

Electronic Supplementary Information

Boosting Li-S battery performance with an in-cell electropolymerized conductive polymer

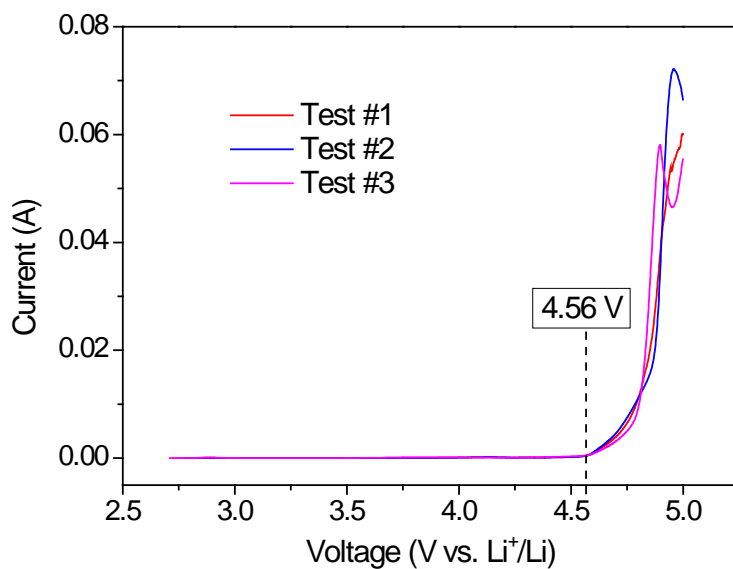


Figure S1 Linear sweep voltammetry (LSV) curves of the electrolyte 1M LiTFSI in 1:1 (v/v) DOL/DME with 2 wt% LiNO₃. Carbon paper was used as the working electrode. Three tests were performed.

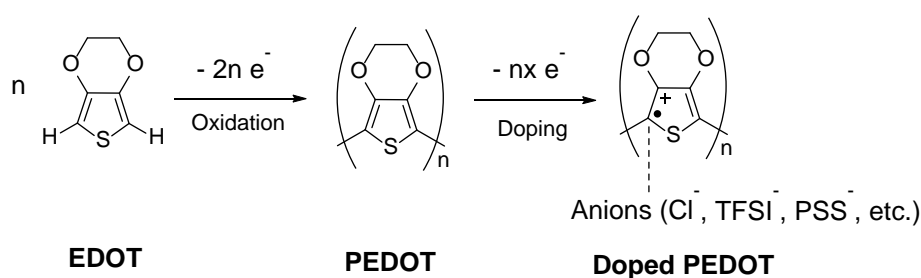


Figure S2 Schematic showing the oxidation of EDOT and the doping of PEDOT via e-polymerization. It should be noted that the oxidation of monomer and the doping of polymer occur simultaneously. The electron transferred per repeat unit during doping or doping level (x) is typically between 0.25 and 0.4.¹ The amounts of charge injected during e-polymerization are calculated as follows.

If 40 μL of 60 mM EDOT-containing electrolyte is used, the amount of charge needed for the oxidation of all the EDOT monomers is:

$$(40 \times 10^{-6} \text{ L}) \times (60 \times 10^{-3} \text{ mol/L}) \times 2 \times \left(96500 \frac{\text{C}}{\text{mol}}\right) = 0.46 \text{ C}$$

The amount of charge needed for the p-doping of the resultant polymers at a doping level of 0.4 is:

$$(40 \times 10^{-6} \text{ L}) \times (60 \times 10^{-3} \text{ mol/L}) \times 0.4 \times \left(96500 \frac{\text{C}}{\text{mol}}\right) = 0.092 \text{ C}$$

Therefore, the total amount of charge needed is: $0.46 \text{ C} + 0.092 \text{ C} = 0.552 \text{ C}$

The amount of the background charge injected into the cell under the potential of 3.8 or 3.9 V when polymerization does not occur is 0.16 C. So the effective charges injected into the cell for polymerization and doping under the potentials of 4.05, 4.10 and 4.15 V are:

$$4.05 \text{ V: } 0.54 \text{ C} - 0.16 \text{ C} = 0.38 \text{ C}$$

$$4.10 \text{ V: } 0.72 \text{ C} - 0.16 \text{ C} = 0.56 \text{ C}$$

$$4.15 \text{ V: } 2.32 \text{ C} - 0.16 \text{ C} = 2.16 \text{ C}$$

Based on the above calculation, the amount (0.56 C) of effective charge injected into the cell at 4.10 V is close to the calculated amount (0.55 C) of charge needed for the oxidation of monomers (polymerization) and the doping of resultant polymer.

