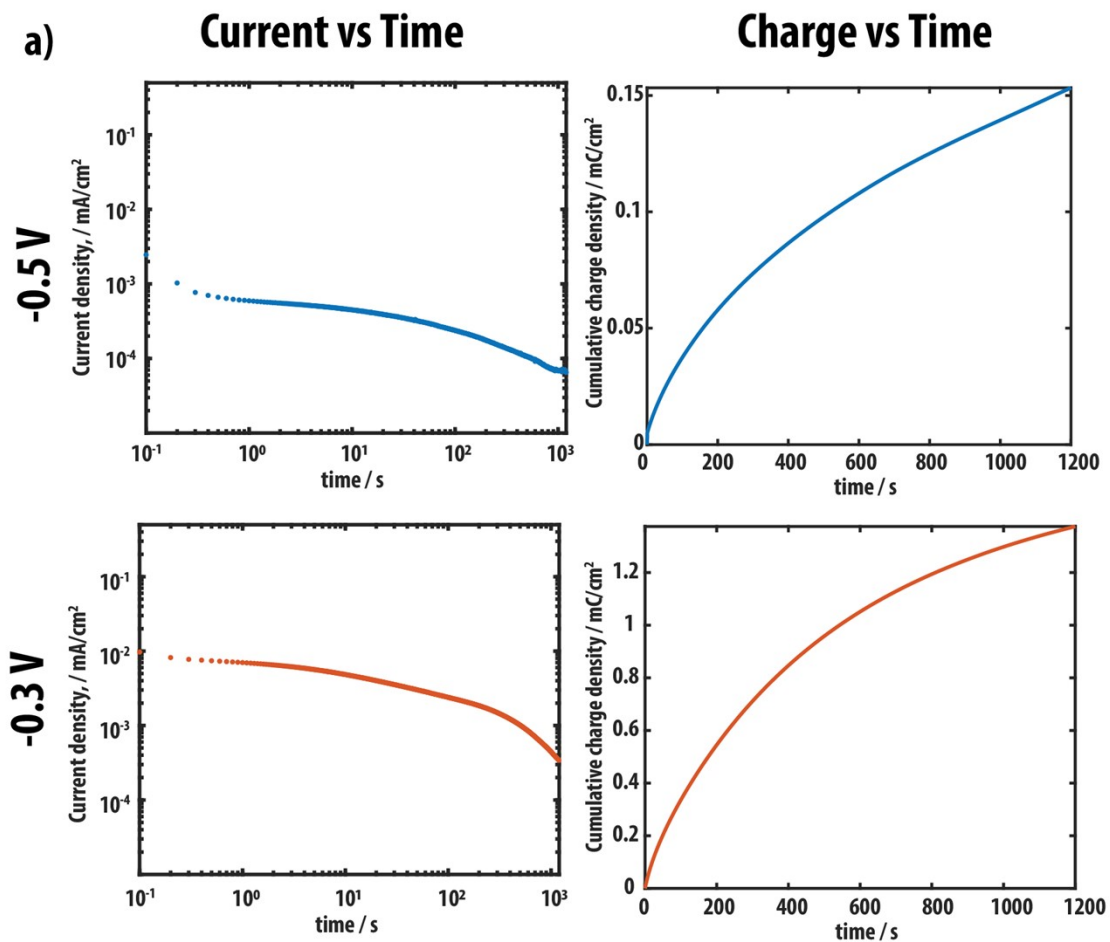


Figure S5a. Chronoamperometry and cumulative charge of 1 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = -0.5$ V and -0.3 V vs. Ag/Ag^+ which are categorized as regime 1.

