ARTICLE

Investigation of low molecular weight sulfur-limonene polysulfide electrodes in Li-S cells

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Lithium-sulfur battery; mechanism; NMR; K-Edge NEXAFS; spectroscopy; cathode materials; inverse vulcanization; elemental sulfur; polymer; limonene; polysulfide

Supporting information

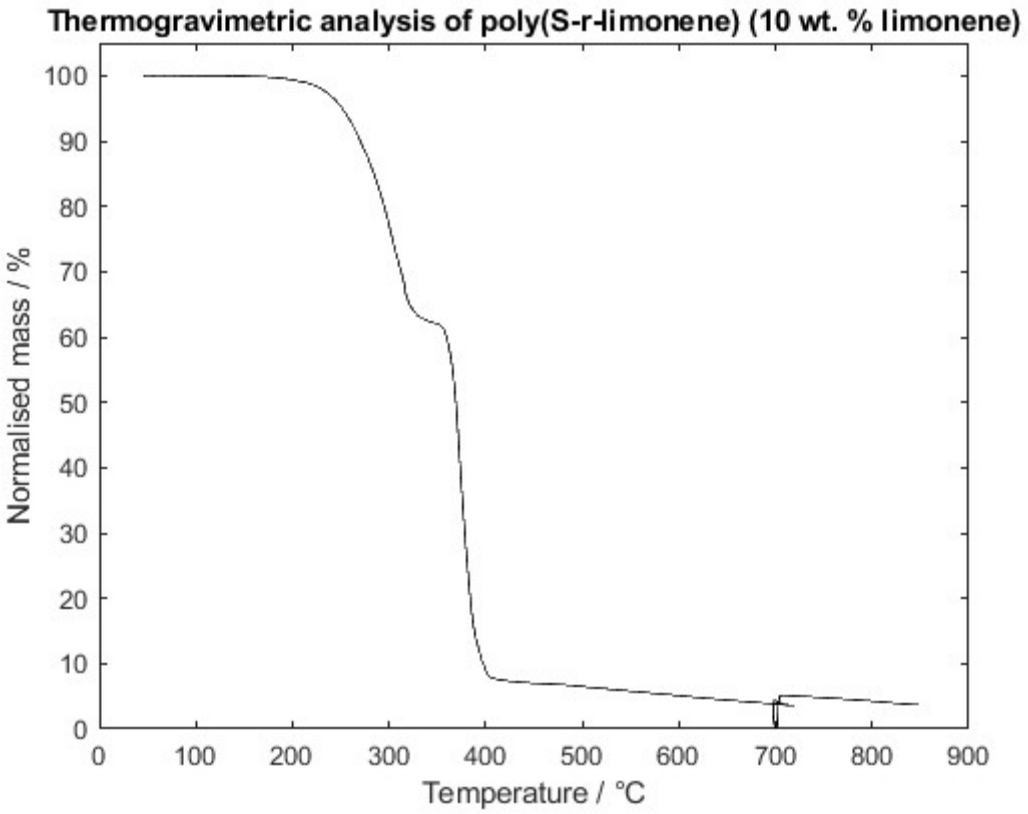

Figure S 1 – Thermogravimetric analysis (TGA) of poly(S-*r*-limonene) prepared with 10 wt. % limonene crosslinker showing true wt. % of sulfur to be > 90 %. The measurement was conducted using a Thermogravimetric Analyzer STAR system (METTLER TOLEDO) under N_2 gas at a heating rate of 10 °C min^{-1}.

