Supporting Information

Design and Characterization of an Adaptive Polymer Electrolyte for Lithium Metal Solid-State Battery Applications

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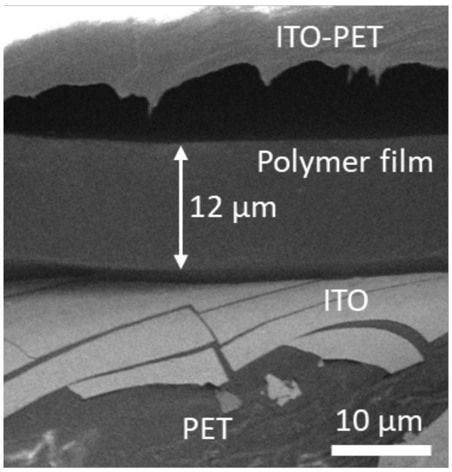

Figure S1. SEM cross-section of thin polymer film (targeting ~10 µm thick) between indium tin oxide (ITO) coated polyethylene terephthalate (PET) sheets. Cross-section obtained by shearing with titanium coated blade. SEM micrograph obtained with backscatter electron mode at an accelerating voltage of 2 kV and beam current of 13 pA.

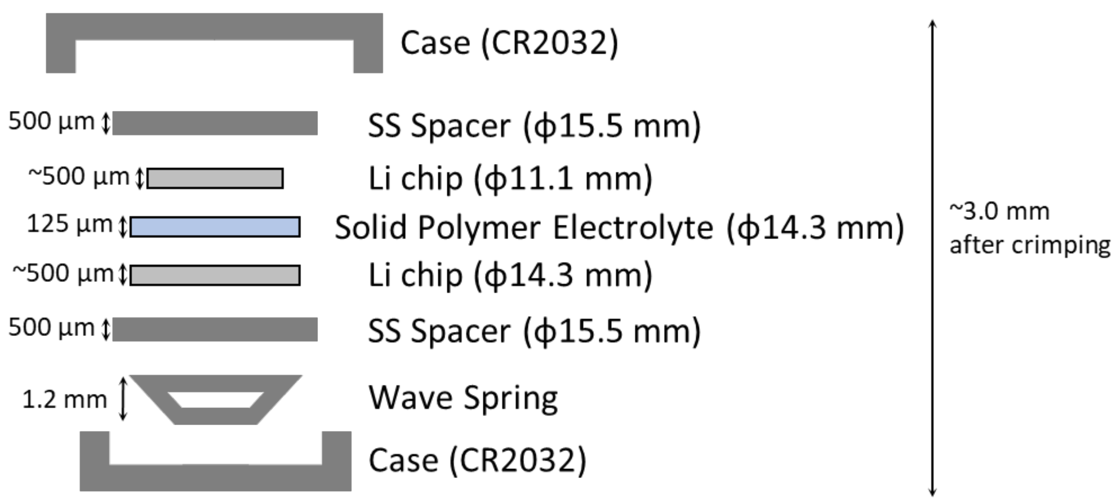

Figure S2. Coin cell stack used for electrochemical impedance spectroscopy and Li symmetric cycling experiments.

