Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Laplace inverted pulsed EPR relaxation to study contact between active material and carbon black in Li-organic battery cathodes

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1 Laplace inversion

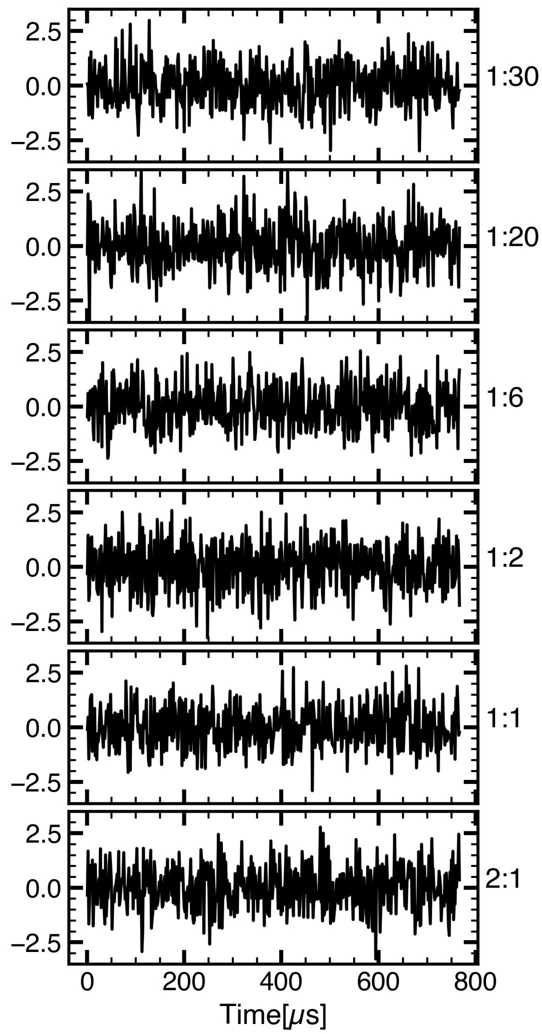

Figure S1: Residuals from inverse Laplace transform (ILT) fits of T_1 data using an exponential kernel. The corresponding distributions are shown in Figure 5 of the main text. Ratios on the right edge denote the PTMA monomer to Super P weight ratio. The residuals were representative of random noise and did not show any apparent systematic features.

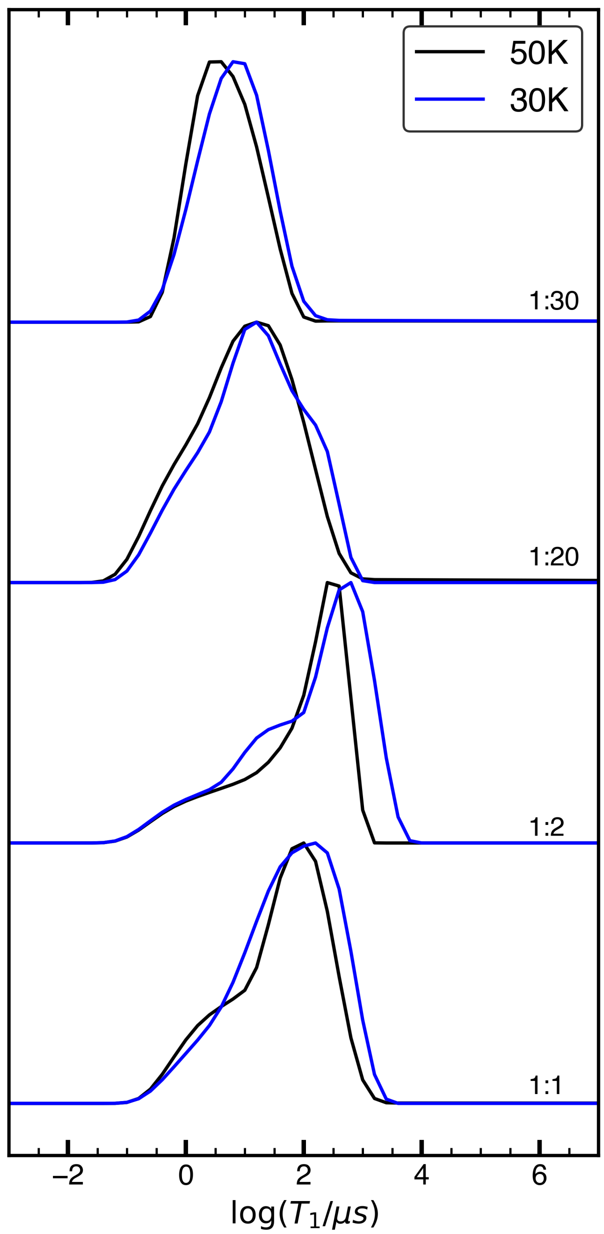

Figure S2: Comparison of relaxation time distributions at 30 K (blue) and 50 K (black), obtained using ILT for composite samples. Ratios on the right edge denote the PTMA monomer to Super P weight ratio. The T_1 distribution at 30 K shows more resolved components, and a shift of the slower relaxing component.