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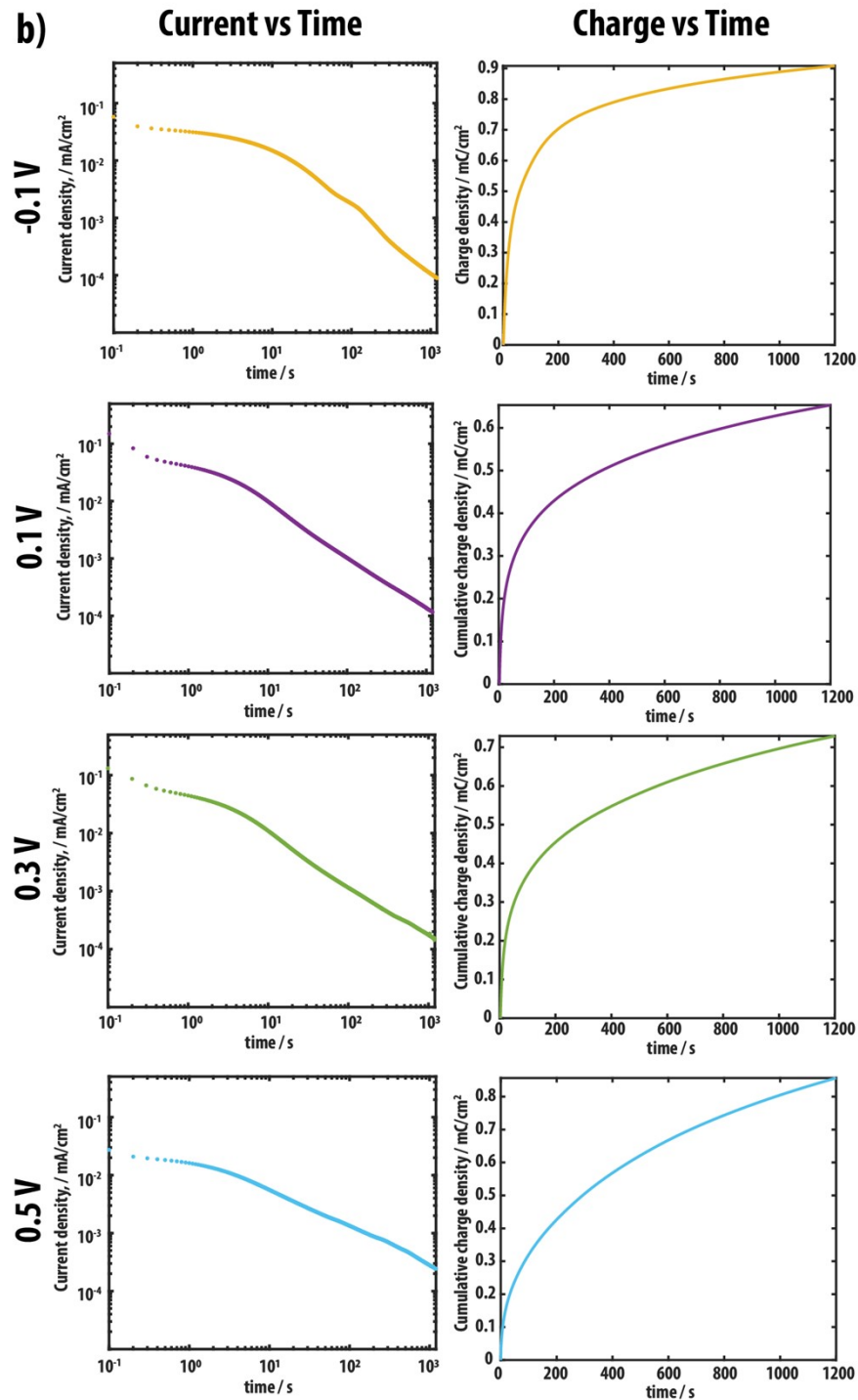


Figure S5b. Chronoamperometry and cumulative charge of 1 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = -0.1 \text{ V}, +0.1 \text{ V}, +0.3 \text{ V}$ and $+0.5 \text{ V}$ vs. Ag/Ag^+ which are categorized as regime 2. *continued on next page...*