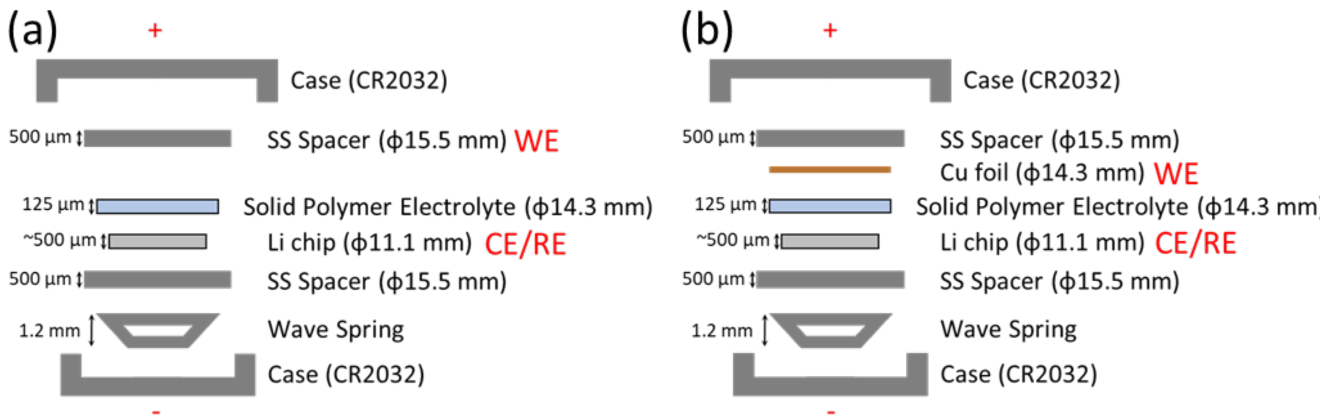

Figure S3. Coin cell stack used for electrochemical stability window experiments with Li-metal as the counter/reference electrode (CE/RE) for (a) anodic scan with 304SS as the working electrode (WE) and (b) cathodic scan with Cu as the WE.

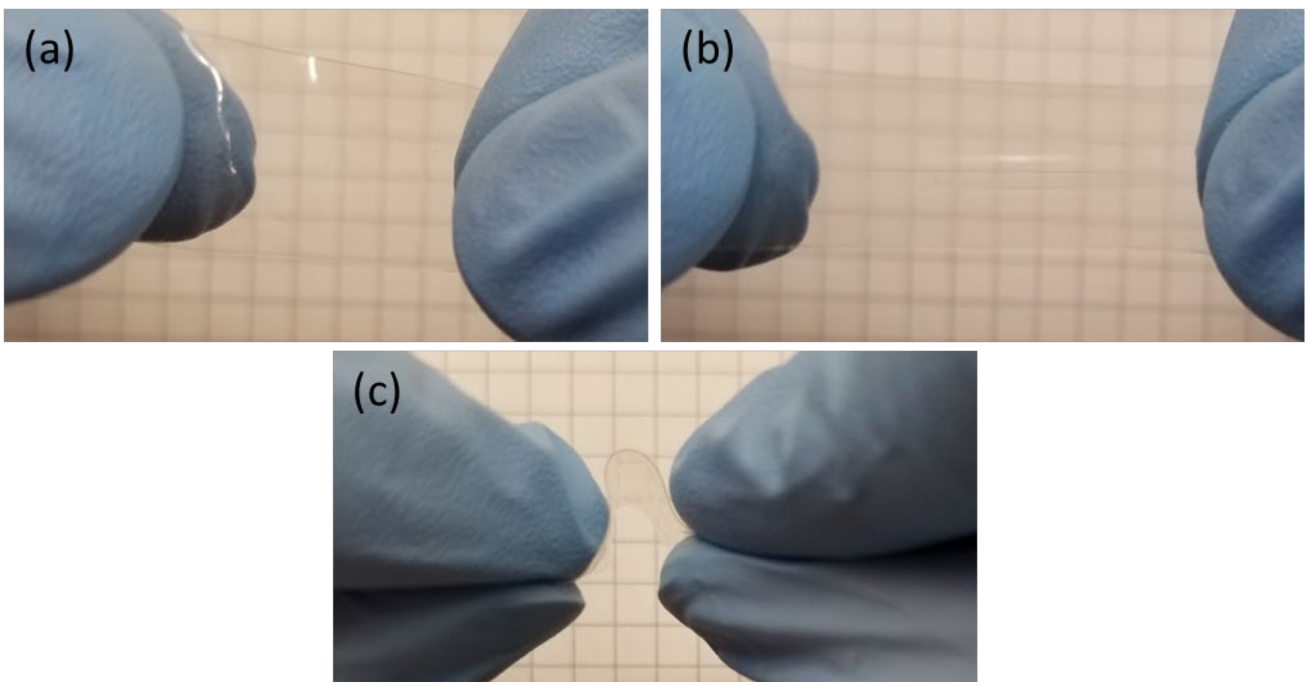

Figure S4. Demonstrating the as produced free-standing polymer electrolyte film for 0 wt% PPy(DBS) composition. (a) Unstretched film, (b) stretching the film and (c) bending the film. Grid size 5 mm.

