

Mechanistic Implications of Li-S Cell Function Through Modification of Organo-Sulfur Cathode Architectures

Lisa Djuandhi,^a Neeraj Sharma,^{*a} Bruce C. C. Cowie,^b Thanh V. Nguyen^a and Aditya Rawal^{*c}

^aSchool of Chemistry, UNSW Sydney, NSW 2052, Australia

^bAustralian Synchrotron, Clayton, Victoria 3168, Australia

^cMark Wainwright Analytical Centre, UNSW Sydney, NSW 2052, Australia.

Supporting Information

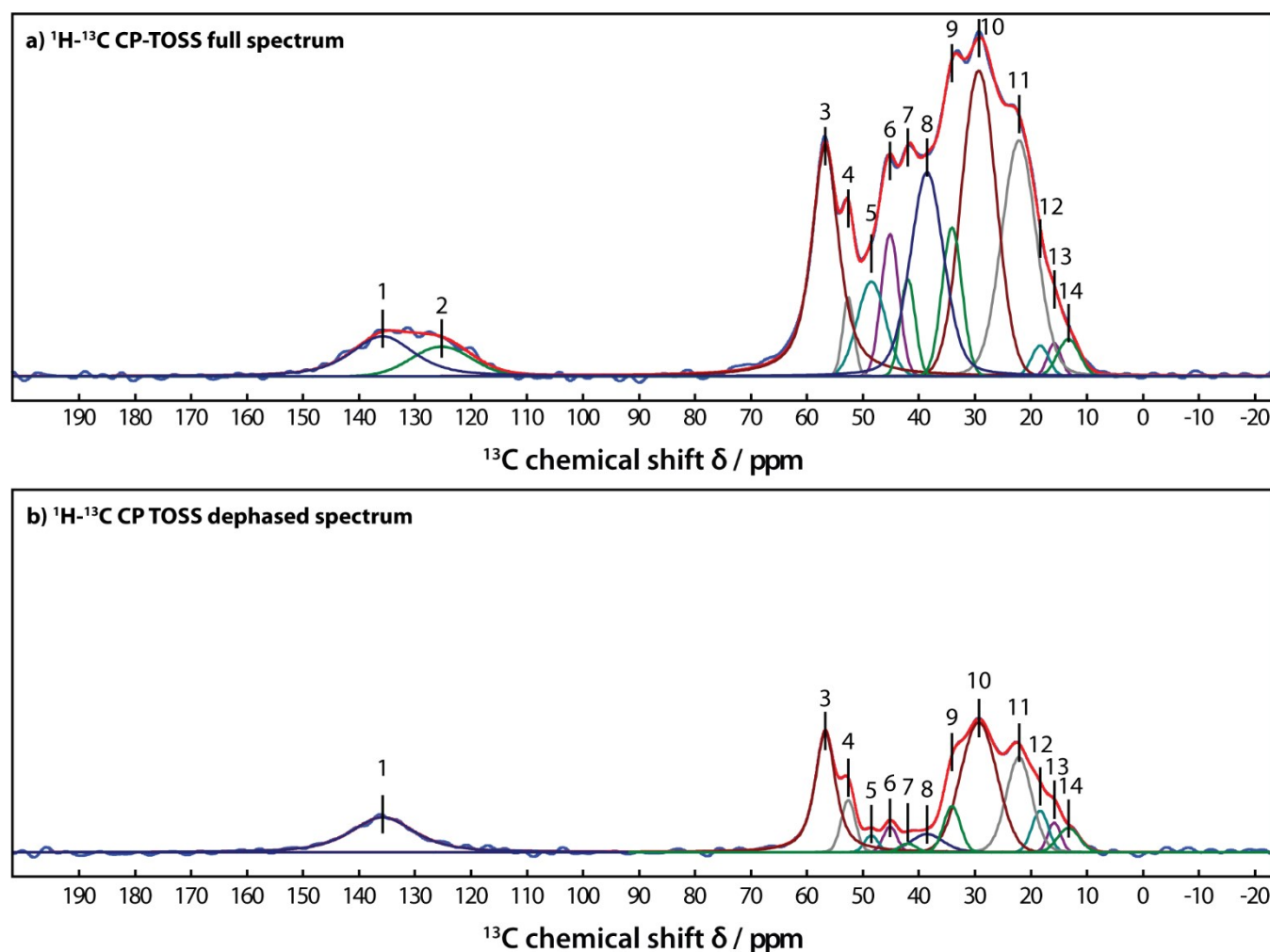


Figure S 1. Deconvolution and elucidation of the peak centres of **a)** the full and **b)** dephased ^1H - ^{13}C CP-TOSS spectra of the as-synthesised poly(S - γ -squalene) copolymer also explored in the main article in **Figure 1a** (blue and red peak areas respectively). Details regarding the profiles and fit results of each peak annotated 1-14 are provided below in the **SI Table S 1**