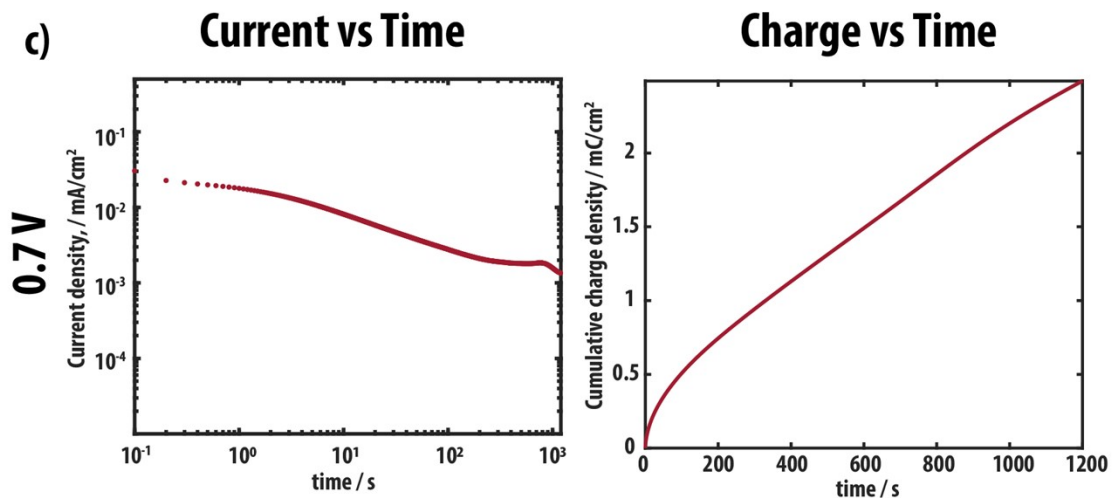


Figure S5c. Chronoamperometry and cumulative charge of 1 mM TEG-DP monomer solution electrodeposited at $E_{\text{dep}} = +0.7$ V vs. Ag/Ag⁺ which are categorized as regime 3.

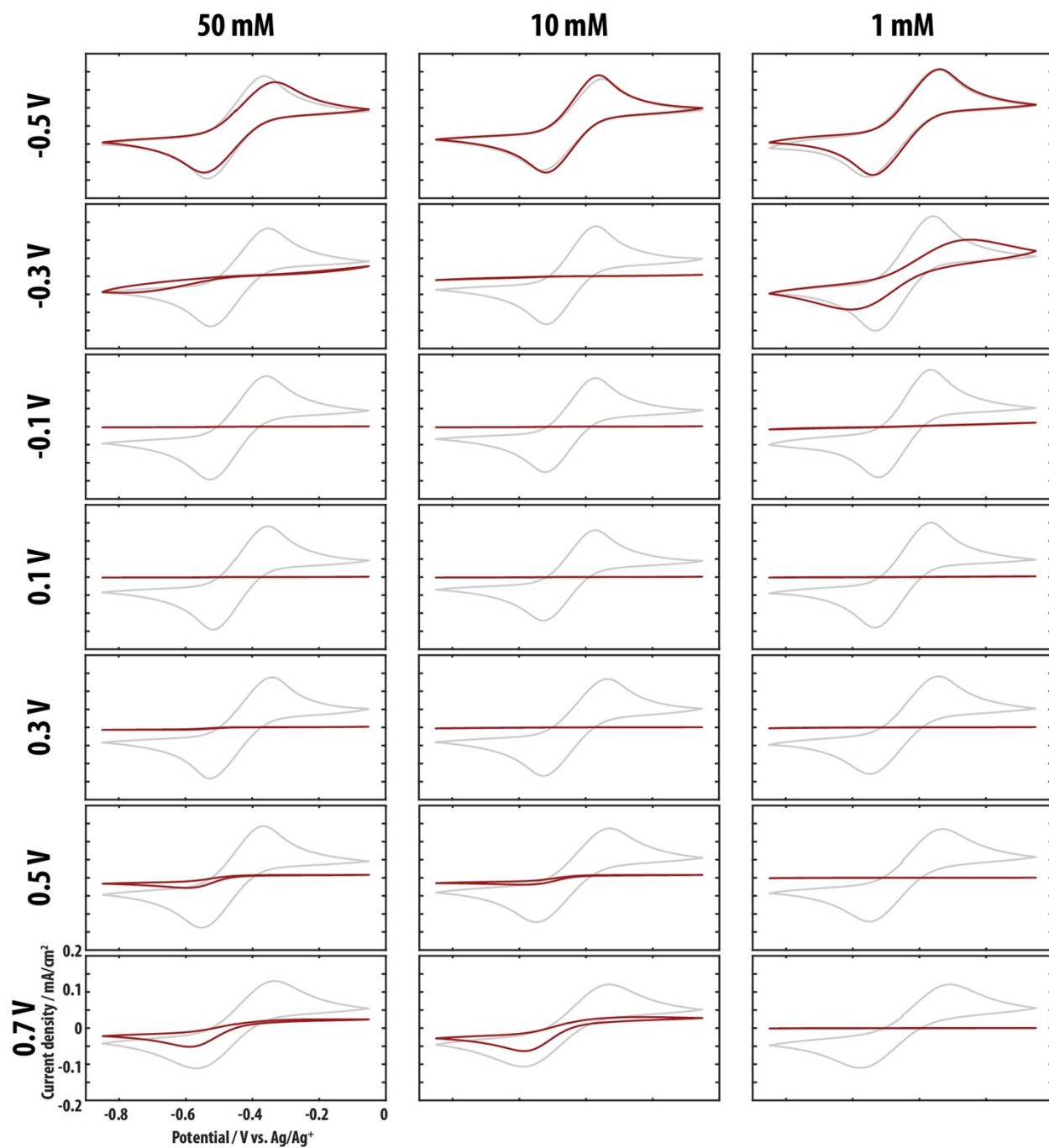


Figure S6. Cyclic voltammetry of decamethylferrocene before (light grey) and after (red) pTEG-DP film deposition on ITO-coated planar electrodes at all conditions. Concentrations are labeled at the top of each column, and E_{dep} are labeled at the left of each row. Universal scale is labeled at the bottom left plot.