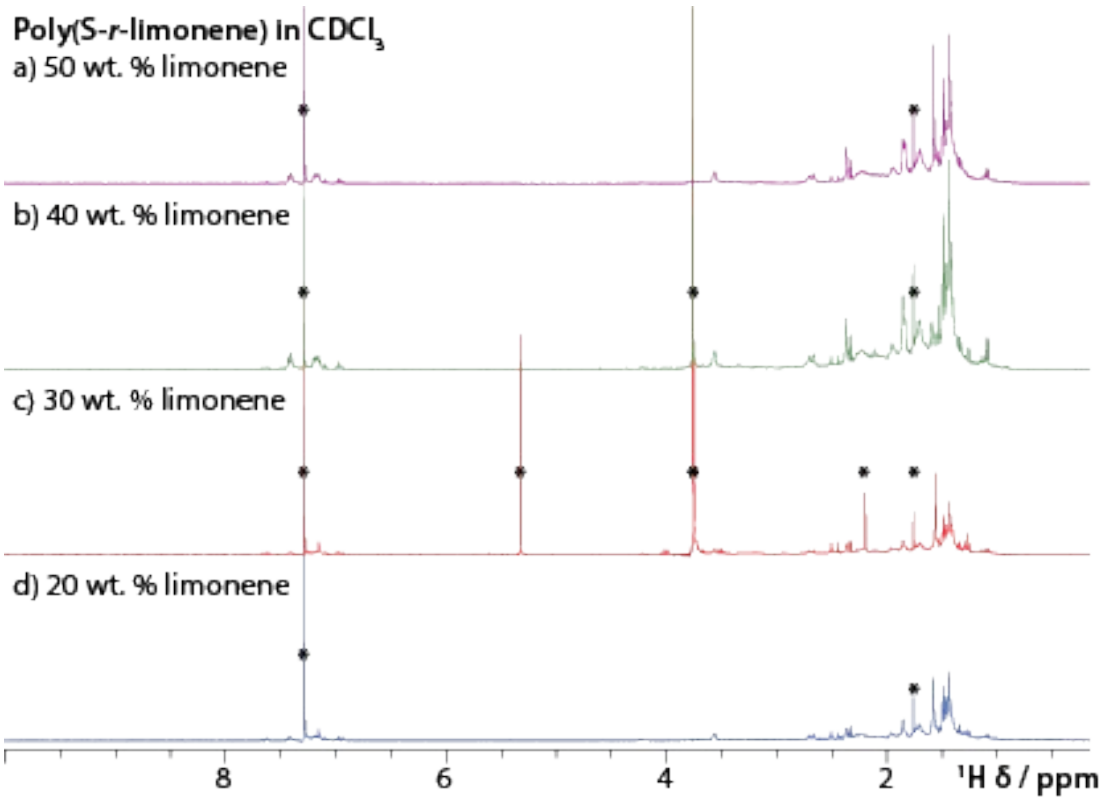

Figure S.2 – Solution state ^{1}H NMR spectra of poly(S-*r*-limonene) in $CDCl_3$ prepared with **a)** 50, **b)** 40, **c)** 30, **d)** and 20 wt. % limonene crosslinking monomer and corresponding elemental sulfur amounts. Asterisks denote residual solvent peaks unrelated to the copolymer analytes.

