Supporting Information: Polymer-based solid electrolyte interphase for stable lithium metal anodes

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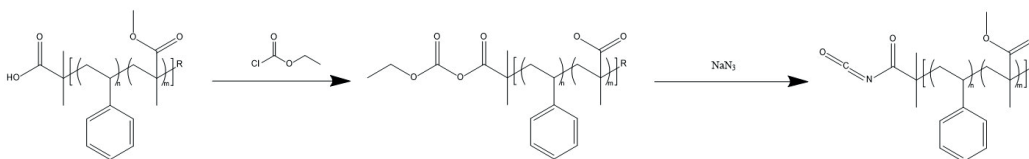43007 Tarragona, Spain

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Figure S1: An isocyanate-driven reaction strategy was implemented to chemically bond the copolymer brush to the lithium hydroxide substrate. The reaction scheme depicts the mechanism of the terminal group conversion from carboxylic acid to isocyanate in the random copolymer brush.
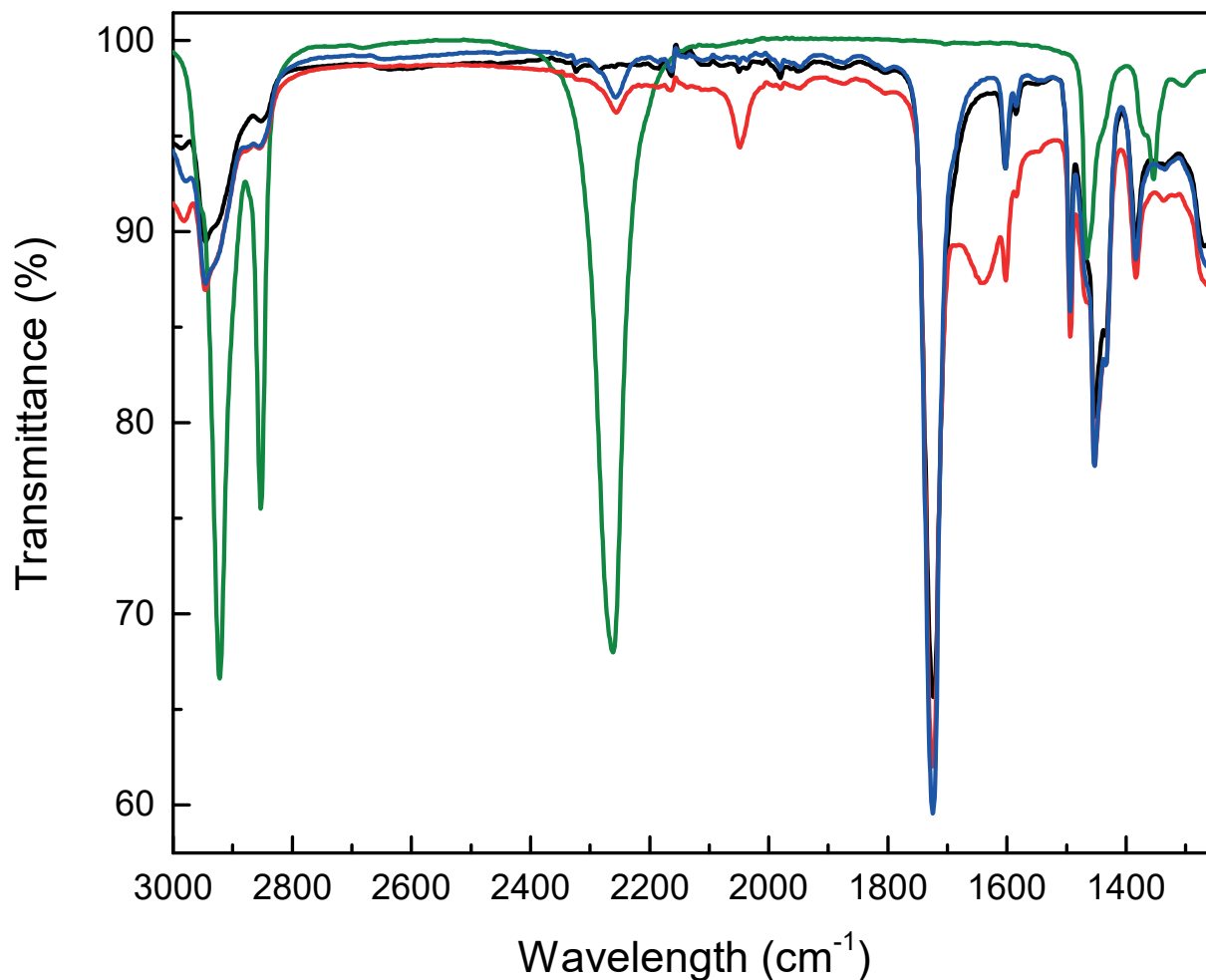
Figure S2: FTIR spectra of the as-received P(S-*r*-MMA) copolymer brush with a carboxylic acid end-group (black trace), after isocyanate end-group conversion (red trace), and after purification (blue trace). The allyl isocyanate reference (green trace) localizes the isocyanate signal, υ_{NCO}, at $2262\,\mathrm{cm}^{-1}$. The isocyanate signal, absent in the carboxylic acid-terminated copolymer, appears in the modified polymer indicating the conversion reaction. The signals at $2047\,\mathrm{cm}^{-1}$ and $1643\,\mathrm{cm}^{-1}$ correspond to impurities and byproducts from the conversion protocol, which vanish following the purification of the final isocyanate-terminated copolymer.
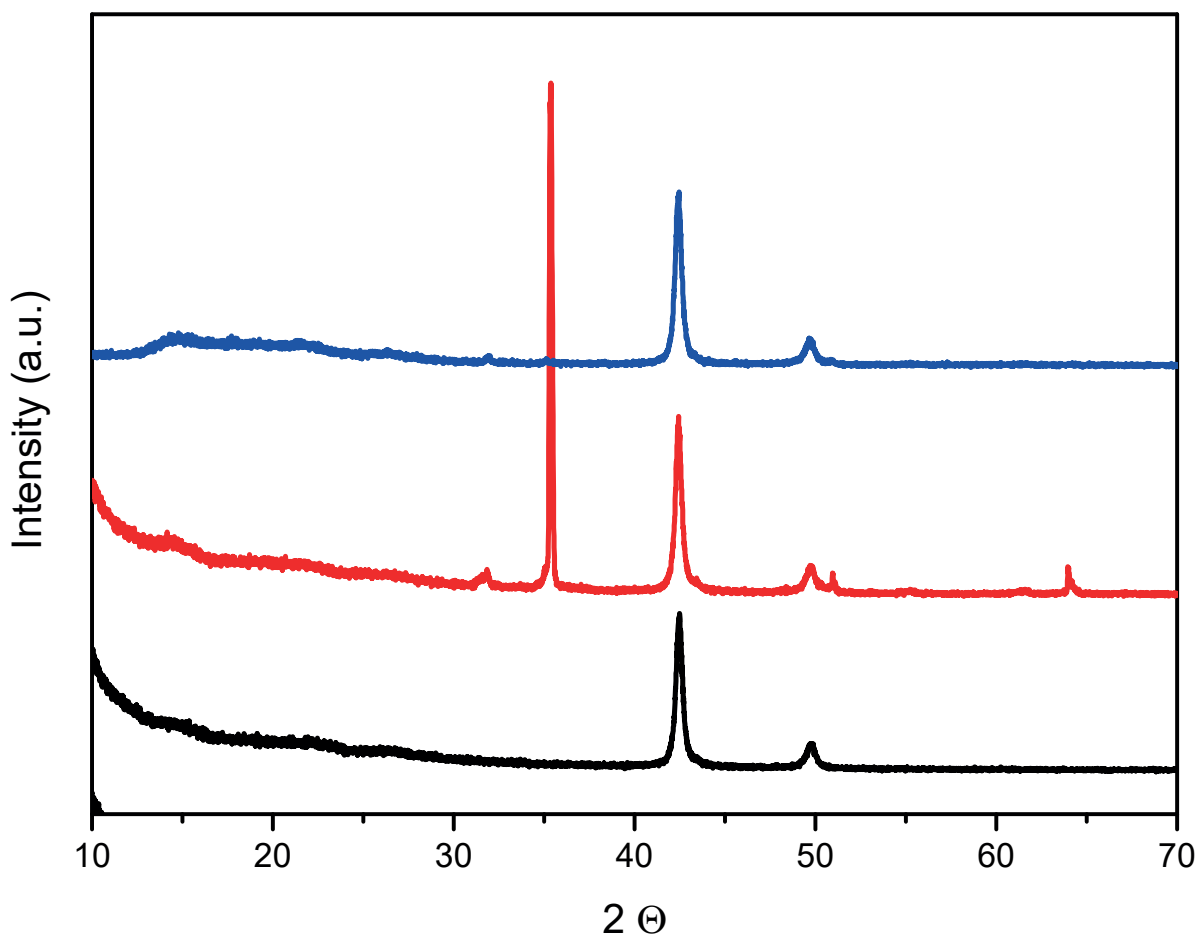
Figure S3: XRD pattern of a P(S-*r*-MMA) copolymer-covered lithium substrate (blue trace) compared with the diffractograms of a pristine lithium substrate (black trace) and a lithium hydroxide-covered substrate (red trace) for peak comparison and assignment. The low scattering angles peaks at 15.58° and 21.5°respectively, indicate the presence of polymeric coverage onto the substrate. Tabulated values of the PMMA and PS homopolymers scattering angles are 15°and 20°.[1]