Table S 1. Peak deconvolution fit results based on ^1H - ^{13}C CP-TOSS of poly(*S*-r-squalene) visualised in the SI **Figure S 1**.

no.	$\delta_{13\text{C}}$ / ppm	a) full spectrum					b) dephased spectrum				
		amp / a.u.	wid / ppm	xG/(1-x)L	Intensity / a.u.	% area	amp / a.u.	wid / ppm	xG/(1-x)L	Intensity / a.u.	% area
1	133.83	99.37	13.28	0.41	131607.4	6.01	86.69	13.43	0.41	116038	15.5
2	123.32	73.45	12.64	1	74502.78	3.4	0	0	1	0	0
3	54.77	573.83	5.67	0.27	346836.3	15.84	299.52	4.32	0.27	138281.4	18.47
4	50.66	195.46	2.37	0.91	38696.28	1.77	129.07	3	0.91	32355.1	4.32
5	46.54	234.44	5.97	1	112332.8	5.13	41.34	2.88	1	9565.02	1.28
6	43.2	351.92	3.74	1	105463.5	4.82	63.13	2.91	1	14762.64	1.97
7	40.03	240.86	3.12	1	60259.95	2.75	21.18	3.5	1	5940.49	0.79
8	36.59	506.55	7	0.73	318384.4	14.54	44.87	6.86	0.73	27630.63	3.69
9	32.14	368.31	4.21	1	124267.2	5.68	113.48	3.56	1	32421.67	4.33
10	27.36	757.05	7.33	1	445192.4	20.34	321.8	7.68	1	198338.9	26.5
11	20.18	584.2	7.27	0.89	356657.4	16.29	235.39	5.38	0.89	106508.9	14.23
12	16.4	75.62	3.64	1	22060.79	1.01	102.13	3.5	1	28686.62	3.83
13	13.87	82.36	2.86	1	18919.01	0.86	73.02	2.73	1	15972.62	2.13
14	11.33	92.14	4.57	1	33807.94	1.54	59.78	4.59	1	22033.4	2.94