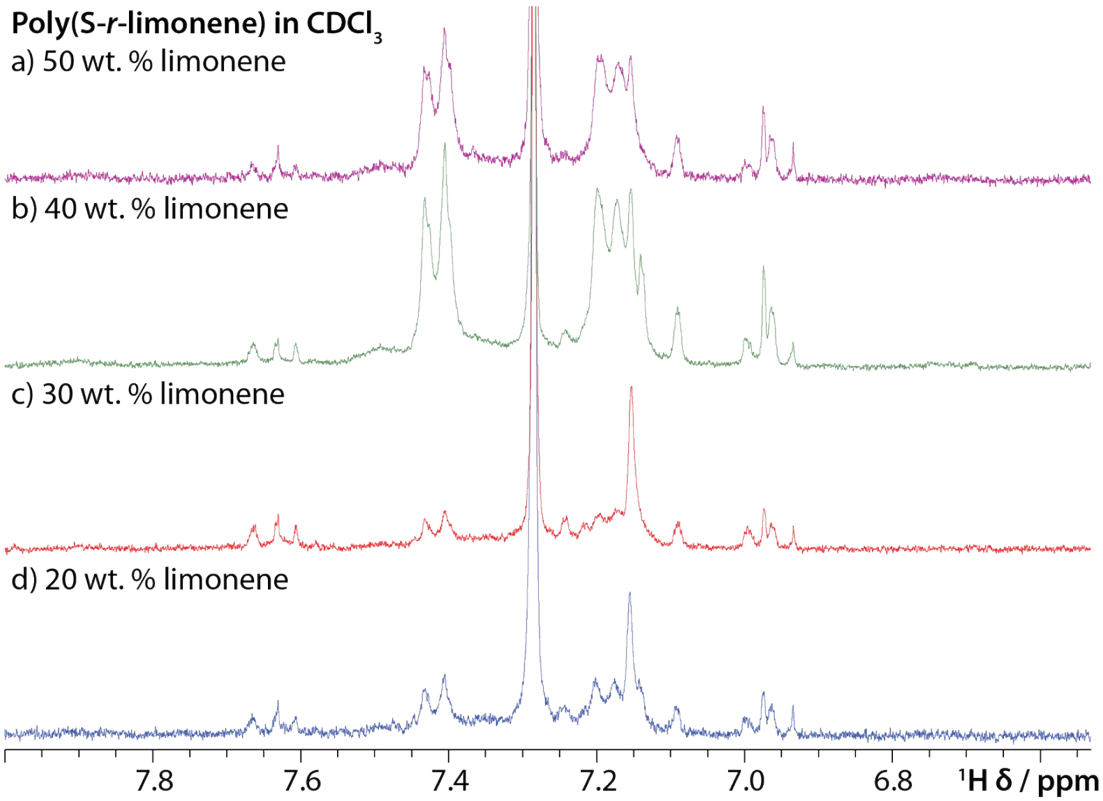

Figure S.3 – Close up on the aromatic region of poly(S-*r*-limonene) spectra shown in **Figure S.2.**