Energy [eV]

LUMO

\- 4.04

\- 4.25

\- 4.55

\- 4.67

HOMO

Pristine
lithium
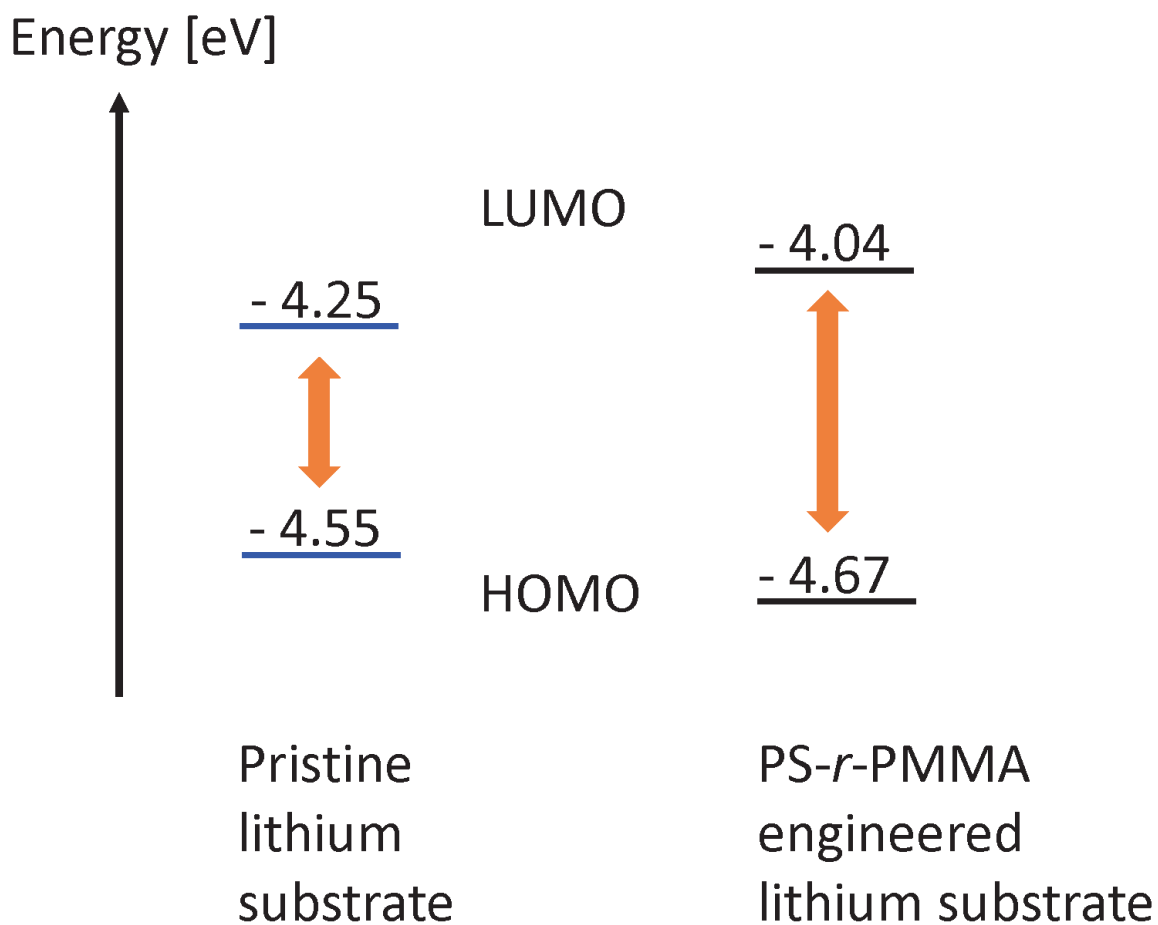substrate

PS-*r*-PMMA
engineered
lithium substrate

Figure S4: Schematic of the HOMO and LUMO energy levels derived from the voltammograms. Quantitative information on the energy levels can be extracted from the empirical equations, $E_{HOMO} = -4.8 - (E_{ox}^{onset} - E_{Ferrocene})$ and $E_{LUMO} = -4.8 - (E_{red}^{onset} - E_{Ferrocene})$.[2,3]