2 T_1 anisotropy

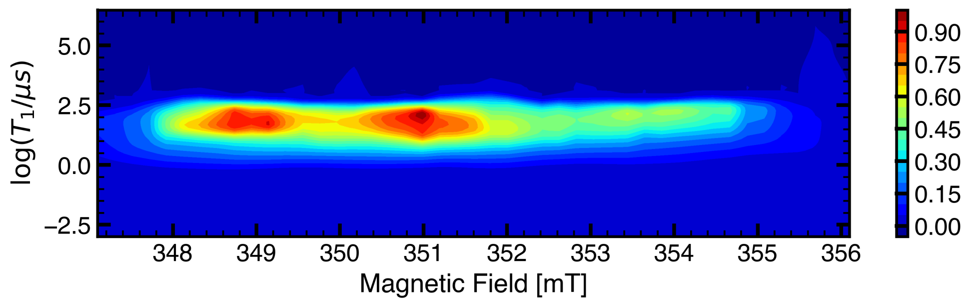

Figure S3: Dependence of ILT-derived T_1 distributions on magnetic field position. The inversion recovery experiments were conducted by sampling 45 field points of the field-swept echo detected spectrum of a 2:1 composite sample. T_1 measurements at various field positions were done at 50 K using the same experimental parameters as described in the Experimental section of the main text. The broad negative component at long T_1 values arises due to a fit of the baseline, since the signal reaches an equilibrium value that is non-zero for recovery delays towards infinity.