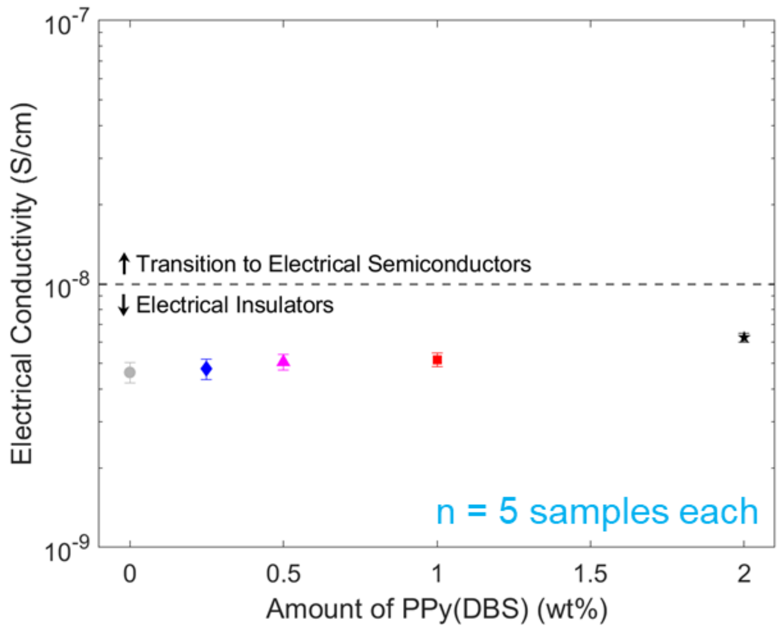

Figure S5. Electrical conductivity measurements of the polymer films with varying amounts of PPy(DBS). Markers indicate average values and error bars indicate standard deviations.

Table S1. Summary of properties from DSC and DMA. T_g from DSC obtained from the inflection point in the slope of the glass transition step, DSC slope of heat flow after glass transition obtained from a linear regression from -20 °C to 120 °C, and T_g from DMA obtained from the peak of the tan delta thermograms.

Sample	T_g from DSC [°C]	DSC slope of heat flow after glass transition [mW/(g °C)]	T_g from DMA tan delta [°C]
0 wt% PPy(DBS)	-37.4	20.1	-43.2
0.25 wt% PPy(DBS)	-38.8	88.6	-53.7
0.5 wt% PPy(DBS)	-39.9	115.0	-53.6
1 wt% PPy(DBS)	-40.9	85.9	-56.6