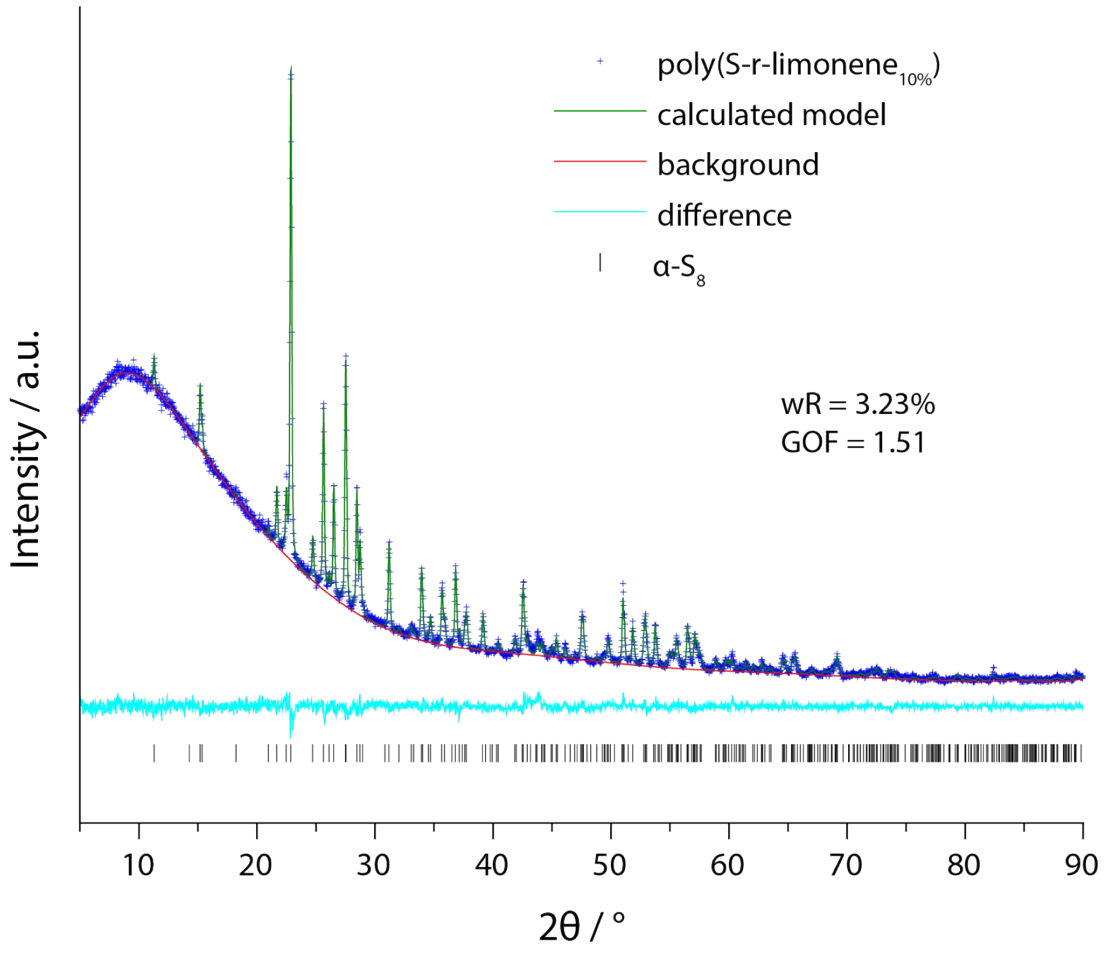

Figure S.4 – X-ray powder diffraction pattern of poly(S-*r*-limonene) prepared using 10 wt. % limonene (blue crosses) and a model of the data (green trace) calculated *via* Rietveld refinement of α-S_8 (orthorhombic α-S_8 F*ddd*, ICDD, No. 01-078-1888) and β-S_8 (monoclinic β-S_8 $P2_1/c$, ICDD No. 01-071-0137). A fit of only the α-S_8 (black peaks markers) with no contributions from β-S_8 adequately represents the data.