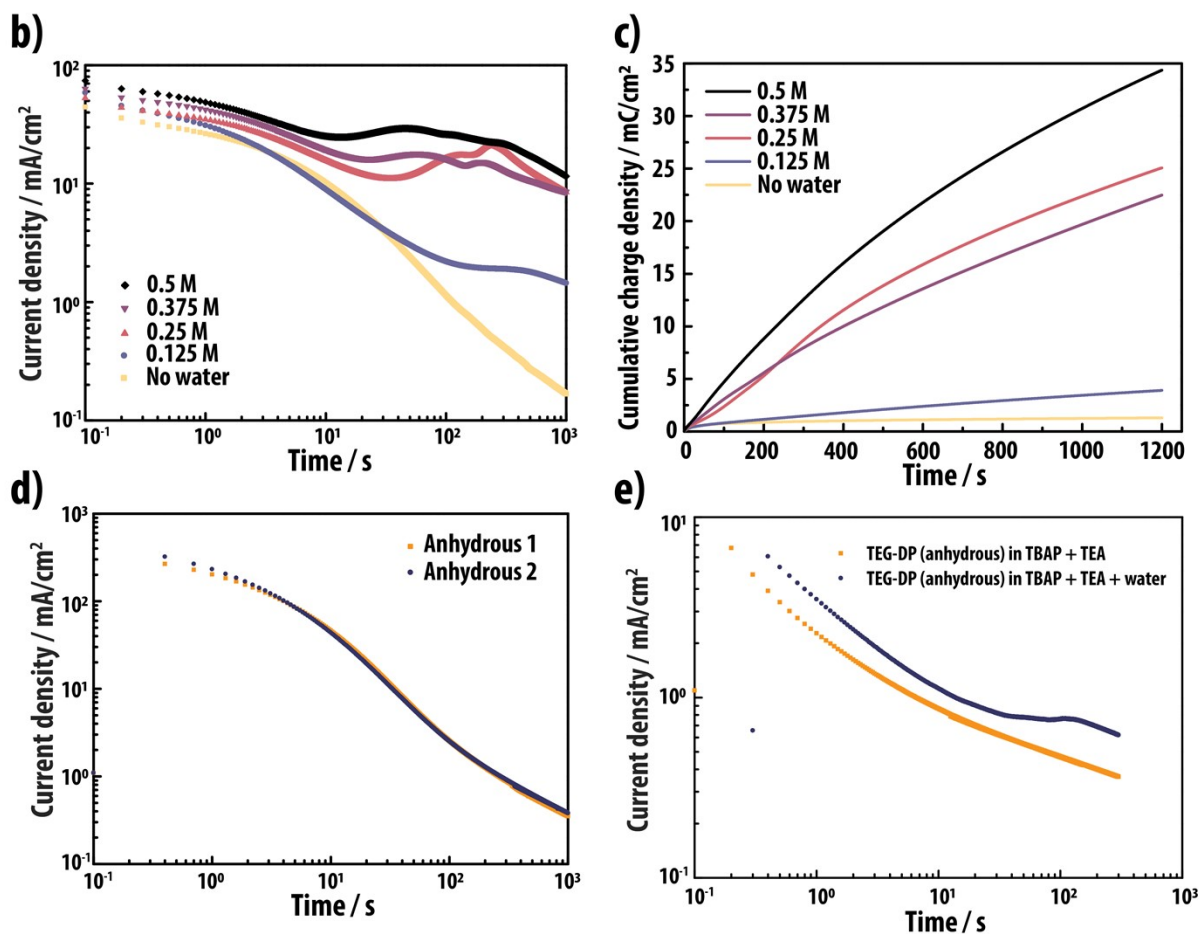
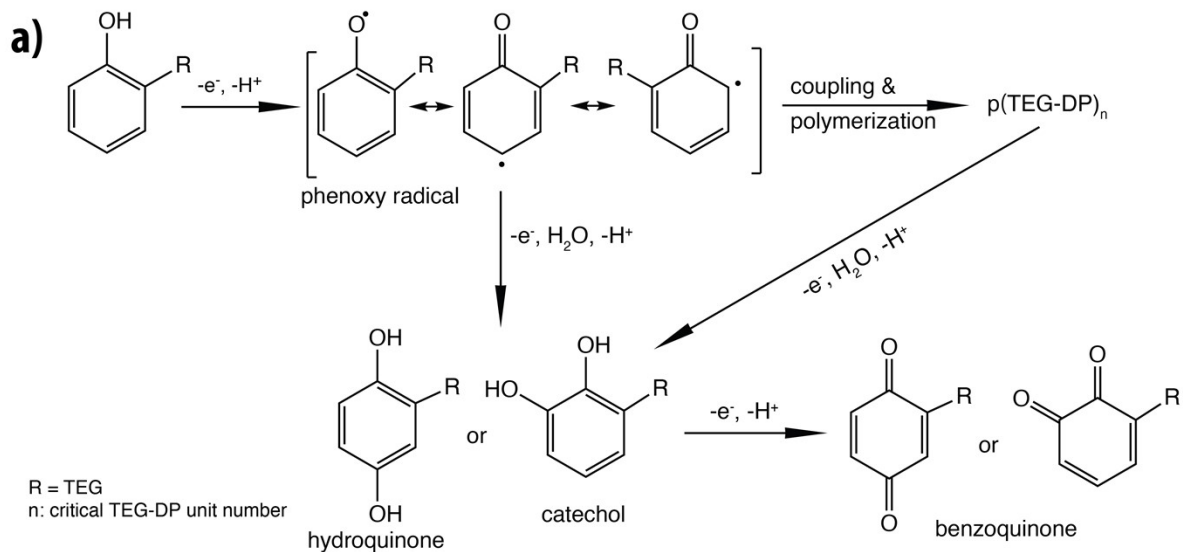