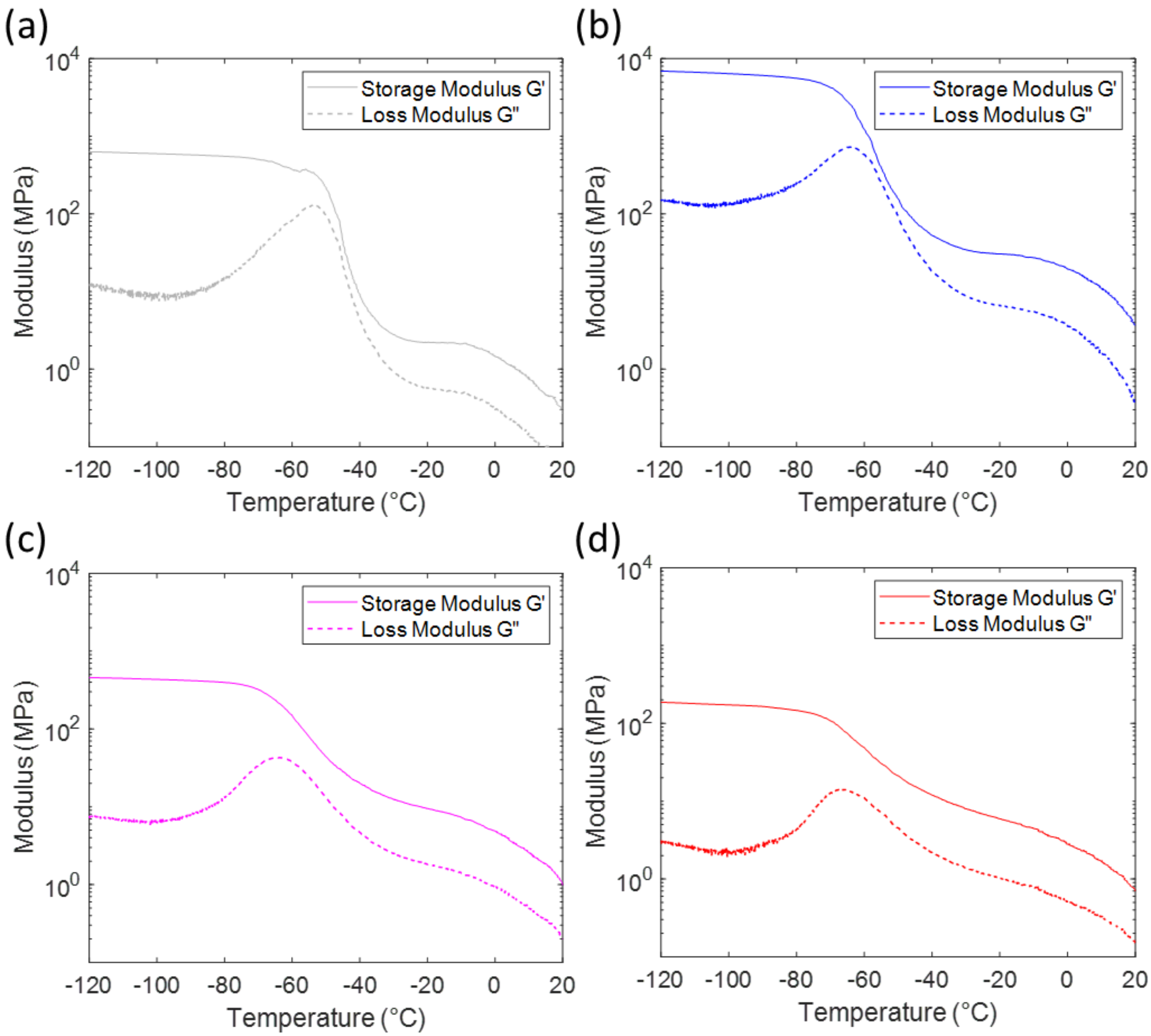

Figure S6. DMA storage (G') and loss modulus (G'') profiles for (a) 0 wt% PPy(DBS), (b) 0.25 wt% PPy(DBS), (c) 0.5 wt% PPy(DBS), and (d) 1 wt% PPy(DBS).