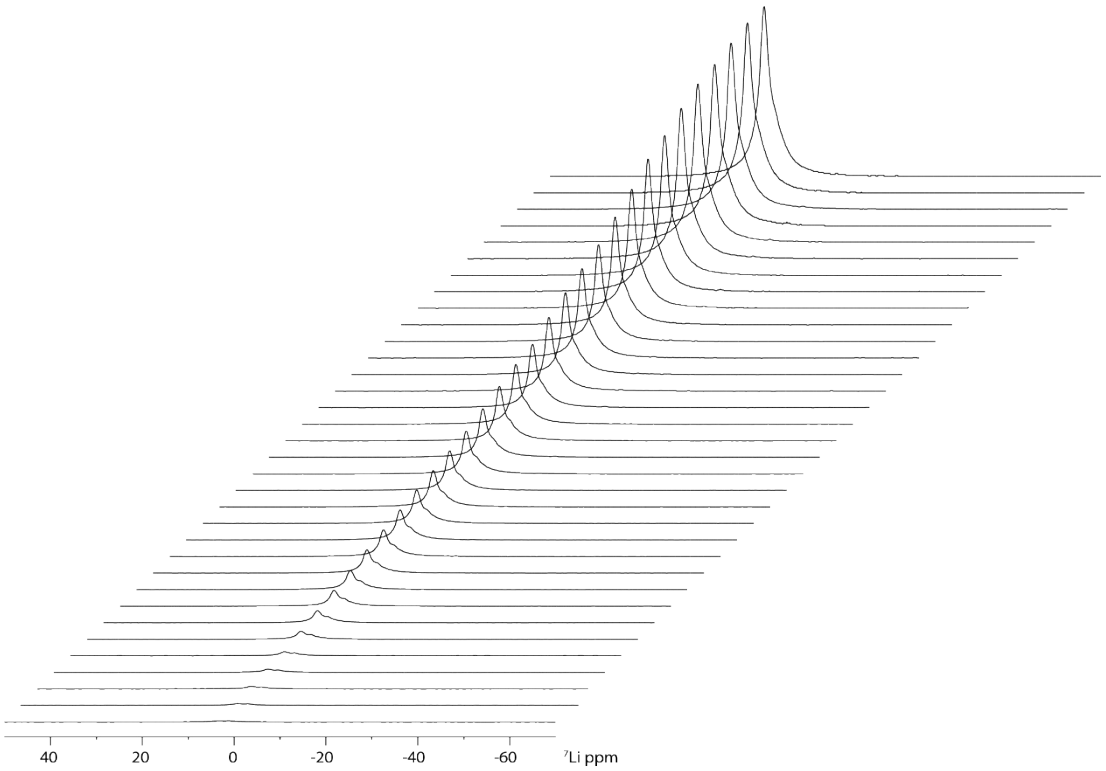

Figure S.5 – Saturation recovery ^{7}Li NMR spectra acquired at τ = 10 ms, 20 ms, 30 ms, 40 ms, 50 ms, 100 ms, 150 ms, 200 ms, 250 ms, 300 ms, 350 ms, 400 ms, 450 ms, 500 ms, 550 ms, 600 ms, 700 ms, 800 ms, 900 ms, 1 s, 1.25 s, 1.5 s, 1.75 s, 2 s, 2.5 s, 3 s, 4 s, 5 s, 7 s, 10 s, and 30 s.