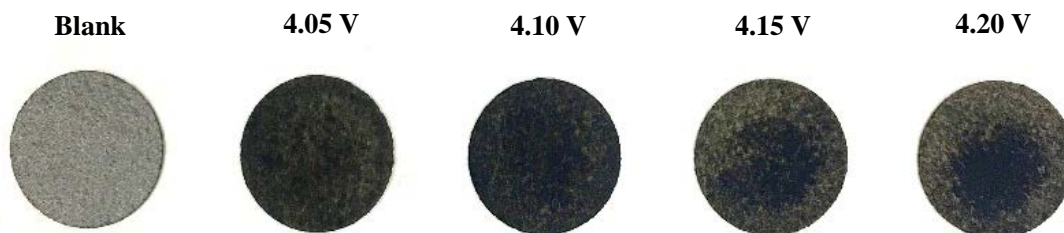


Figure S3 Photos of carbon papers with e-PEDOT synthesized at different potentials.

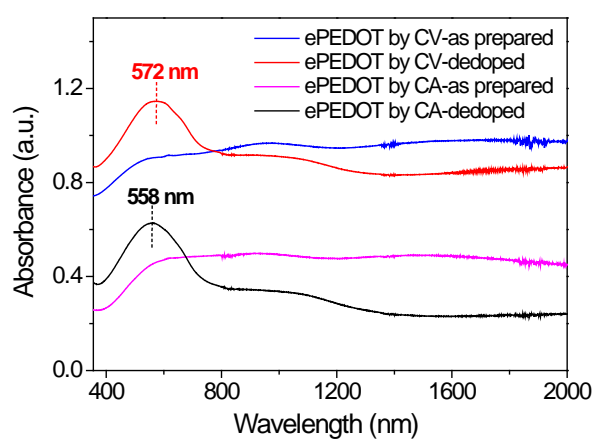


Figure S4 Comparison of the UV-Vis-NIR spectra of the e-PEDOT prepared by the CV and CA methods. The conditions for the CV and CA methods are 3~4.2 V for 10 cycles with a scan rate of 20 mV s^{-1} and 4.1 V for 800 s, respectively.

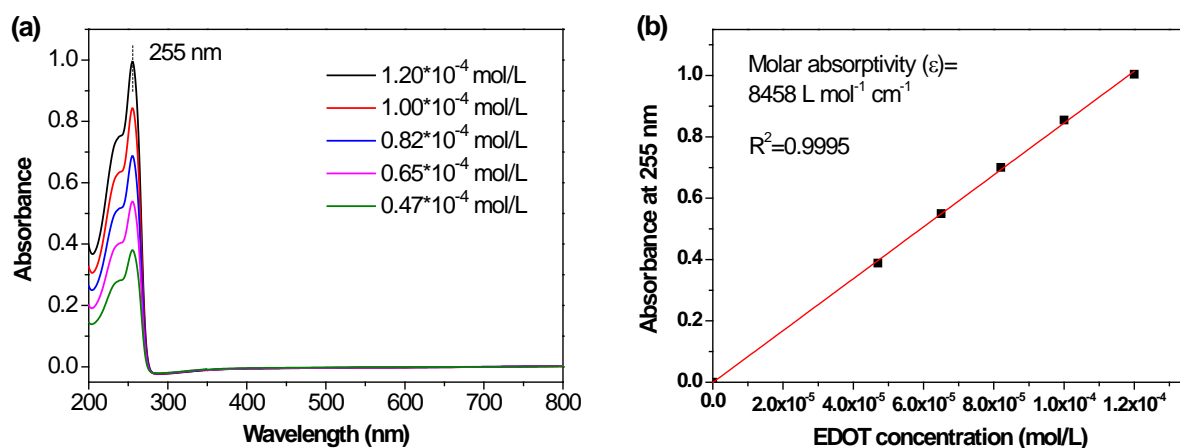


Figure S5 (a) UV-Vis spectra of a series of EDOT aqueous solutions with different concentrations. (b) Linear plot of the absorbance (at 255 nm) of EDOT at different concentrations. Details follow.