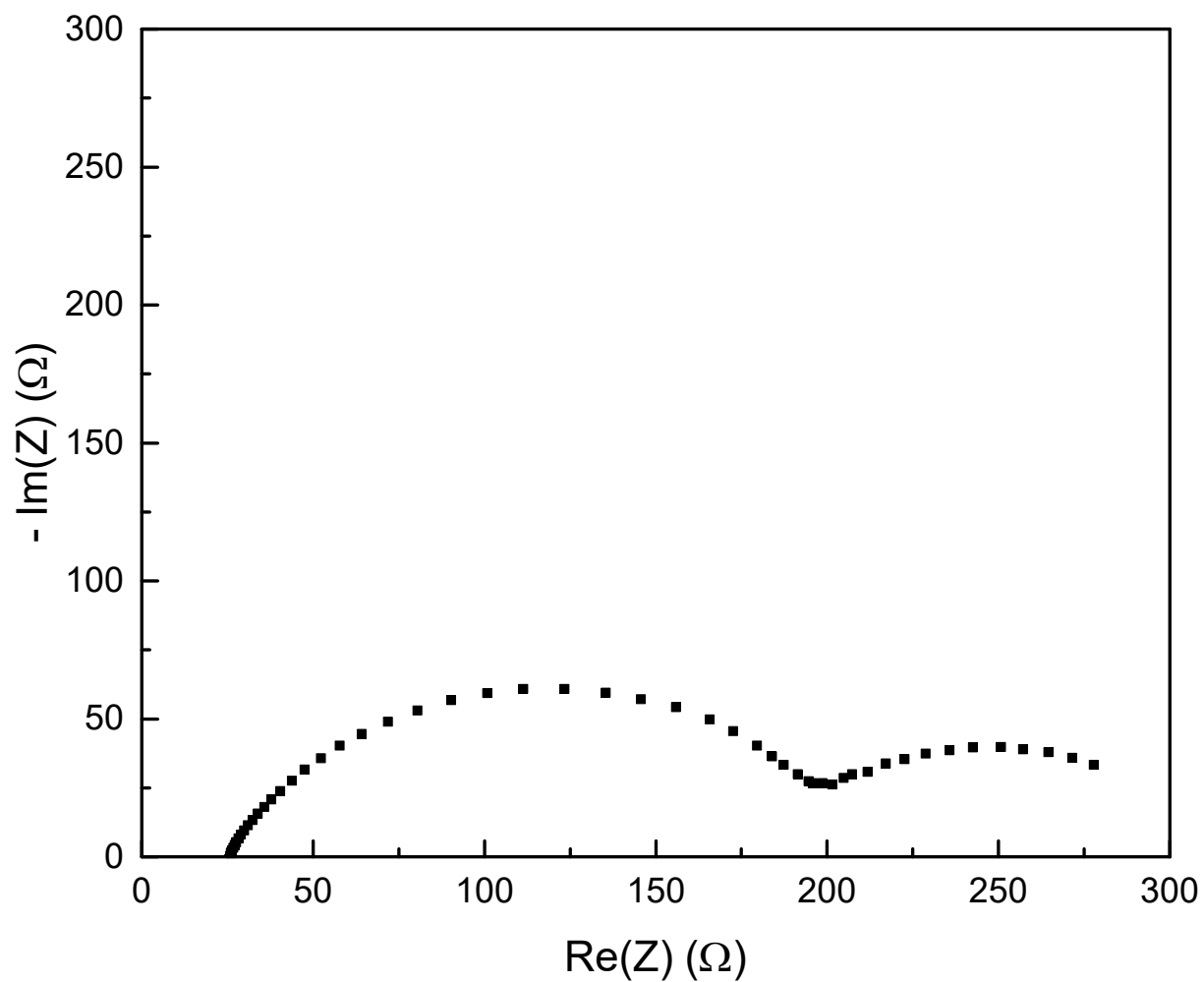
Figure S5: Nyquist plot of a pristine lithium substrate before electrochemical cycling. The trace displays two semicircles. The intrinsic resistance of the metallic substrate is inferred from the intersection with the real axis at an impedance value around ca. 200 Ω, and the second semicircle arises from the native passivation of the lithium substrate.