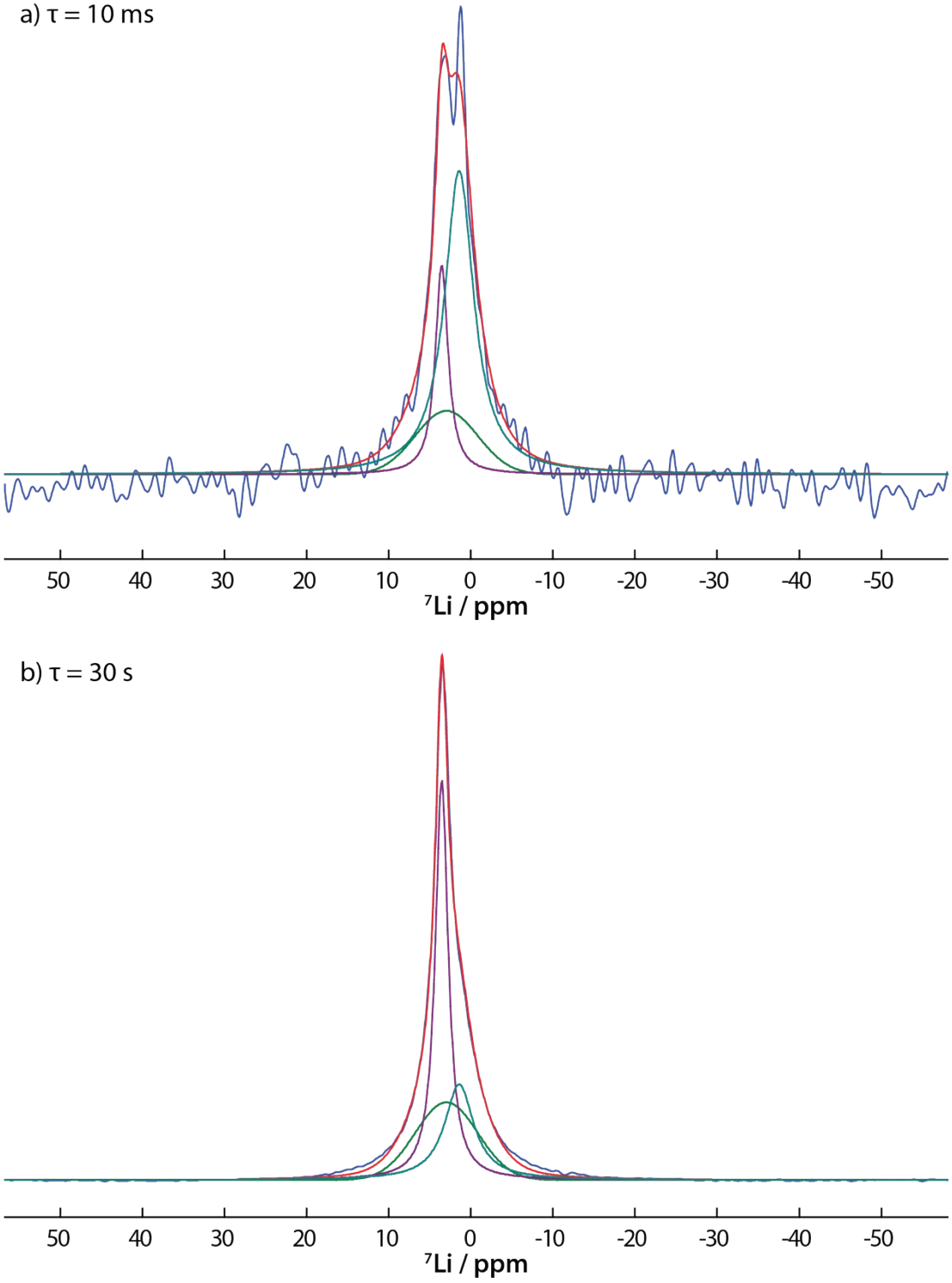

Figure S.6 – Peak deconvolution of ^{7}Li spectra acquired with **a)** τ = 10 ms signal recovery and **b)** τ = 30 s signal recovery for T_1 saturation recovery measurements.