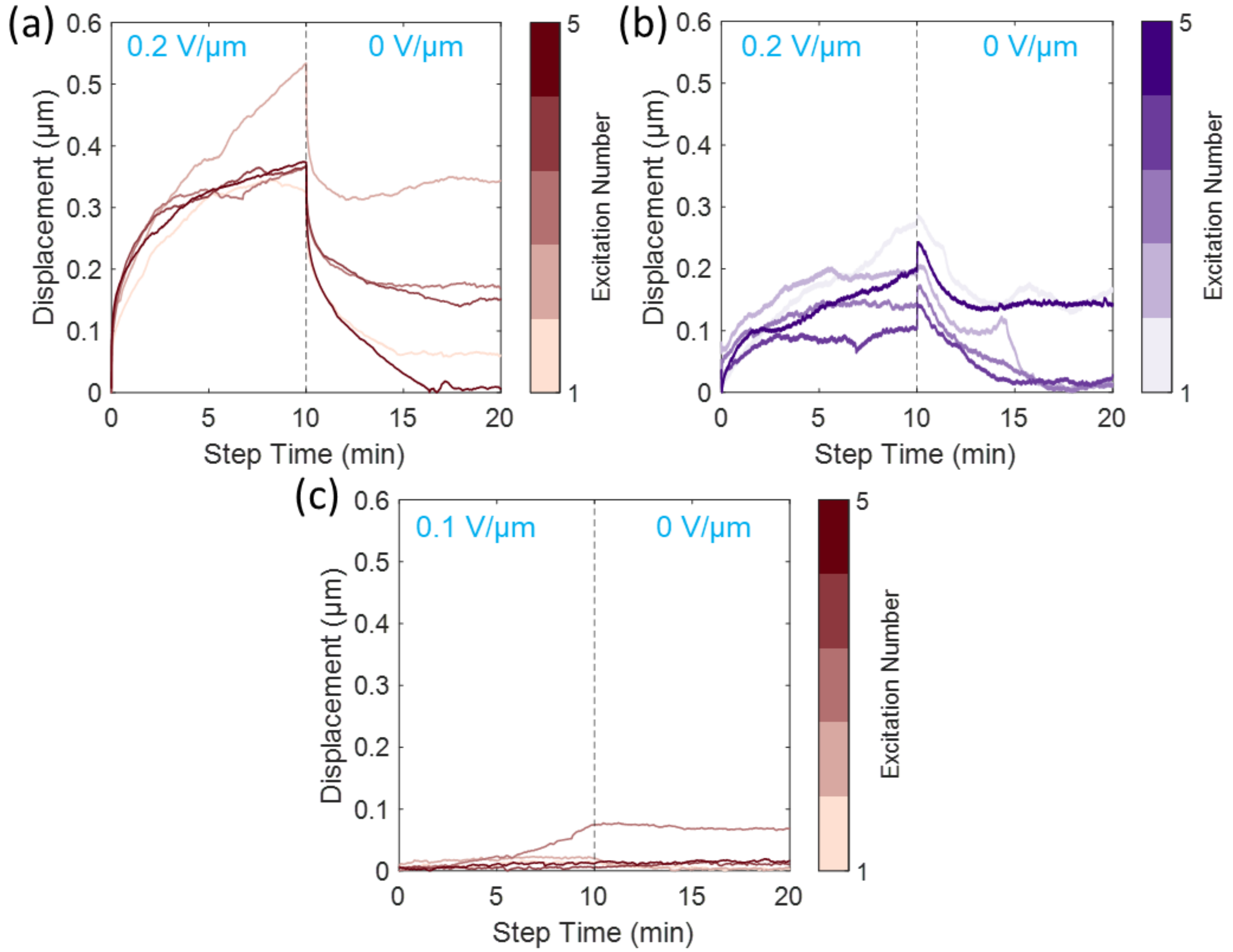

Figure S7. AFM continuous point measurement of polymer film under 0.1-0.2 V/μm followed by 0 V/μm electric field strength for (a) 1 wt% PPy(DBS) with 0.2 V/μm excitations, (b) 0.5 wt% PPy(DBS) with 0.2 V/μm excitations, and (c) 1 wt% PPy(DBS) with 0.1 V/μm excitations.