A series of EDOT aqueous solutions with known concentrations were prepared. The UV-Vis spectra of the as-prepared standard solutions were measured (Figure S6a). The peak position of EDOT in the aqueous solution is the same as the reported value.² The linear plot of the absorbance at different concentrations is performed. The molar absorptivity (ϵ) of EDOT is determined to be $8.458 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ based on the Beer-Lambert law.

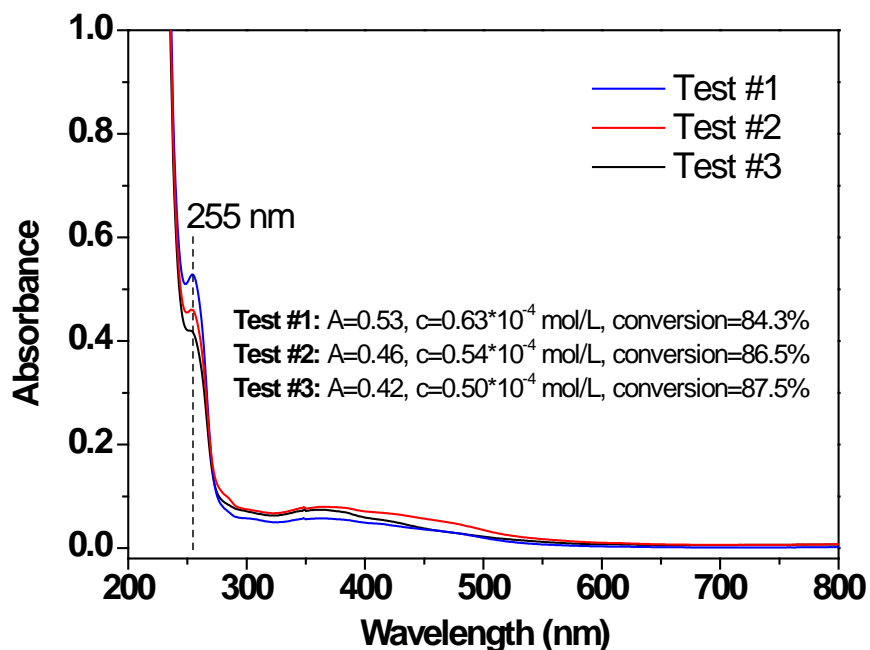


Figure S6 UV-Vis spectra of the diluted electrolyte solutions after e-polymerization at 4.10 V vs. Li/Li⁺ for 800 s using the CA method with electrodes having Super P/H-PSS (weight ratio of 4:1) on carbon-coated Al substrates. Three experiments were performed to obtain an average EDOT monomer conversion of 86%. Details follow.

After e-polymerization, the coin cells were opened and all the cell parts (cathode case, anode case, cathode film, separator, lithium foil) were soaked in 3 mL of DME with gentle shaking. Then the solution was treated with a rotovap to remove the majority of DME solvent. The residual solution was about 0.1 mL. After that the residual solution was diluted with 3 mL water and the UV-Vis spectra was measured.