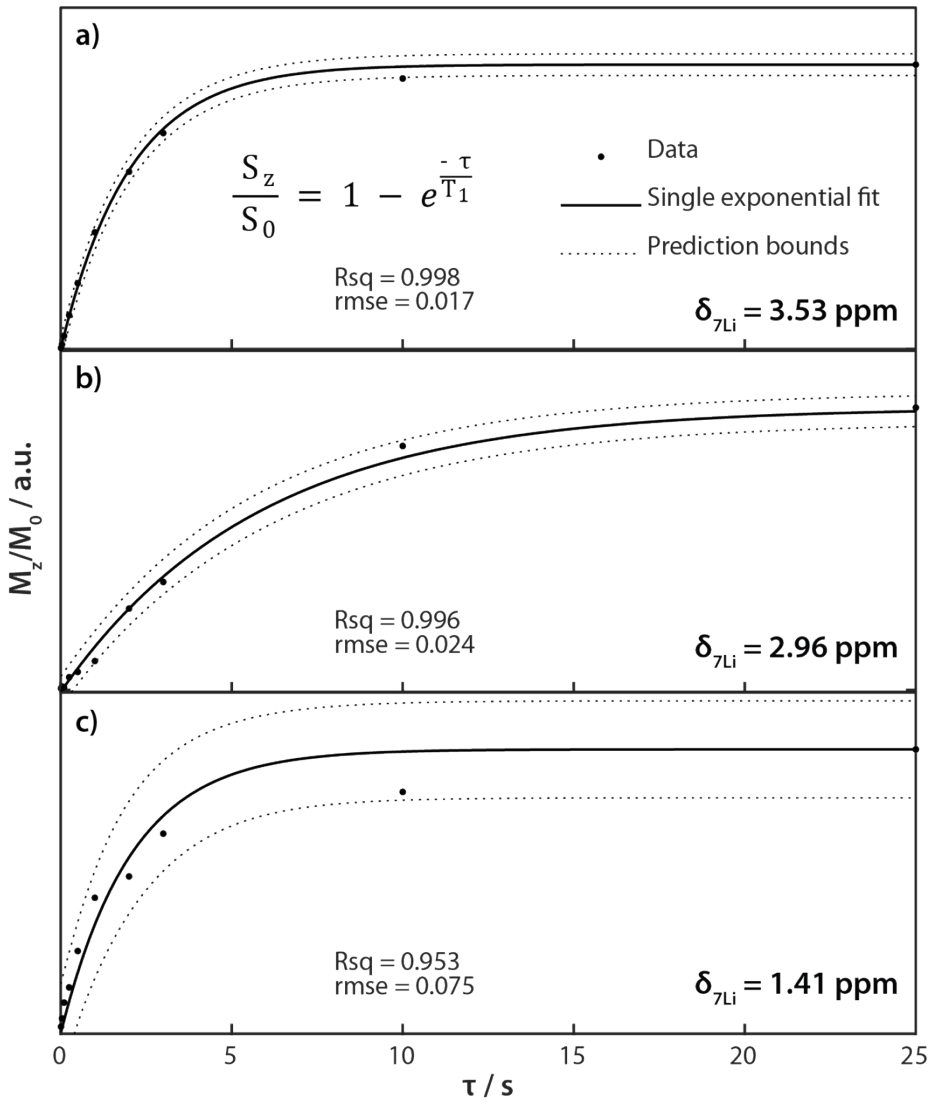

Figure S.7 – Single- phase exponential decay fits to normalized solid-state ^{7}Li saturation recovery NMR signal intensity values (M_z/M_0, black crosses) at peak *centers* δ_{7Li} = 3.51, 2.86, 2.39, and 1.23 ppm plotted *vs* τ = 10 ms, 20 ms, 30 ms, 40 ms, 50 ms, 100 ms, 150 ms, 200 ms, 250 ms, 300 ms, 350 ms, 400 ms, 450 ms, 500 ms, 550 ms, 600 ms, 700 ms, 800 ms, 900 ms, 1 s, 1.25 s, 1.5 s, 1.75 s, 2 s, 2.5 s, 3 s, 4 s, 5 s, 7 s, 10 s, and 30 s. The black traces represent fits to the function $\frac{M_z}{M_0} = 1 - e^{\frac{-\tau}{T_1}}$ to determine T_1 relaxation times. The dotted lines represent 95% confidence intervals.