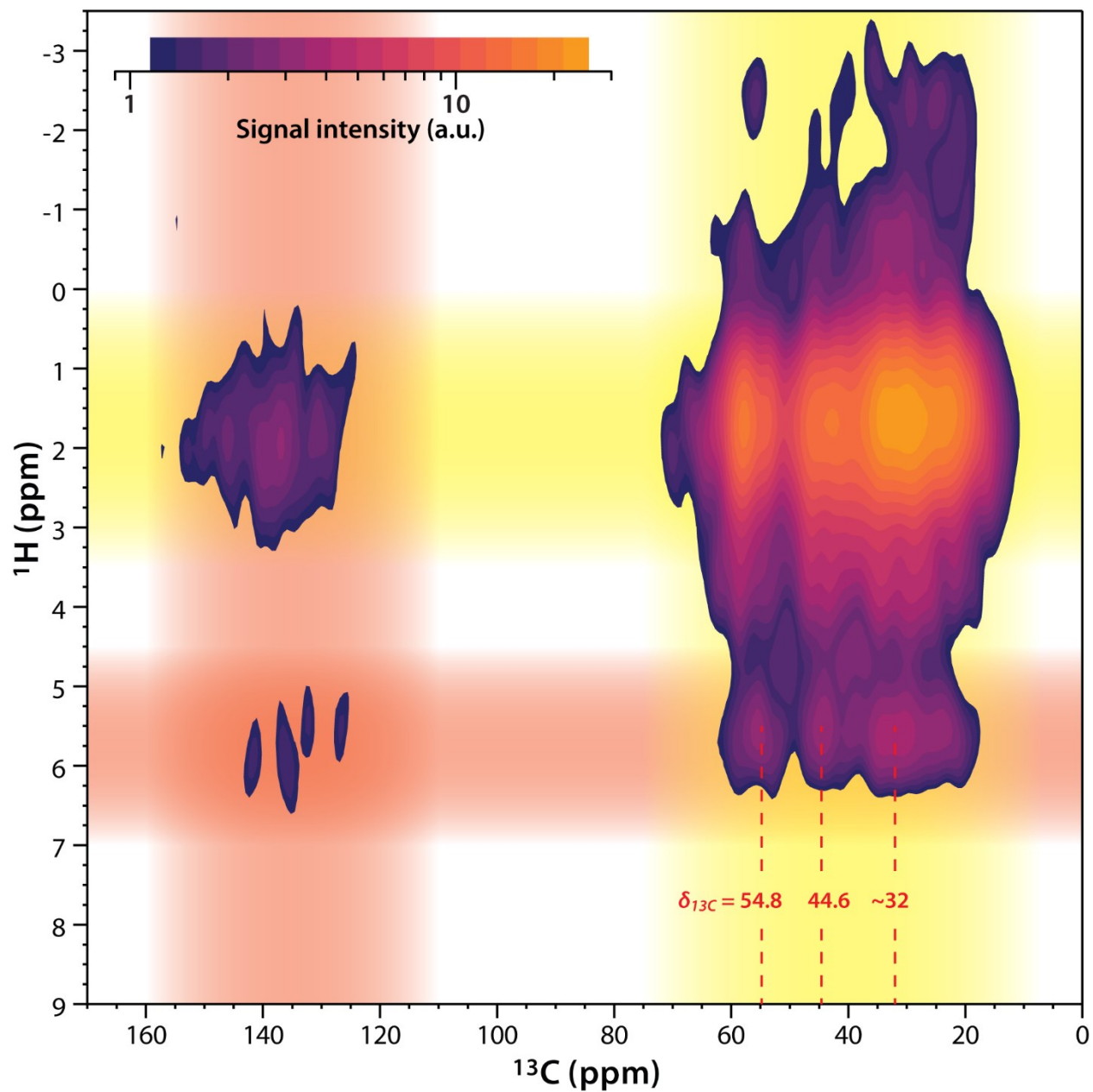


Figure S2. ^1H - ^{13}C HETCOR NMR spectrum of poly(*S-r*-squalene), also shown in the main article in **Figure 8b**.

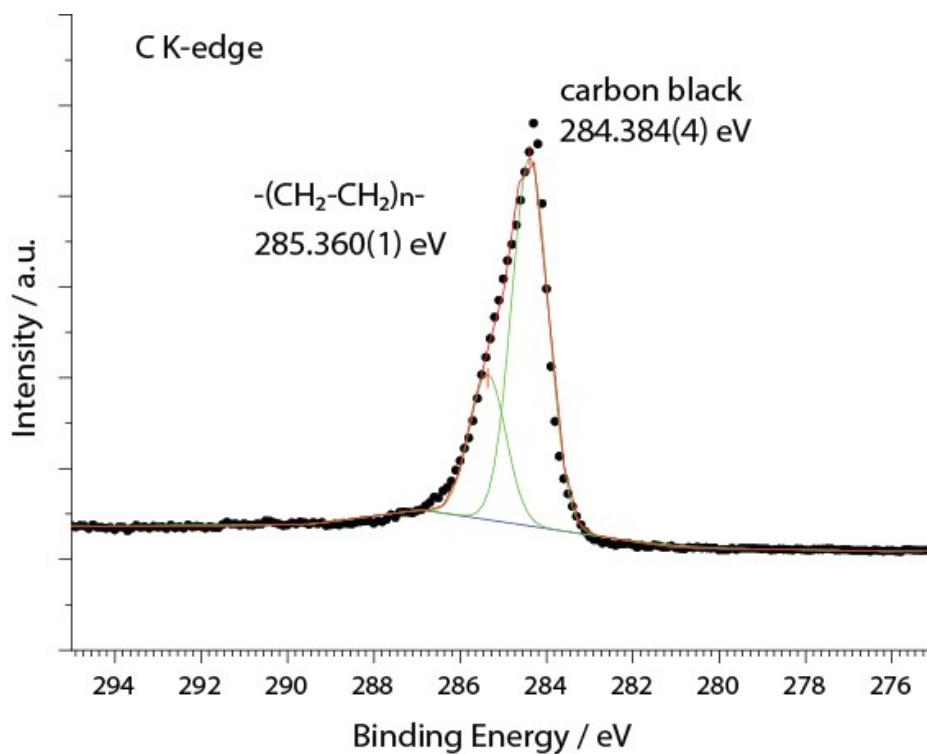


Figure S3. High resolution carbon K-edge soft-XPS spectrum collected using synchrotron radiation energy set at 730 eV of a poly(S-r-squalene) cathode. The black dots indicate collected data points, blue trace calculated baseline, green traces are the gaussian peak fits, and the red trace is the cumulative fit of the peaks. Red peak markers denote the peak centres.