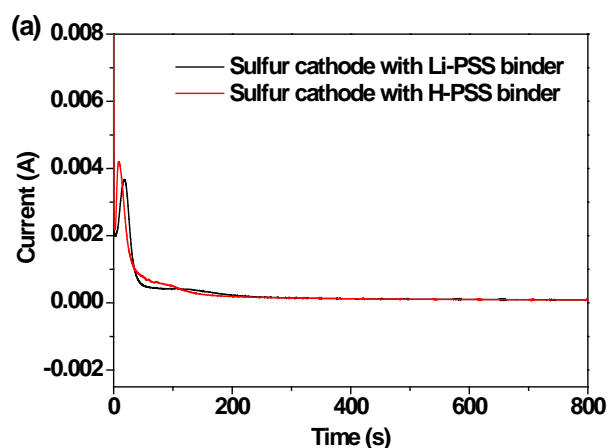


Figure S7 Chronoamperograms for the sulfur cathodes with Li-PSS or H-PSS binder. The Li-S cells were held at 4.10 V vs. Li/Li⁺ for 800 s.

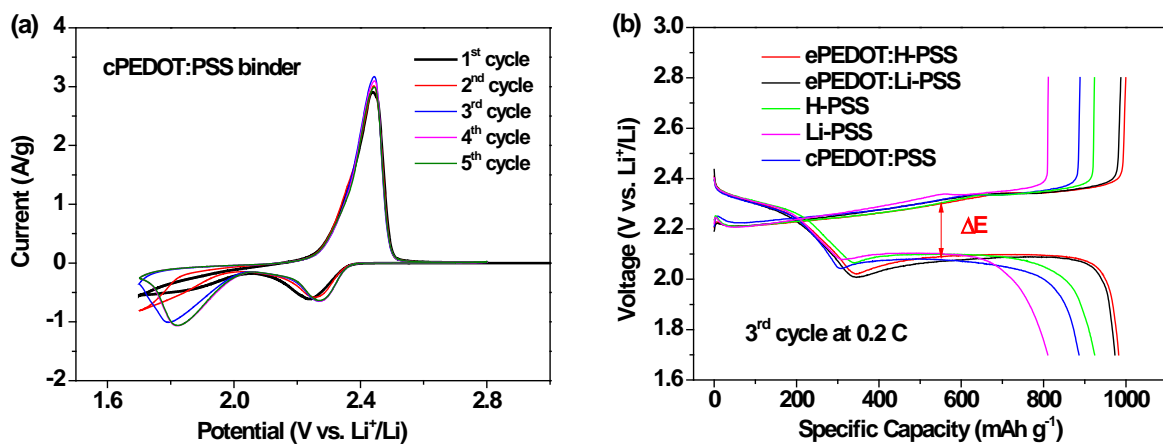


Figure S8 (a) CV of a sulfur cathode using cPEDOT:PSS binder. (b) Charge/discharge profiles of sulfur cathodes using ePEDOT:H-PSS, ePEDOT:Li-PSS, H-PSS, Li-PSS and cPEDOT:PSS binders for the third cycle 0.2 C. The potential difference between the charge and discharge curves at the capacity of 550 mAh/g was used to calculate the polarization potentials at 0.2 C for the sulfur cathodes using different binders.

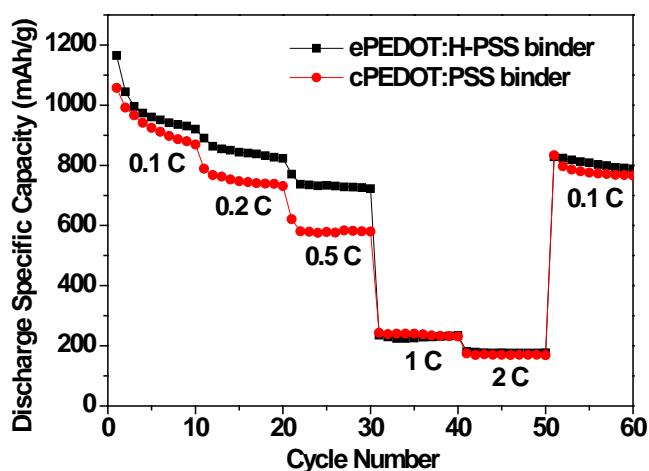


Figure S9 Rate performance of sulfur cathodes using ePEDOT:H-PSS and cPEDOT:PSS binders.