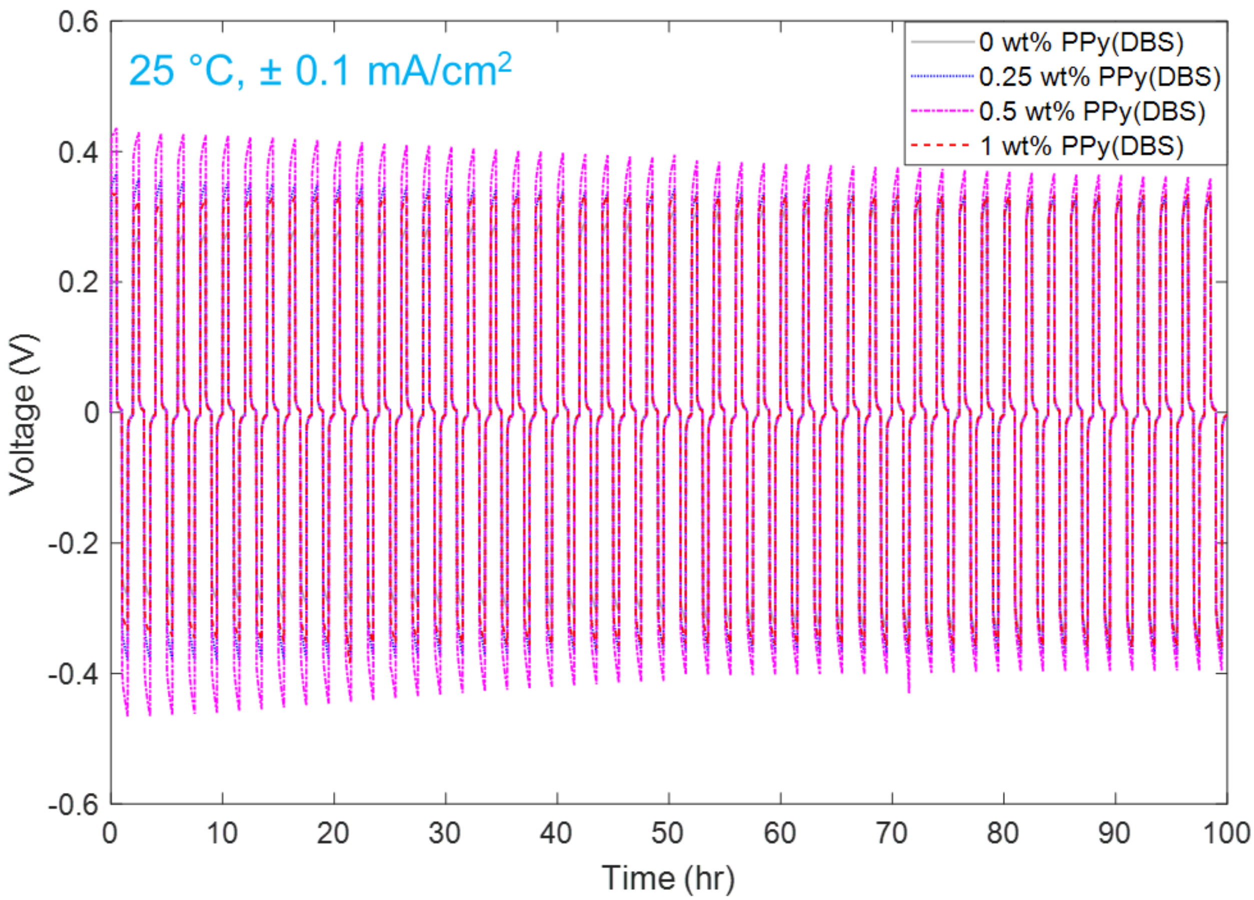

Figure S8. Li symmetric cycling overpotentials for a representative Li/polymer/Li coin cell from each composition at 25 °C under ± 0.1 mA/cm^2 for 30 min each direction with 30 min rests for 50 cycles.

Table S2. Equivalent circuit model parameters from EIS fitting of the representative cells in Figure S9. Parameters are series resistance (R_s), solid electrolyte interphase resistance (R_{SEI}), charge transfer resistance (R_{ct}), constant phase elements (CPE_1, CPE_2), and exponent of the CPEs to account for the non-ideal capacitive behavior (α). $\alpha < 1$ for non-ideal capacitive behavior, $\alpha = 1$ for ideal capacitor.

Representative Coin Cell	0 wt% PPy(DBS)			0.25 wt% PPy(DBS)			0.5 wt% PPy(DBS)			1 wt% PPy(DBS)		
Cycles	0	25	50	0	25	50	0	25	50	0	25	50
R_s [Ω]	76	79	83	92	108	102	99	107	109	78	82	82
R_{SEI} [Ω]	760	710	966	973	1088	1054	1164	866	800	1232	966	962
CPE_1 [S*s$^\alpha$]	3.07 * 10^{-6}	4.30 * 10^{-6}	4.98 * 10^{-6}	2.75 * 10^{-6}	4.85 * 10^{-6}	6.25 * 10^{-6}	1.95 * 10^{-6}	4.81 * 10^{-6}	6.77 * 10^{-6}	2.42 * 10^{-6}	5.38 * 10^{-6}	6.55 * 10^{-6}
α_1	0.79	0.76	0.74	0.80	0.73	0.71	0.81	0.72	0.69	0.77	0.69	0.68
R_{ct} [Ω]	2494	2402	3080	2667	2637	2147	4128	3274	2790	2463	2817	2626
CPE_2 [S*s$^\alpha$]	3.11 * 10^{-6}	3.13 * 10^{-6}	3.06 * 10^{-6}	2.49 * 10^{-6}	3.27 * 10^{-6}	3.56 * 10^{-6}	2.07 * 10^{-6}	2.79 * 10^{-6}	2.97 * 10^{-6}	3.34 * 10^{-6}	2.78 * 10^{-6}	2.68 * 10^{-6}
α_2	0.89	0.88	0.87	0.90	0.88	0.88	0.87	0.85	0.85	0.88	0.86	0.88