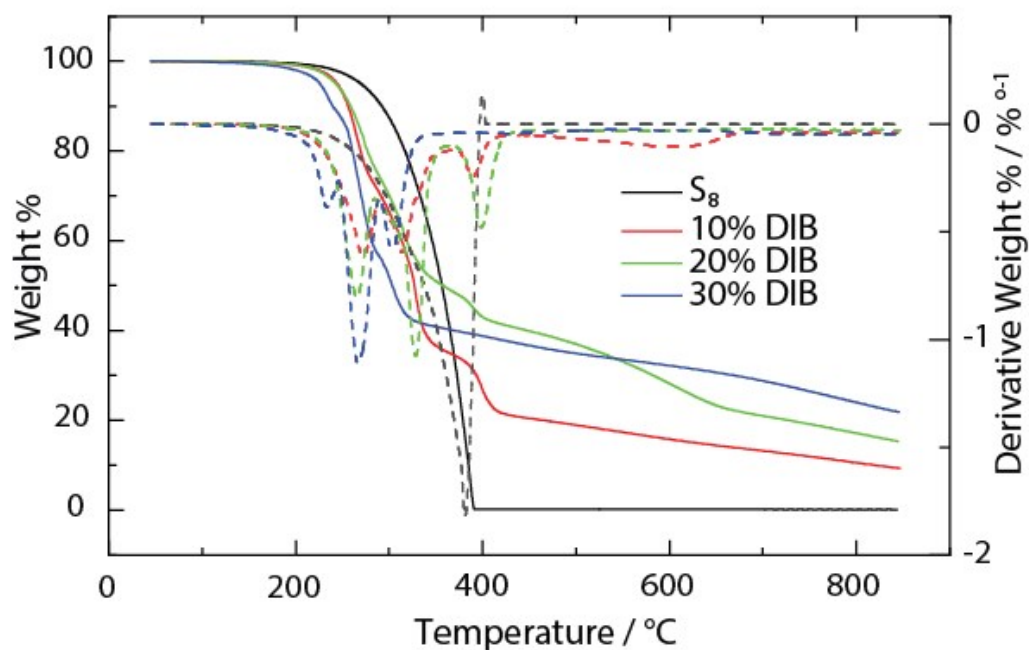


Figure S4. Thermogravimetric analysis data (bold lines) and the first derivative (DTG, dashed lines) of elemental sulfur (black), and poly(S-r-DIB) synthesised using 10% (red), 20% (green), and 30% (blue) weight DIB feeds.