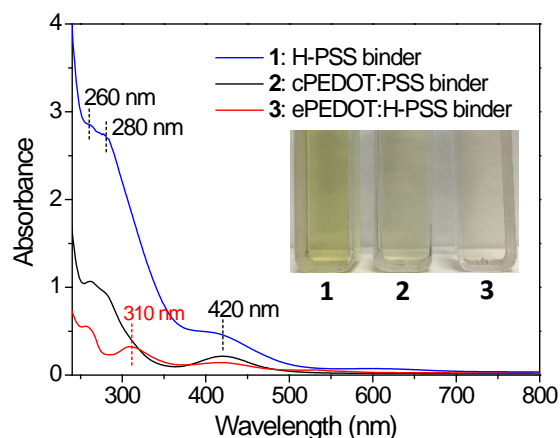


Figure S10 Comparison of lithium polysulfide dissolution in the electrolyte for the sulfur cathodes using different binders. Inset shows the photos of polysulfide solutions in the cuvettes. The respective batteries, cycled for 100 cycles and stopped in the charged state, were disassemble in a glovebox. For each cell, all the components were soaked in 5 mL of DOL/DME (v/v=1/1) and shaken manually for 3 min. After that the UV spectra of the supernatant were recorded. Both ePEDOT and cPEDOT showed obvious polysulfide trapping effects although the absorption profiles of their electrolyte solutions are somehow different, which might be due to the different chain stacking of ePEDOT and cPEDOT in the cathode composites.

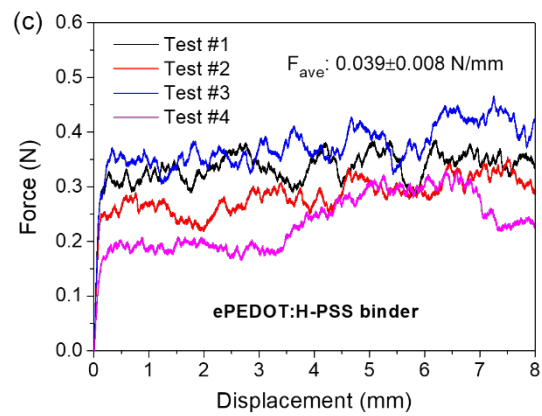
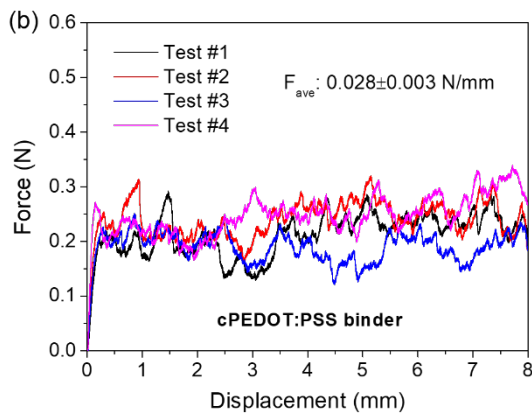
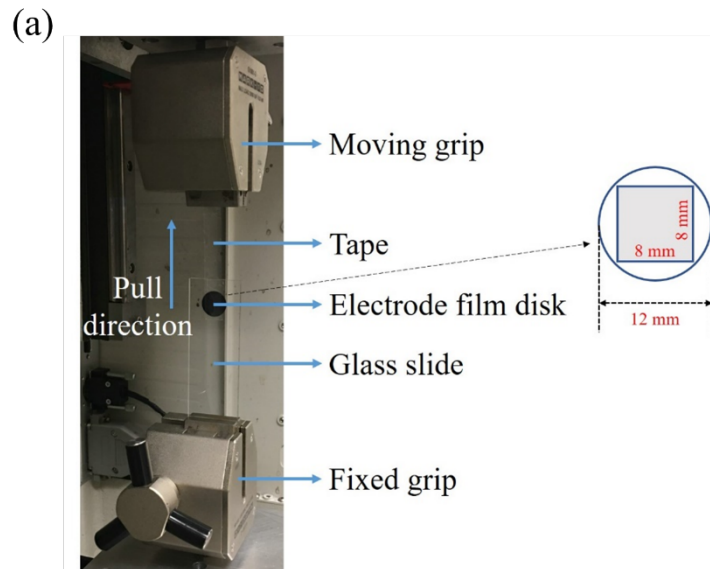


Figure S11 (a) Photos of the mechanical tester for peel test. Load force vs. displacement curves for sulfur cathode films using (b) cPEDOT:PSS binder and (c) ePEDOT:H-PSS binder.

