Electronic Supplementary Material (ESI) for Faraday Discussions.

Ion Counting in Supercapacitor Electrodes using NMR Spectroscopy

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Supporting Information

S1. Spectral deconvolutions: ^{19}F NMR adsorption study

Deconvolutions for the ^{19}F NMR spectra of 4 mg pieces of YP-50F film soaked in different amounts of NEt_4-BF_4 electrolyte (Figures 1a and 1c in the main text) are shown in Figure S1. Deconvolution parameters for each fitted lineshape are summarized in Table S1.

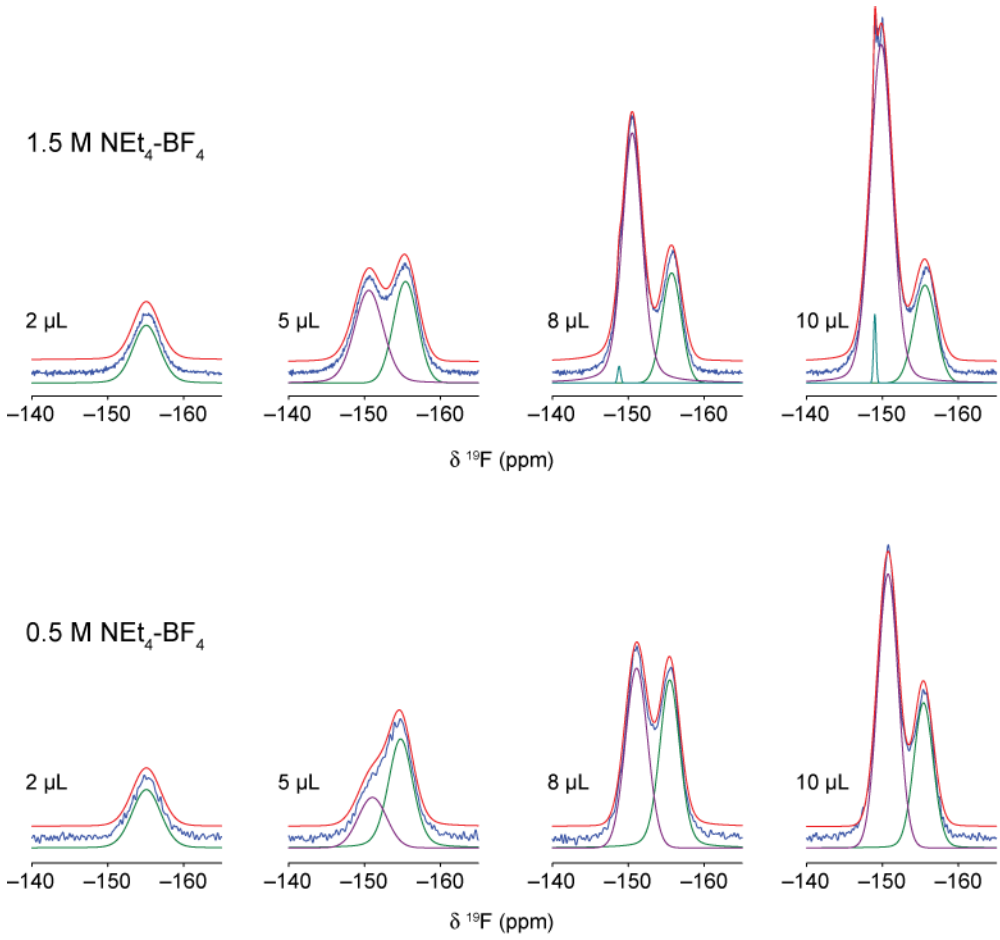

Figure S1. Deconvolutions of ^{19}F NMR spectra recorded for 4 mg pieces of YP-50F film soaked in different amounts of NEt_4-BF_4 electrolyte. Experimental lineshapes are shown in blue, individual fitted components are shown in green and purple, and the total fitted lineshape is shown in red.

Table S1. Deconvolution parameters for fits shown in Figure S1.