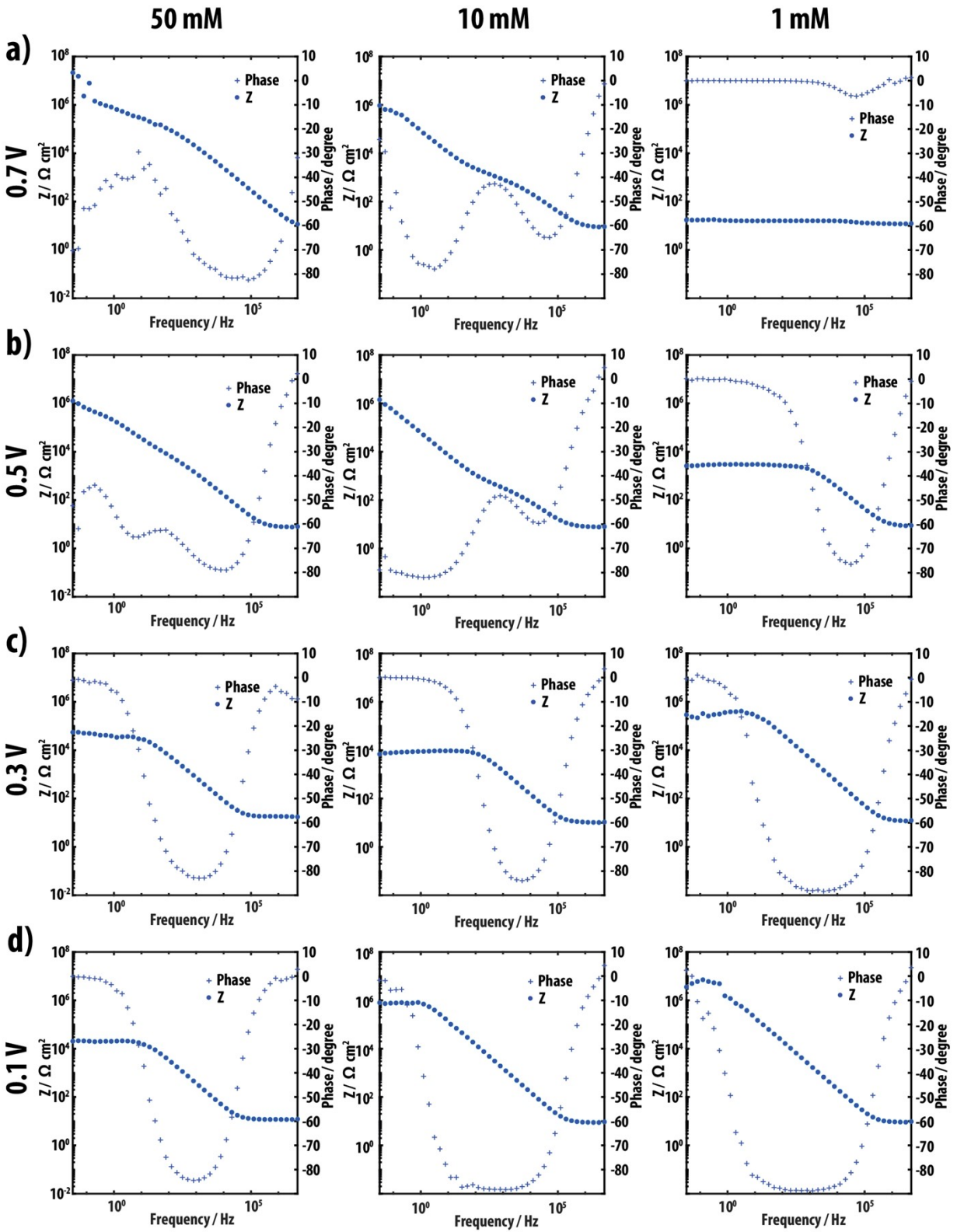