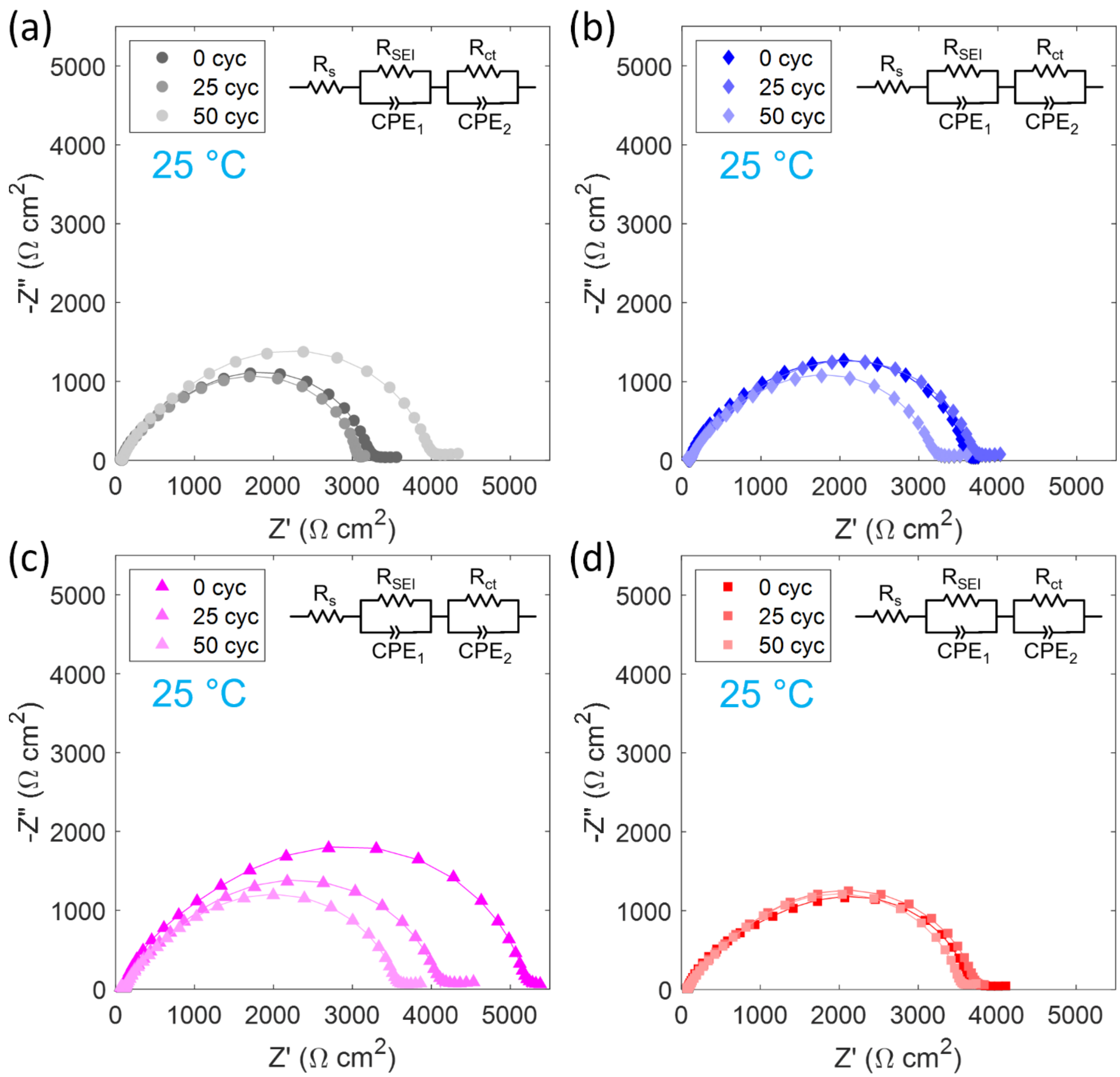

Figure S9. EIS spectra at 25 °C of representative Li/polymer/Li coin cells after 0, 25, and 50 Li symmetric cycles for (a) 0 wt% PPy(DBS), (b) 0.25 wt% PPy(DBS), (c) 0.5 wt% PPy(DBS), and (d) 1 wt% PPy(DBS). Markers indicate measured values and solid lines represent the equivalent circuit fit. Equivalent circuit elements