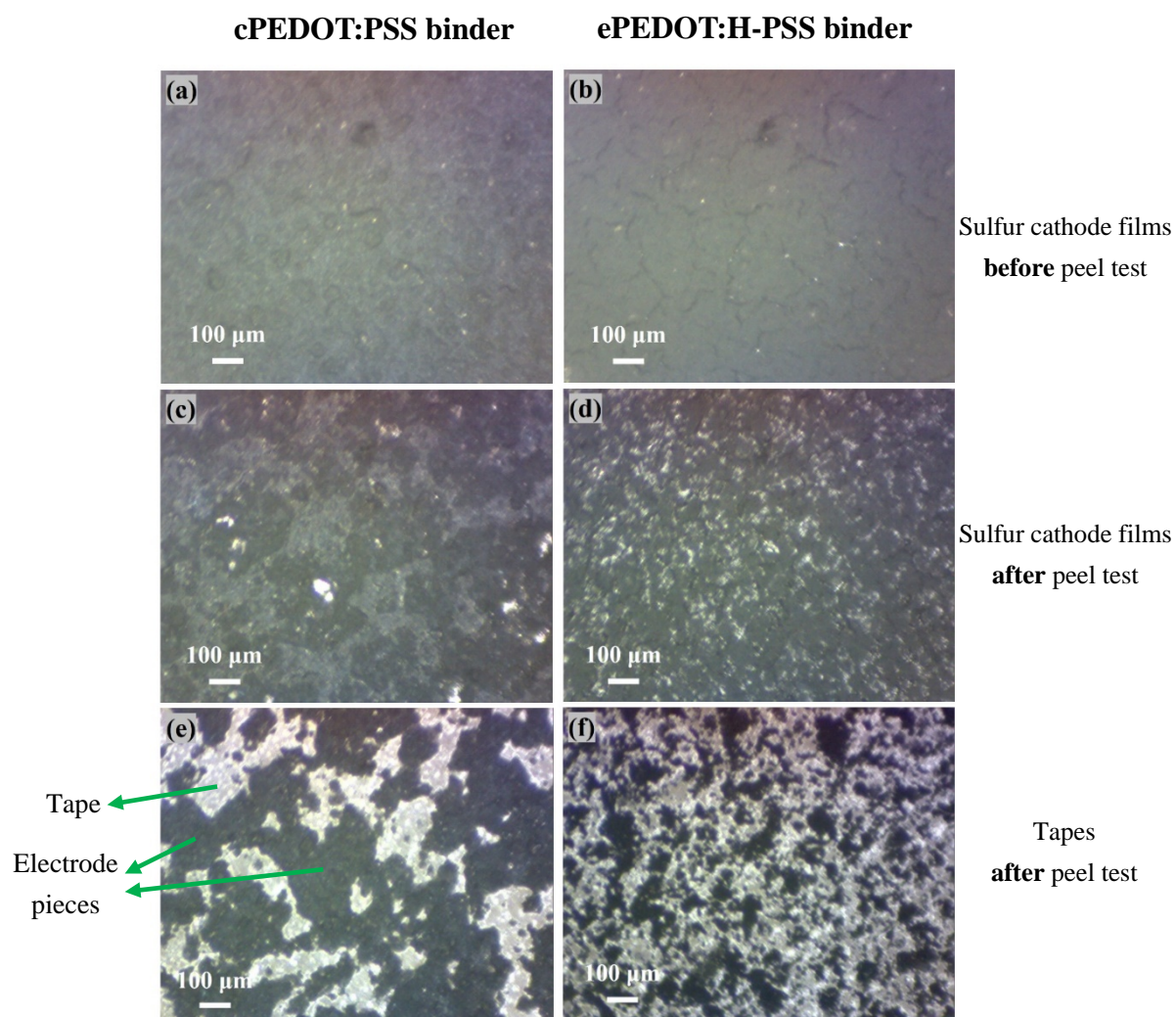


Figure S12 Optical images of sulfur cathode films before and after peel test, and tapes after peel test. Sulfur cathode film with the cPEDOT:PSS binder (a) before peel test, (c) after peel test, and (e) tape after peel test. Sulfur cathode film with the ePEDOT:H-PSS binder (b) before peel test, (d) after peel test, and (f) tape after peel test.