Figure S7. (a) Mechanism of phenol group oxidation pathways with water presence (M. Gattrell and D. W. Kirk, *J. Electrochem. Soc.*, **1992**, 139, 2736). (b) Chronoamperometry (CA) of

monomer solution composed of 25 mM TEG-DP, 50 mM TEA (anhydrous), 100 mM TBAP along with varying concentration of DI water ($E_{\text{dep}} = +0.2 \text{ V vs. Ag/Ag}^+$ for 1200 s). (c) Corresponding cumulative charge passed during electrodeposition. (d) CA of two potentiostatic electrodepositions of TEG-DP in anhydrous monomer solution (25 mM TEG-DP, 50 mM anhydrous TEA, 100 mM TBAP, $+0.2 \text{ V vs. Ag/Ag}^+$ for 1200 s) that are used for post-deposition oxidation tests in d. (e) CA of the pTEG-DP films deposited under anhydrous conditions in (d) now exposed to monomer-free solutions with and without water, respectively.



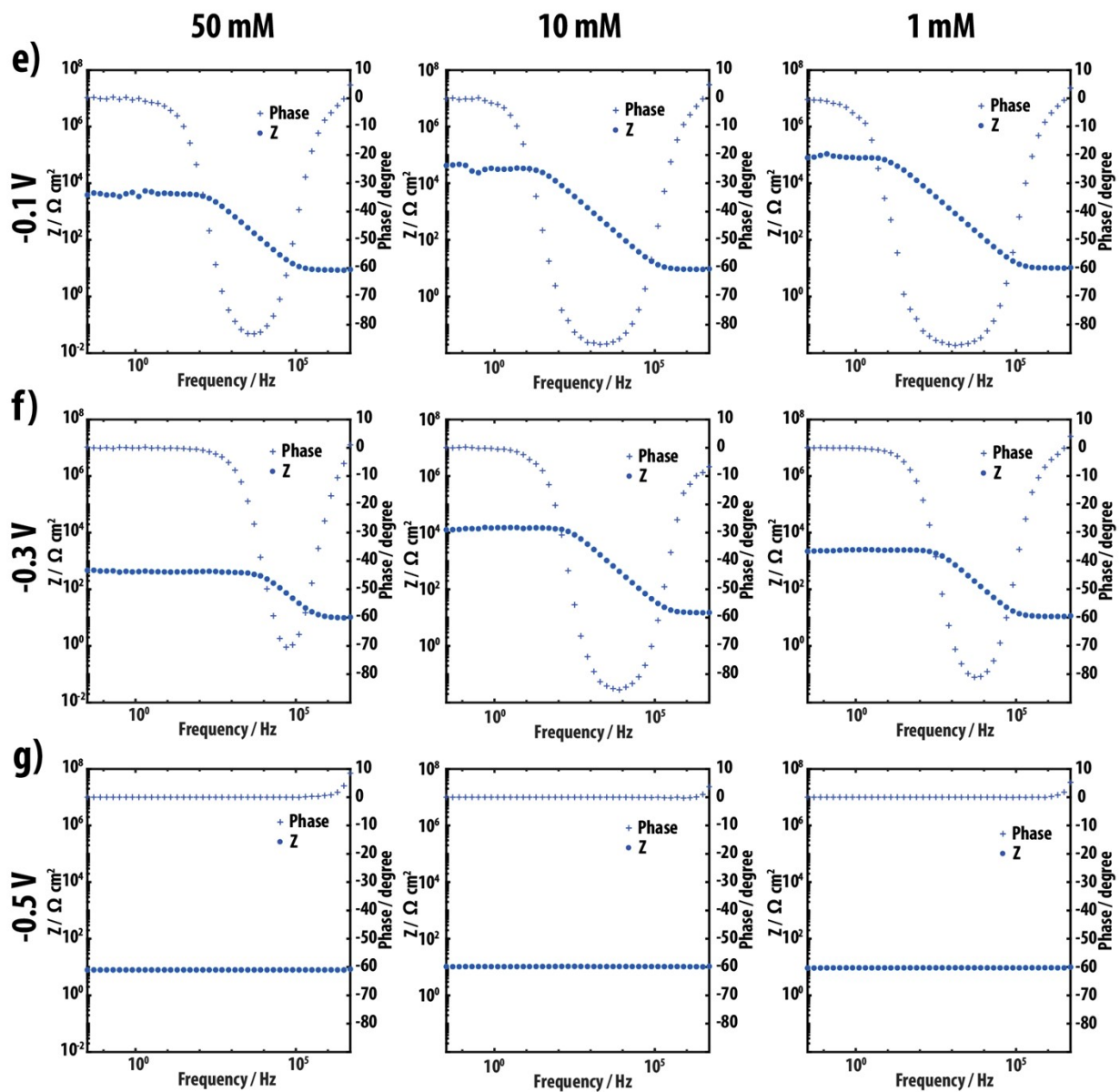


Figure S8. (a-g) Bode plot of solid-state EIS measurement of pTEG-DP films deposited at all conditions. TEG-DP concentrations are labeled at the top of each column, and the potentials are labeled at the left of each row.