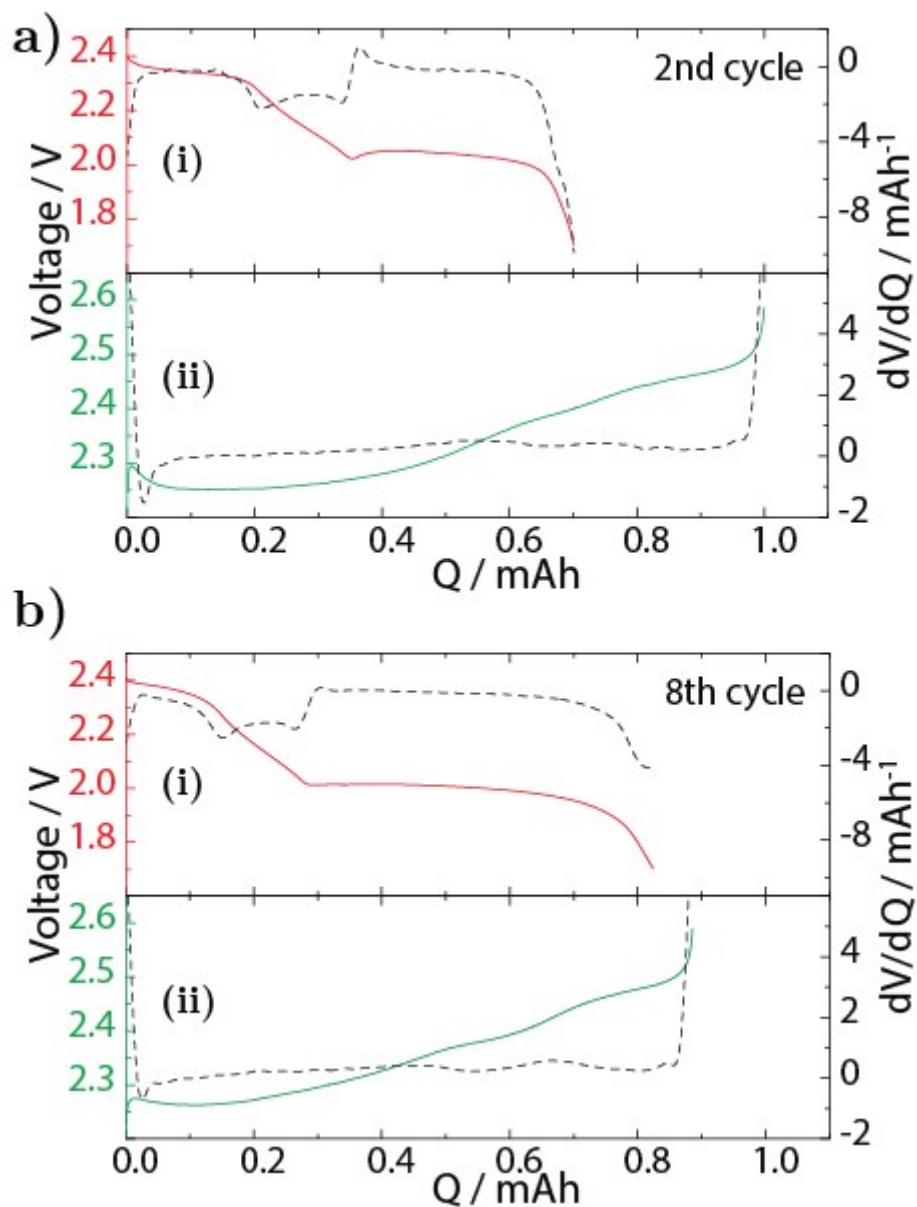


Figure S5. Voltage capacitance plots (discharge and charge plots correspond to red and green traces respectively) and the derivative (dV/dQ , dashed black traces) of Li-S cells using poly(S-r-squalene) as the active cathode material extracted at **a)** the 2nd cycle **i)** discharge and **ii)** charge and **b)** the 8th cycle. **i)** discharge and **ii)** charge. This data corresponds to samples used for ex-situ XANES characterisation featured in Figure 6 of the main article, with a)i) corresponding to the red traces in Figure 6ai and bi, a)ii) to the green traces in Figure 6ai and bi, b)i) to the red traces in Figure 6aii and bii, and b)ii) the green traces in Figure 6aii and bii.

Table S2. Fit results of peak deconvolution via least-squares method using Gaussian/Lorentzian line shapes to the 1D ^7Li MAS spectrum measured for 20th discharge (spectrum in **Figure 8ai**). The Gaussian/Lorentzian ratio is included in the fitting protocol by the $xG/(1-x)L$ parameter wherein G = Gaussian, L = Lorentzian, meaning that when $x = 1$ the line shape is purely Gaussian and when $x = 0$ the line shape is purely Lorentzian.

^7Li (ppm)	% Peak	$xG/(1-x)L$
3.5	68.9(6)	0
1.1	30.1(7)	0
0.0	1.0(1)	0

Table S3. Fit results of peak deconvolution via least-squares method using Gaussian/Lorentzian line shapes to the 1D ^1H - ^7Li CP-MAS spectrum measured for 20th discharge (spectrum in **Figure 8ai**). The Gaussian/Lorentzian ratio is included in the fitting protocol by the $xG/(1-x)L$ parameter wherein G = Gaussian, L = Lorentzian, meaning that when $x = 1$ the line shape is purely Gaussian and when $x = 0$ the line shape is purely Lorentzian.