consist of series resistance (R_s), solid electrolyte interphase resistance (R_{SEI}), charge transfer resistance (R_{ct}), and constant phase elements (CPE_1, CPE_2).

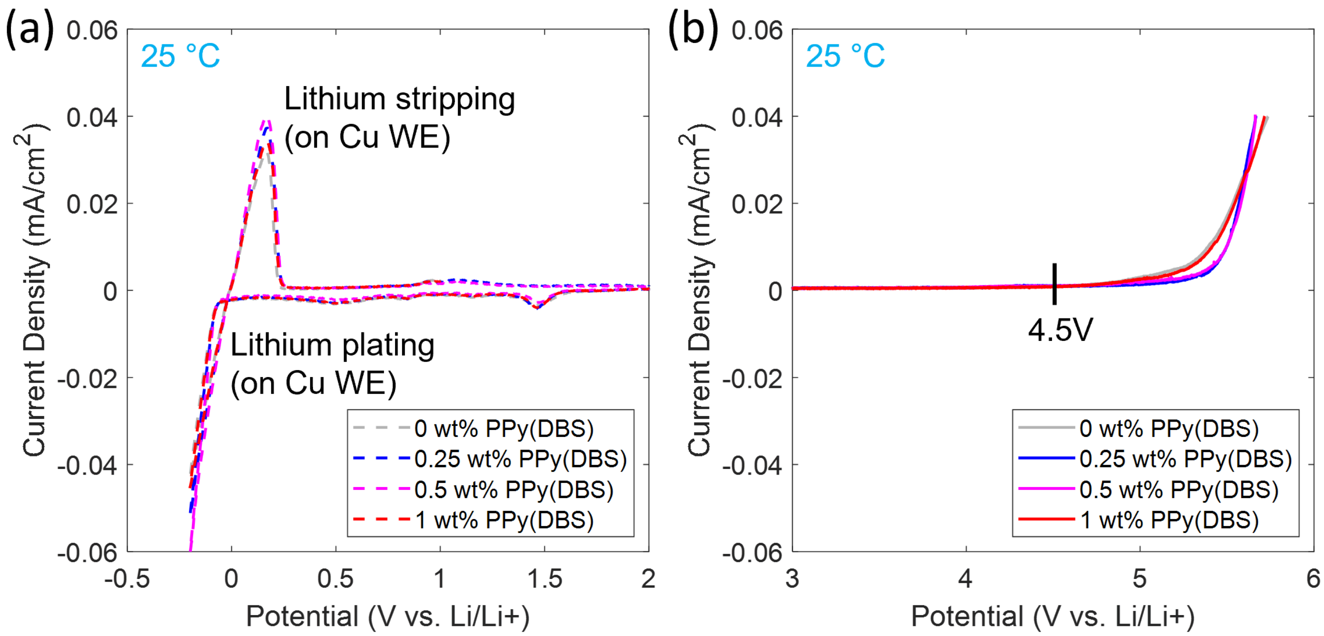

Figure S10. Zoomed-in plots of (a) the cathodic CVs and (b) the anodic LSV for determining ESW of the polymer electrolyte compositions with 0-1 wt% PPy(DBS).