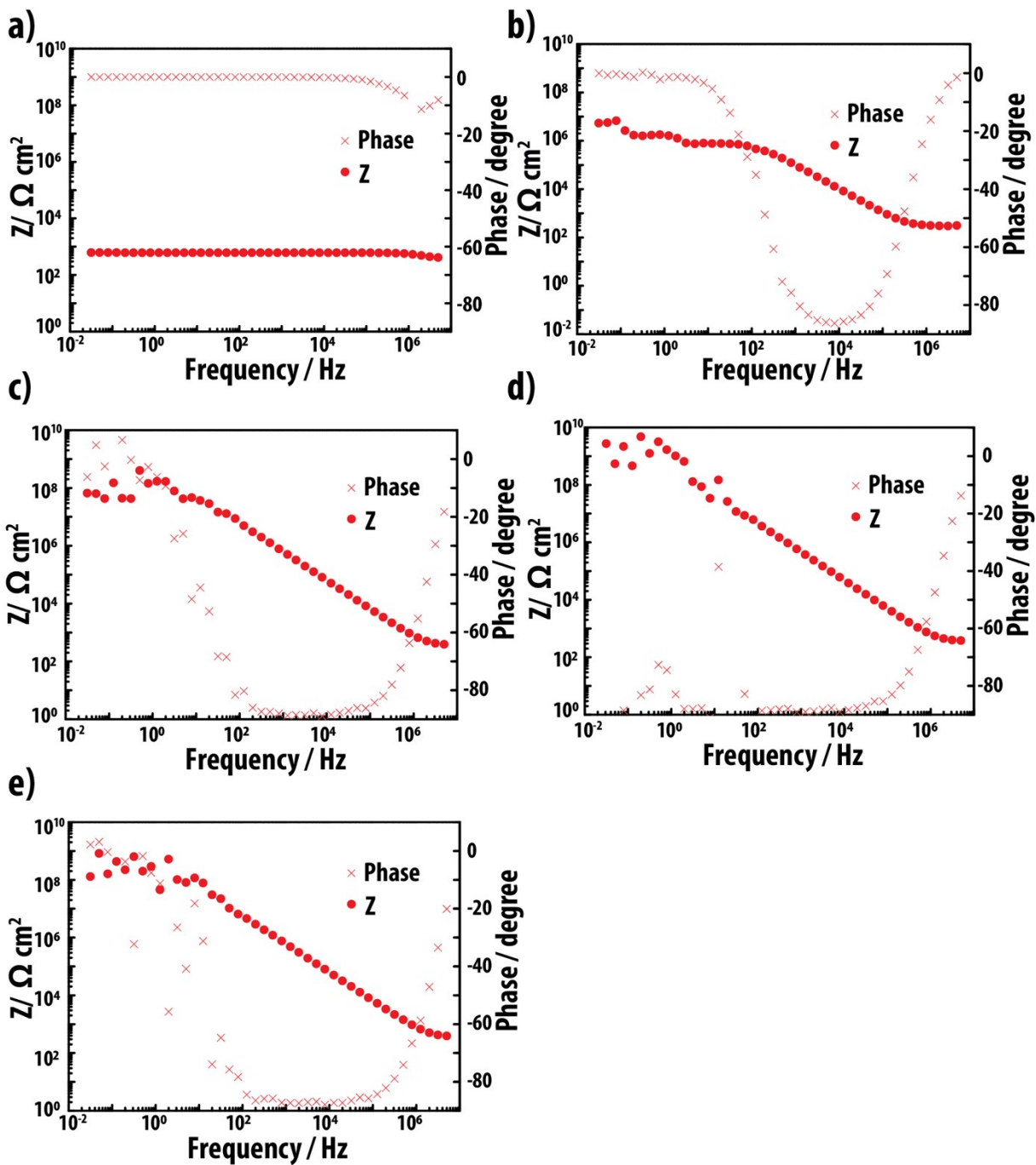


Figure S9. Bode plot of solid-state EIS measurement of films obtained from solutions composed of 25 mM TEG-DP 50 mM TEA, 100 mM TBAP with (a) no DI water, (b) 0.125 M DI water, (c) 0.25 M DI water, (d) 0.375 M DI water and (e) 0.5 M DI water.

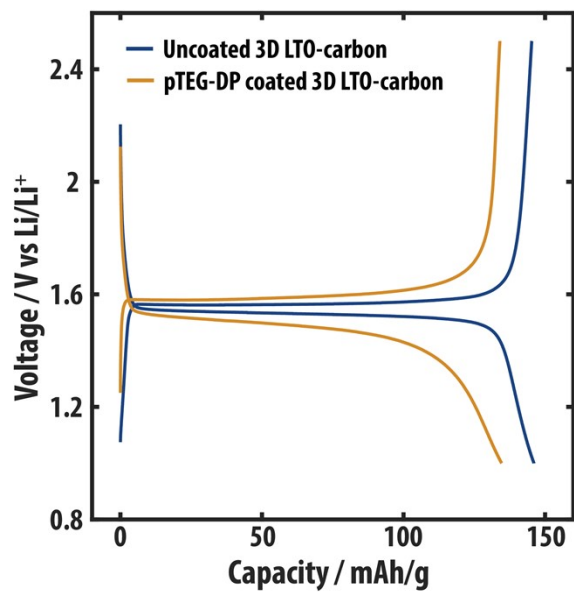


Figure S10. Charge and discharge curves (5th cycle) of pTEG-DP coated and uncoated 3D LTO-carbon electrodes (9.1 mA/g, 0.05 C, C-rate is calculated based on the theoretical LTO capacity of 175 mAh/g).

Table S1. Characterization data of all pTEG-DP films.

Conc. / mM	E_{dep} /V vs. Ag/Ag⁺	Thickness / nm	Root-mean-square roughness / nm	Low-frequency Impedance / $\Omega \text{ cm}^2$	Resistivity / $\Omega \text{ cm}$	Relative Permeability to DMFc