^7Li (ppm)	% Peak	$xG/(1-x)L$
3.5	34.3(6)	1
1.1	65.7(6)	0.5

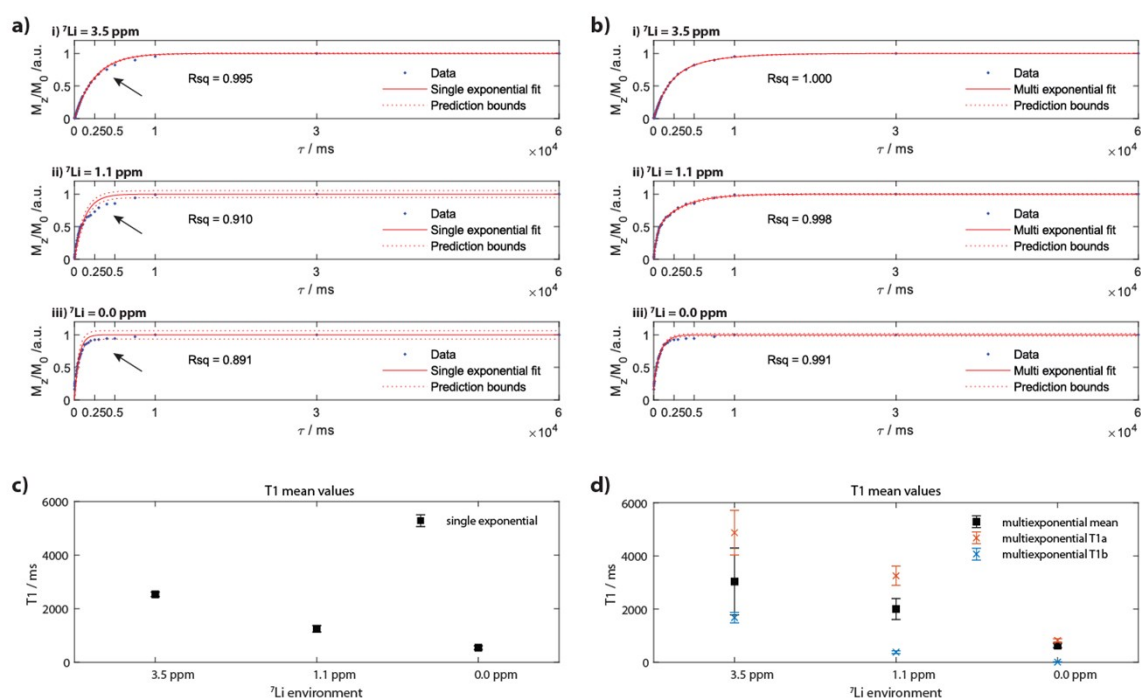


Figure S 6. Spin-lattice (T_1) relaxation times of lithium environments measured for the poly(*S-r-squalene*) electrode extracted after 20th discharge via a series of saturation recovery experiments conducted with various delays $\tau = 10$ ms to 60 s. **a)** Single-exponential function fitting regime and **b)** multi-exponential function fitting regime used to model the data of each lithium environment. **c)** T_1 values extracted from the fits based on the **i)** single-exponential fit function model and **ii)** multi-exponential fit function model

Table S 4. T1 relaxation times of three main lithium environments observed in electrochemically lithiated poly(S-r-squalene) extrapolated

from a single exponential fitting regime, $\frac{S_z}{S_0} = 1 - e^{-\frac{\tau}{T1}}$, wherein S_z is the signal absolute value, S_0 signal anticipated at equilibrium taken as the signal measured at the longest delay $\tau = 60$ s, τ the applied T1 relaxation delay before the final $\pi/2$ pulse is applied. This tabulated data relates to the fitting regime visualized in the ESI Figure S 5a.