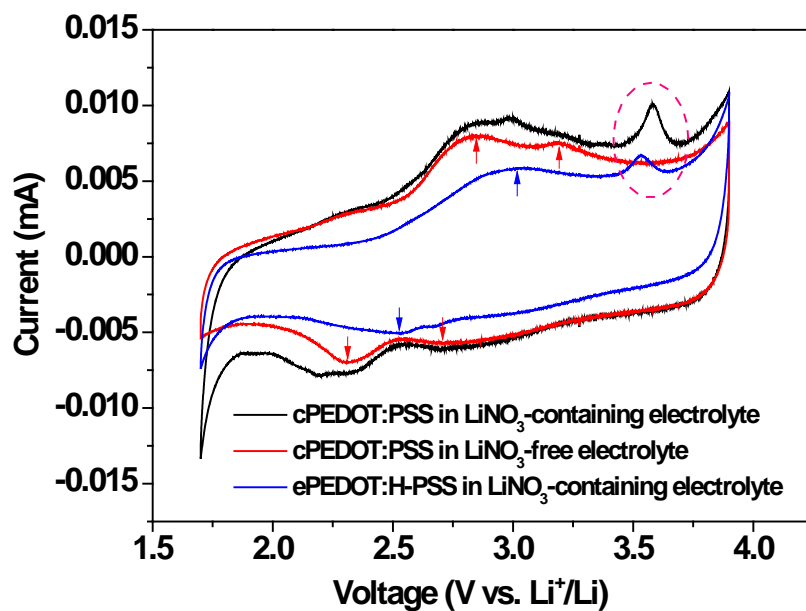


Figure S13 Comparison of the CV curves of ePEDOT:H-PSS and commercial cPEDOT:PSS in LiNO_3 -containing and LiNO_3 -free electrolytes. The ePEDOT was deposited on a Super P/H-PSS substrate via the chronoamperometry method, while the commercial cPEDOT:PSS was blended with Super P and coated on a Al foil via the slurry coating method. The peak at ~ 3.56 V originates possibly from the oxidation of LiNO_2 that is formed from the reduction of LiNO_3 by Li metal as suggested in the literature.^{3,4}