50	-0.5	N/A	N/A	~10	N/A	0.995
50	-0.3	15.28	0.72	~4000	~10 ⁹	0.338
50	-0.1	15.2	1.34	~1000	~10 ⁸	0.0167
50	0.1	15.1	1.19	~2000	~10 ¹⁰	0.014
50	0.3	16.76	2.74	~50000	~10 ¹⁰	0.064
50	0.5	39.6	4.34	>10 ⁶	>10 ¹¹	0.218
50	0.7	80.31	3.48	>10 ⁷	>10 ¹²	0.374
10	-0.5	N/A	N/A	~10	N/A	0.934
10	-0.3	10.61	0.76	~800	~10 ⁸	0.060
10	-0.1	8.82	1.54	~40000	~10 ¹⁰	0.015
10	0.1	8.29	0.863	~20000	~10 ¹⁰	0.011
10	0.3	9.95	0.233	~50000	~10 ¹⁰	0.016
10	0.5	13.43	3.29	>10 ⁶	>10 ¹¹	0.175
10	0.7	12.09	2.39	>10 ⁶	>10 ¹¹	0.472
1	-0.5	N/A	N/A	~10	N/A	1
1	-0.3	N/A	N/A	~2000	N/A	0.809
1	-0.1	N/A	N/A	~100000	N/A	0.045
1	0.1	7.18	0.88	>10 ⁶	>10 ¹²	0.010
1	0.3	9.63	1.52	~300000	~10 ¹¹	0.012
1	0.5	8.96	0.75	~2000	~10 ⁹	0.007
1	0.7	9.53	1.31	~400	~10 ⁸	0.008