3 Non-negativity constraint

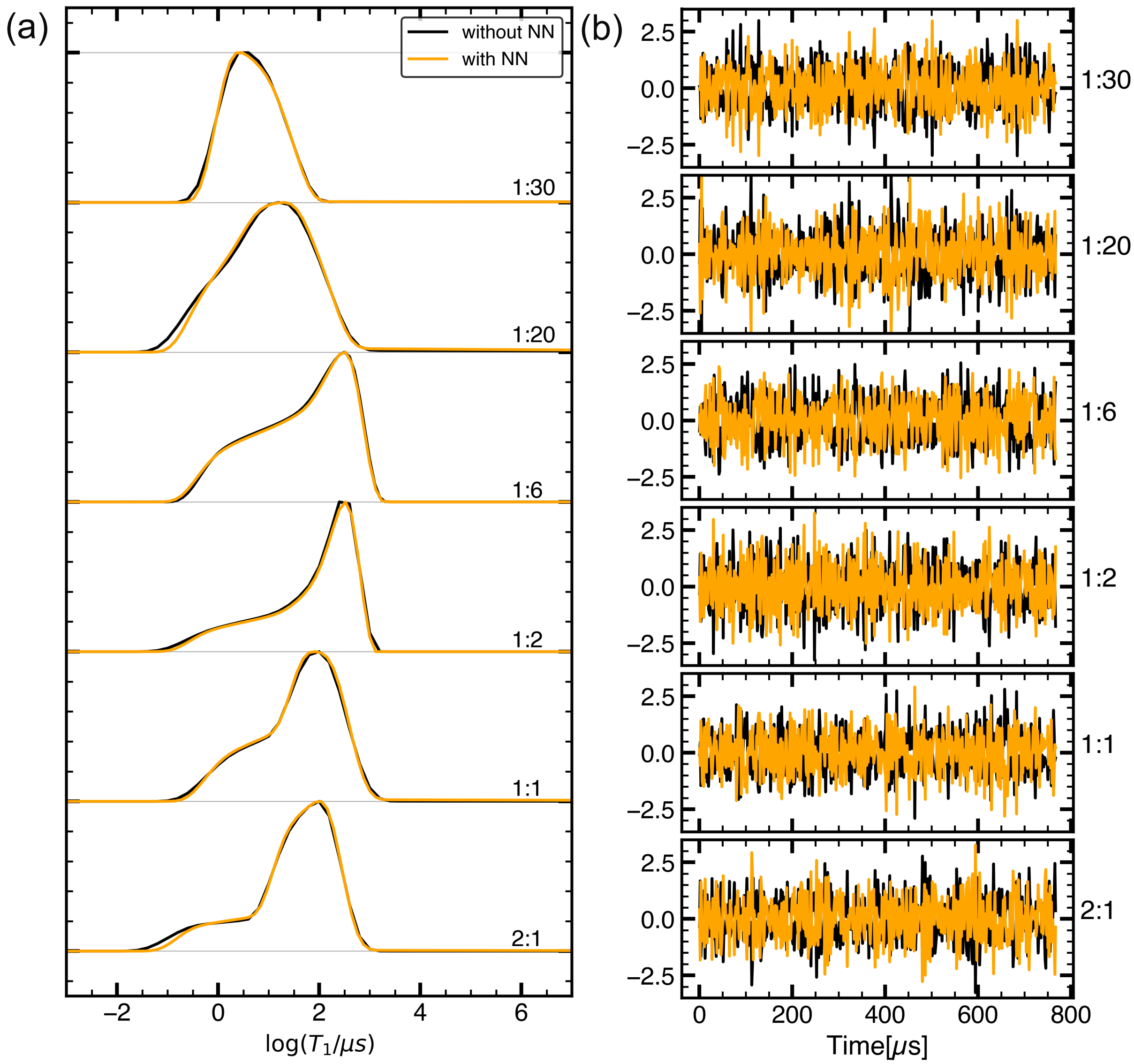

Figure S4: (a) Comparison of T_1 distributions obtained using ILT with (black) and without (orange) non-negativity penalty. The use of a non-negativity penalty did not show significant differences in the obtained T_1 distributions. (b) Residuals from ILT fits of $T1$ data using an exponential kernel with (black) and without (orange) non-negativity penalty. The two sets of residuals are shown with opposite sign for better visibility.

4 Laplace inversion of T_m

Figure S5a shows T_m curves for some of the composite samples. Laplace inversion of T_m data in the presence of oscillations on the spin echo decay curve due to electron spin echo envelope modulation (ESEEM) leads to fits as shown in Figure S5b, where the 2:1 sample is shown as an example. Oscillations at short echo times, which are not inconsistent with inversion using an exponential kernel, are overfitted. This can be circumvented by employing a weighted Laplace inversion, using a guess of the non-uniform amplitude of the ESEEM oscillations as a noise estimate, thereby treating ESEEM modulations as noise on the relaxation curve (Figure S5c). Then distribution as shown in Figure S5d are obtained. While the T_m distributions also show multiple components, similar to T_1, in the presence of ESEEM an accurate quantification of the relative contributions of relaxation components is not feasible.

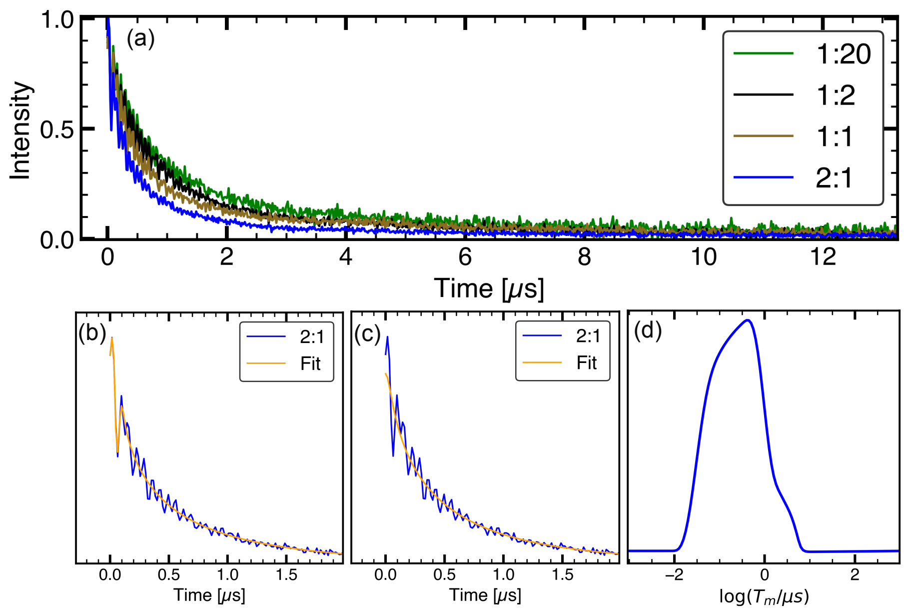

Figure S5: (a) Comparison of spin echo decay time traces for varying ratios of PTMA monomer to Super P, acquired at 50 K. The 2:1 composite sample shows the fastest T_m rate, owing to the highest amount of nitroxide spins and small inter-spin distances. For better comparison of spin echo decay curves from different composite samples, the data was scaled between 0 and 1. (b) Fit of T_m curve for the 2:1 sample using ILT in the presence of ESEEM oscillations. (c) Fit of T_m curve for 2:1 obtained using weighted ILT with the amplitude of ESEEM oscillations treated as a noise estimate. (d) T_m distribution obtained using ILT with the fitting approach shown in (c).