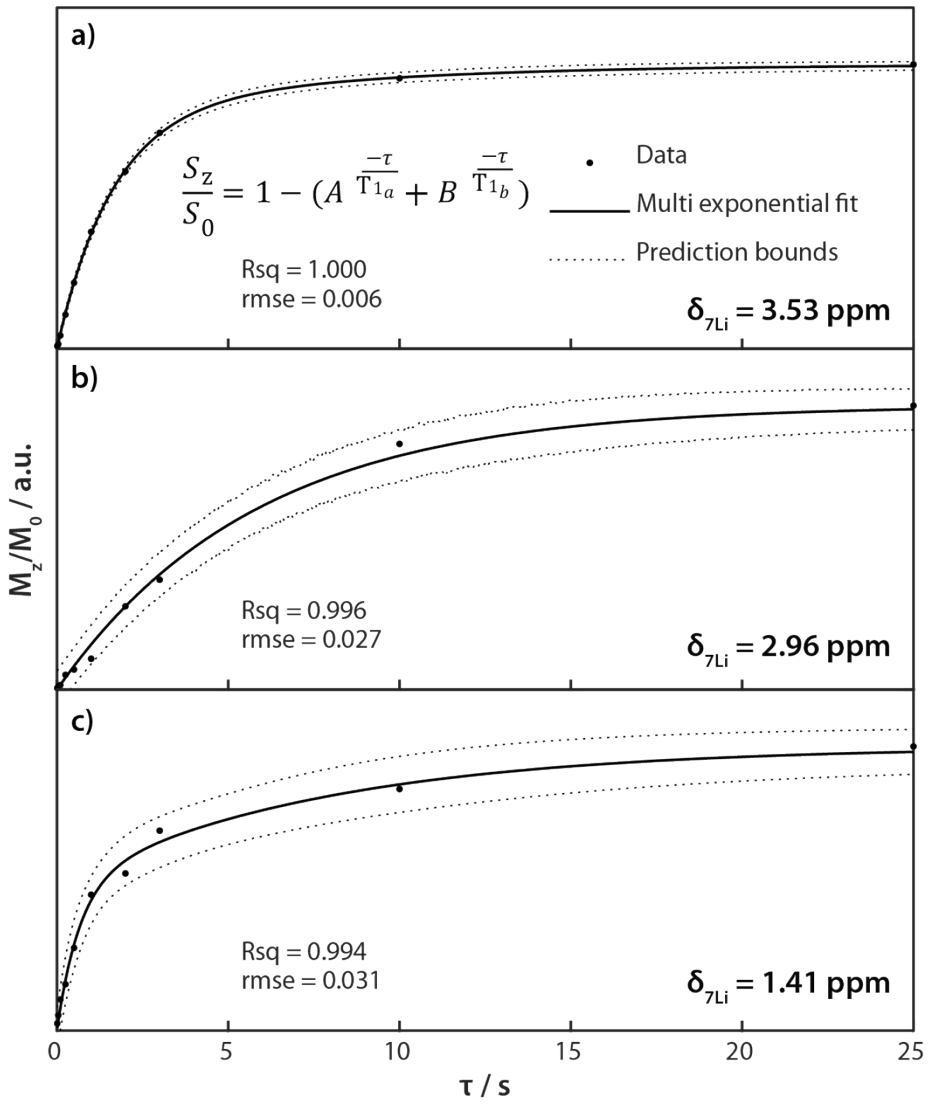

Figure S.8 – Two-phase exponential decay fits to normalized solid-state ^{7}Li saturation recovery NMR signal intensity values (M_z/M_0, black crosses) at peak *centers* δ_{7Li} = 3.51, 2.86, 2.39, and 1.23 ppm plotted *vs* τ = 10 ms, 20 ms, 30 ms, 40 ms, 50 ms, 100 ms, 150 ms, 200 ms, 250 ms, 300 ms, 350 ms, 400 ms, 450 ms, 500 ms, 550 ms, 600 ms, 700 ms, 800 ms, 900 ms, 1 s, 1.25 s, 1.5 s, 1.75 s, 2 s, 2.5 s, 3 s, 4 s, 5 s, 7 s, 10 s, and 30 s. The black traces represent fits to the function $\frac{M_z}{M_0} = 1 - (Ae^{\frac{-\tau}{T_{1_a}}} + (1-A)e^{\frac{-\tau}{T_{1_b}}})$ to determine T_1 relaxation times. The dotted lines represent 95% confidence intervals.

Table S.1 – T_1 values calculated from **a)** single-phase and **b)** two-phase exponential decay fits to the saturation recovery measurements for lithium environments I, II, and III shown in the appendix **Figure S.7** and **Figure S.8** respectively. A fit to lithium environment II using the two-phase exponential decay function did not yield conclusive parameter values which have been omitted.

a) Single-phase exponential decay $\frac{M_z}{M_0} = 1 - e^{\frac{-\tau}{T_1}}$

	δ_{7Li} (ppm)	T_1 (ms)	R_{sq}
I	3.53	2070(90)	0.993
II	2.96	5200(300)	0.9823
III	1.41	2800(700)	0.6303

b) Two-phase exponential decay $\frac{M_z}{M_0} = 1 - (Ae^{\frac{-\tau}{T_{1_a}}} + (1-A)e^{\frac{-\tau}{T_{1_b}}})$

	δ_{7Li} (ppm)	A (%)	T_{1a} (ms)	T_{1b} (ms)	R_{sq}	T_{1mean} (ms)
I	3.53	18(4)	8000(1000)	1590(60)	1.000	2600(600)
II	2.96	-	-	-	-	-
III	1.41	48(4)	15000(3000)	700(100)	0.985	8000(2000)