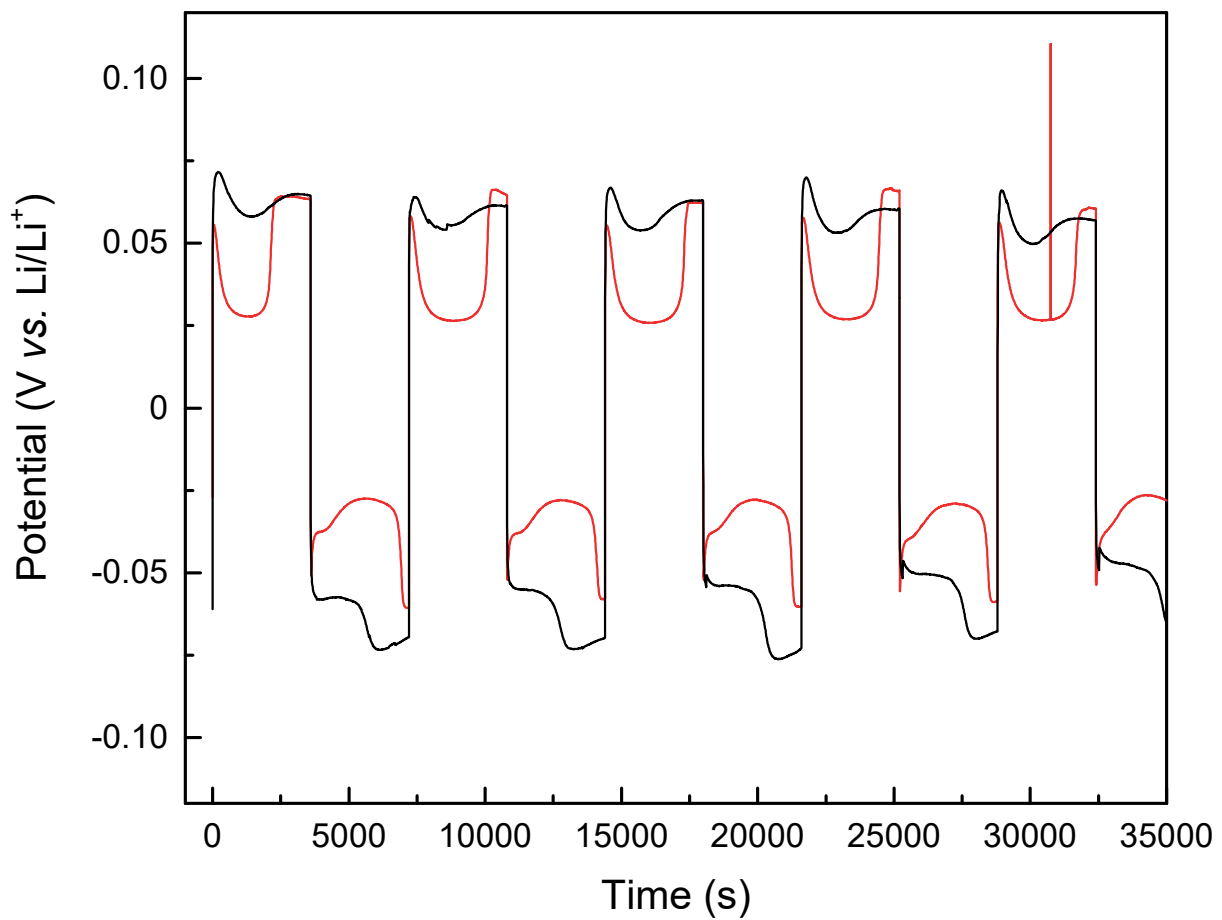
Figure S6: Galvanostatic cycling traces of a pristine lithium substrate (red) and a P(S-*r*-MMA) covered lithium electrode (black), with current of $0.5\,\mathrm{mA}$ (0.25 mA cm^{-2}).
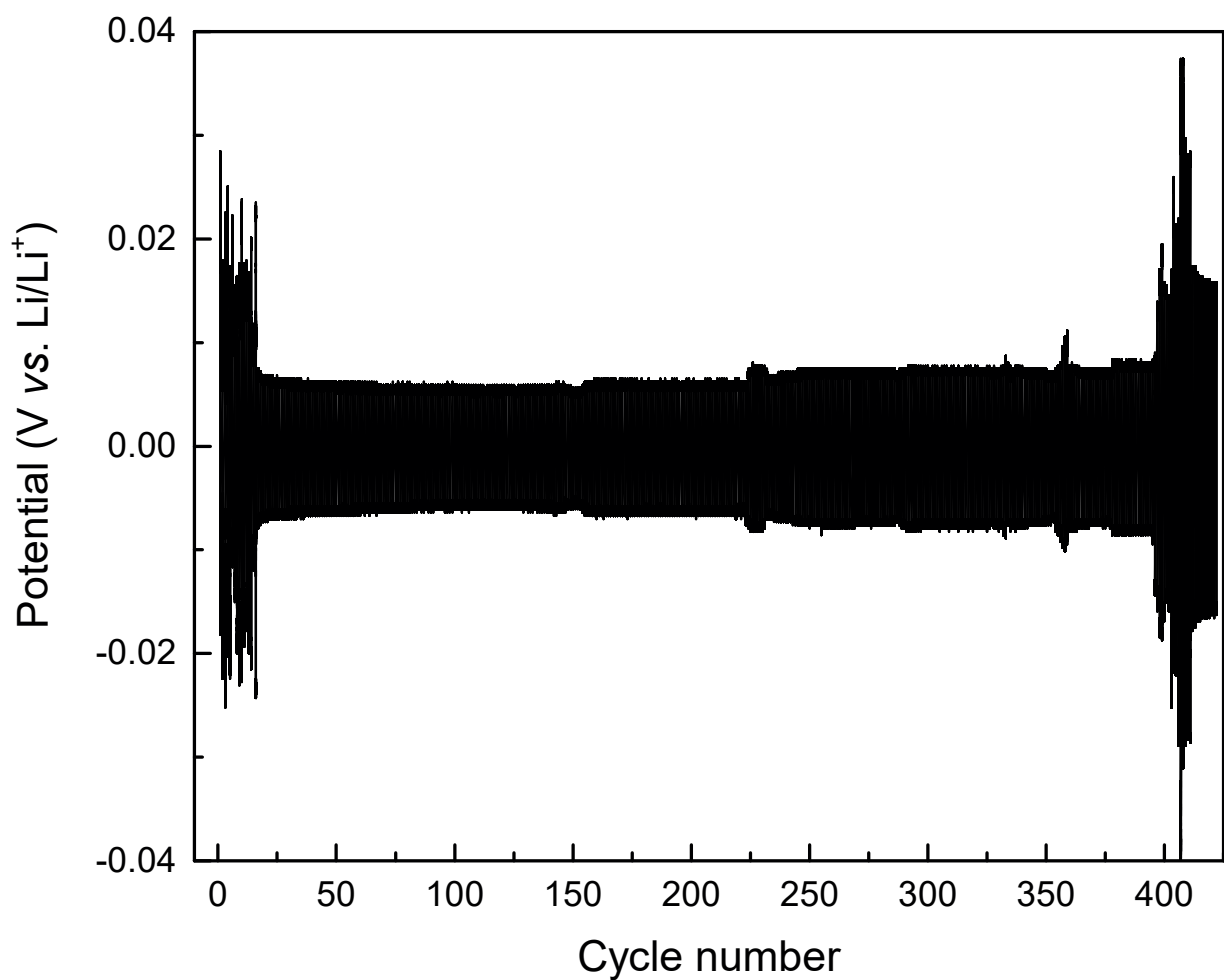
Figure S7: Galvanostatic cycling trance of symmetric P(S-*r*-MMA) covered lithium electrodes, with the commercial liquid electroylte (EC/DMC = 50/50(V/V), 1 M LiPF$_6$) and current of $0.2\,\text{mA}$ (0.1 mA cm^{-2}).

References

(1) Huang, G.; Xu, J.; Geng, P.; Li, J. Carrier Flotation of Low-Rank Coal with Polystyrene. *Minerals* **2020**, *10*.

(2) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Advanced Materials* **2011**, *23*, 2367–2371.

(3) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. Efficient Two Layer LEDs on a Polymer Blend Basis. *Advanced Materials* **1995**, *7*, 551–554.