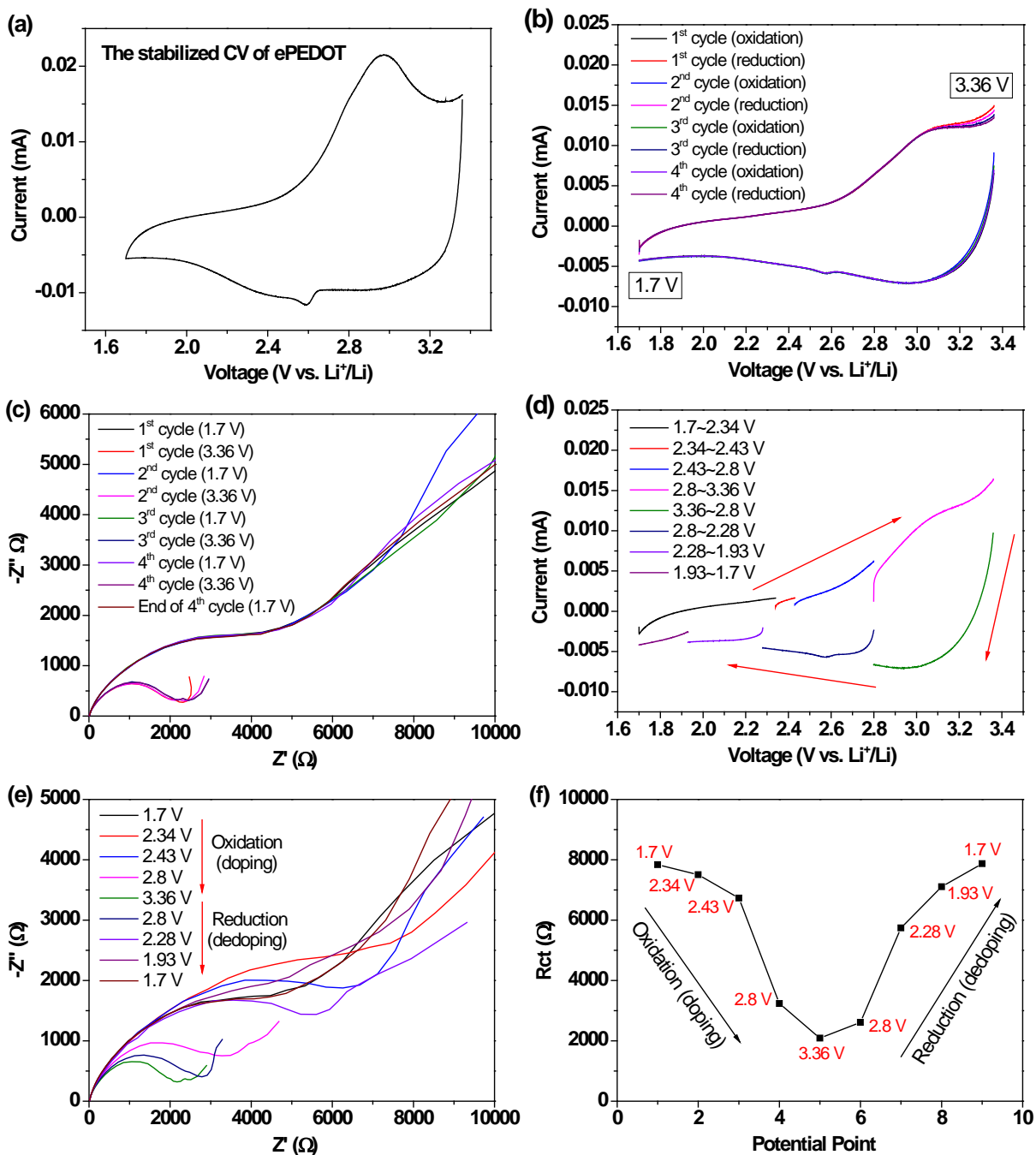


Figure S14 (a) The stabilized CV curve (20th cycle) of a cell having ePEDOT grown on an ITO-coated glass substrate. The ePEDOT-containing cell was prepared by e-polymerization of EDOT in a two-electrode coin cell with ITO and Li as electrodes in 60 mM EDOT-containing electrolyte using the CA method at 4.10 V vs. Li/Li⁺ for 800 s. The cell was subjected to CV cycling between 1.7 and 3.36 V for 20 cycles to obtain a stable CV curve. (b) Combined CV

(or LSV) segments (oxidation and reduction processes) for four consecutive cycles for the same cell in (a). The cell was switched from CV testing to EIS testing at 1.7 V and 3.36 V, respectively. (c) EIS spectra of the cell measured at 1.7 and 3.36 V vs. Li/Li⁺, respectively, for four consecutive CV cycles. (d) Combined CV segments during one cycle of oxidation and reduction processes for the same cell in (a). The cell was switched from CV testing to EIS testing sequentially at 1.7, 2.34, 2.43, 2.8, and 3.36 V for the oxidation process and 2.8, 2.28, 1.93, and 1.7 V for the reverse reduction process. (e) EIS spectra of the cell collected at the potential points shown in (d) during one cycle of oxidation (doping) and reduction (dedoping) processes. (f) Rct values at different potential points derived from the EIS spectra in (e).

References

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- 2 Z. Cui, C. Coletta, T. Bahry, J. L. Marignier, J. M. Guigner, M. Gervais, S. Baiz, F. Goubard and S. Remita, *Mater. Chem. Front.*, 2017, **1**, 879–892.
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