Volume /μL	Resonance	Shift (ppm)	Width (ppm)	G/L ratio	Absolute integrated intensity (arb.)	Relative integrated intensity*
1.5 M concentration						
2	in-pore	-155.09	4.19	0.83	62598	0.16
5	in-pore	-155.40	3.75	1.00	92204	0.24
	ex-pore	-150.57	4.45	0.84	106621	0.28
8	in-pore	-155.71	2.99	1.00	79599	0.21
	ex-pore 1	-150.51	3.11	0.69	212061	0.55
	ex-pore 2	-148.79	0.46	1.00	1874	0.00
10	in-pore	-155.59	3.40	1.00	80544	0.21
	ex-pore 1	-149.83	3.42	0.83	298478	0.77
	ex-pore 2	-148.99	0.40	1.00	6618	0.02
0.5 M concentration						
2	in-pore	-155.10	4.45	0.25	24952	0.21
5	in-pore	-154.76	3.81	0.77	41882	0.35
	ex-pore	-151.04	4.41	1.00	20341	0.17
8	in-pore	-155.45	3.12	0.77	51856	0.43
	ex-pore	-151.08	3.44	1.00	56501	0.47
10	in-pore	-155.40	3.02	0.92	41294	0.34
	ex-pore	-150.72	3.17	1.00	79424	0.66

*Integrated intensity relative to the total intensity of the 10 μL spectrum for each concentration.

S2. Spectral deconvolutions: In Situ NMR studies of supercapacitor cells

Representative deconvolutions of ^{19}F *in situ* NMR spectral recorded for cells held at 0 V are shown in Figure S2. In each case, a single component was used to model the in-pore resonance, while a minimum of 3 - 4 components were required to accurately model the ex-pore / free electrolyte feature. For Li-TFSI, more components were required owing to the more complex appearance of the ex-pore / free electrolyte feature.