^7Li (ppm)	T1 / ms	Rsq
3.5	2500(90)	0.995
1.1	1300(100)	0.910
0.0	550(70)	0.891

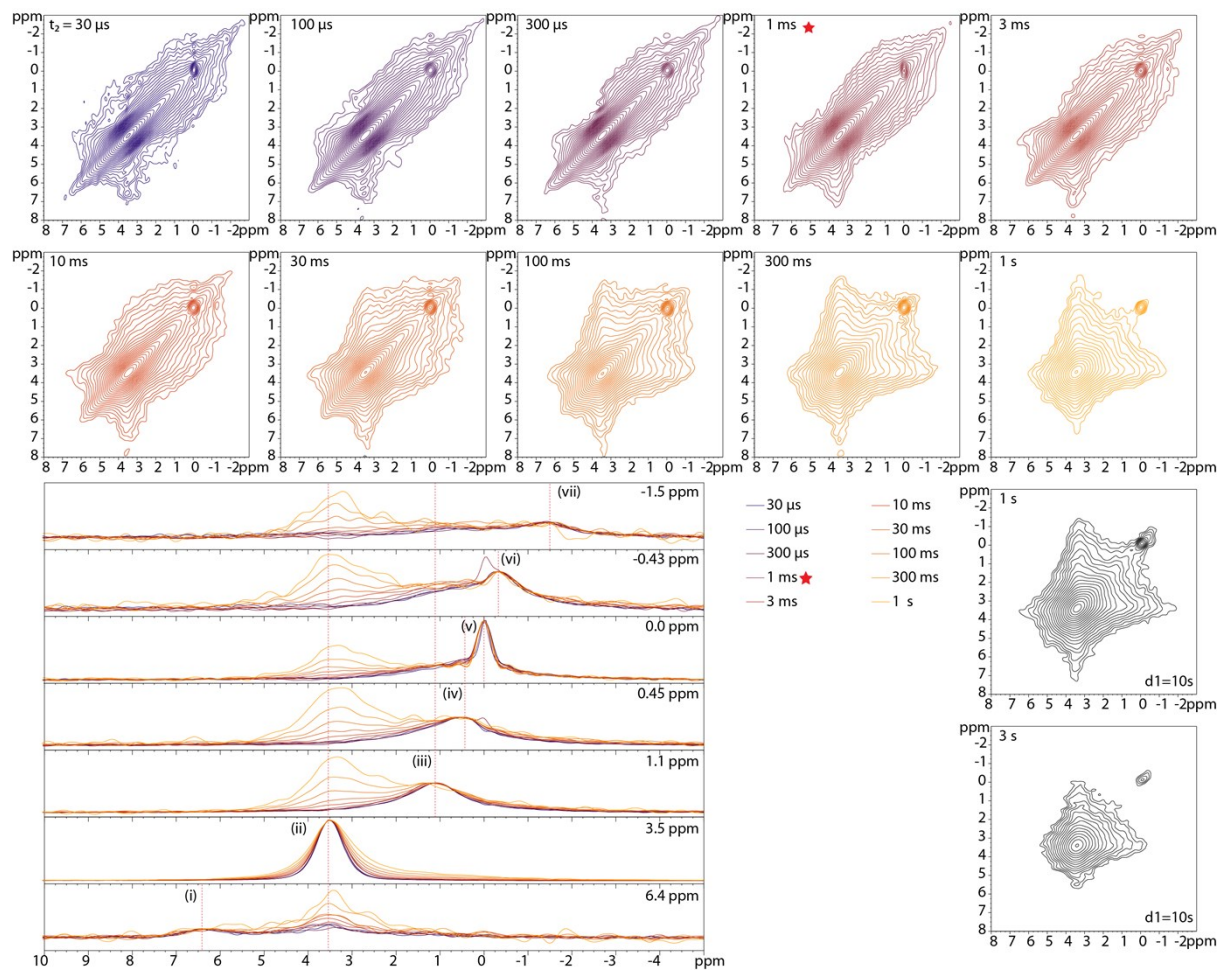


Figure S 7. a) ^7Li - ^7Li EXSY spectra of electrochemically treated poly(S-r-squalene) electrode powder extracted after 20th discharge collected at mixing times $d_8 = 30 \mu\text{s}, 100 \mu\text{s}, 300 \mu\text{s}, 1 \text{ ms}, 3 \text{ ms}, 10 \text{ ms}, 30 \text{ ms}, 100 \text{ ms}, 300 \text{ ms}$ and 1 s (30 kHz spin rate, $d_1 = 3 \text{ s}$). **b)** are slices of each spectrum in a) taken at **(i)** 6.4, **(ii)** 3.5, **(iii)** 1.1, **(iv)** 0.45, **(v)** 0.0, **(vi)** -0.43, and **(vii)** -1.5 ppm. **c)** Spectra of the same sample measured with a longer recycle delay $d_1 = 10 \text{ s}$ at mixing times **(i)** $d_8 = 1 \text{ s}$ and **(ii)** $d_8 = 3 \text{ s}$.