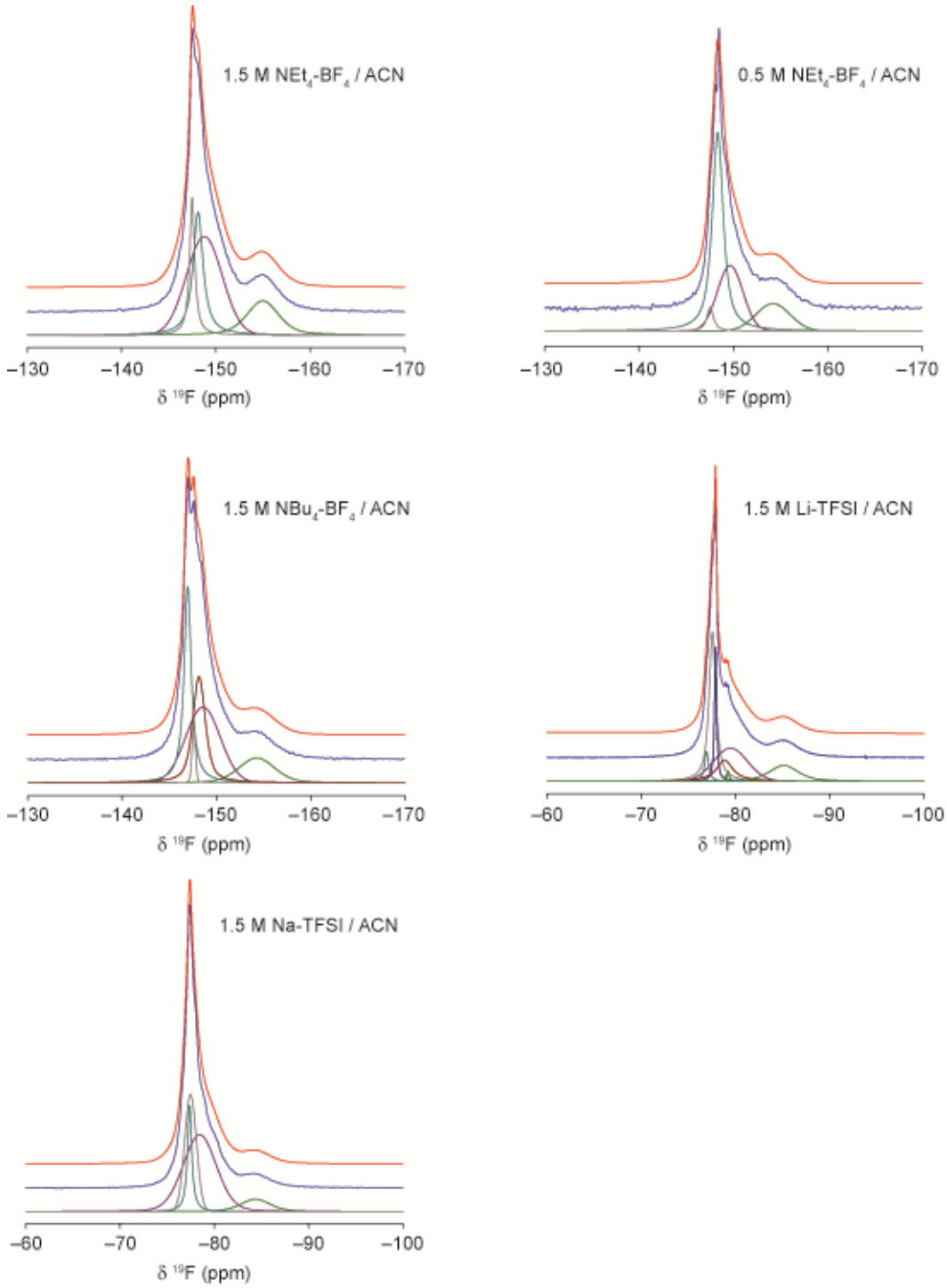

Figure S2. Representative deconvolutions of ^{19}F in situ NMR spectra recorded for cells held at 0 V. Experimental lineshapes are shown in blue, while the sum of individual fitted components is shown in red.

S3. Charge stored during *in situ* NMR experiments

Figure S3 shows the cumulative charge stored for each cell at each voltage step in the ^{19}F *in situ* NMR experiments. The stored charge varies approximately linearly with the applied cell voltage in each case and is fully discharged during the 1.5 V → 0 V step.

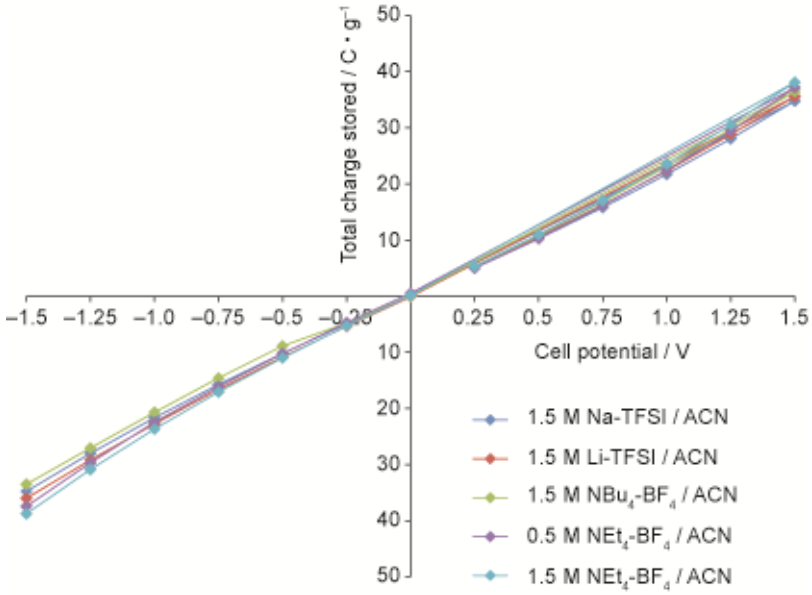

Figure S3. Plot showing cumulative charge stored as a function of voltage in supercapacitor bag cells used in *in situ* NMR experiments.