



Understanding the Capacity Decay of Si/NMC622 Li-Ion Batteries Cycled in Superconcentrated Ionic Liquid Electrolytes: A New Perspective

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Supporting Information

Understanding the Capacity Decay of Si/NMC622 Li-ion Batteries Cycled in Superconcentrated Ionic Liquid Electrolytes: A New Perspective

Khryslyn Araño^{a,b,c}, Nicolas Gautier^a, Robert Kerr^b, Bernard Lestriez^a, Jean Le Bideau^a, Patrick C. Howlett^b, Dominique Guyomard^a, Maria Forsyth^b, and Nicolas Dupré^{a,}*

^aUniversité de Nantes, CNRS, Institut des Matériaux Jean Rouxel (IMN), F – 44000, Nantes, France

^bInstitute for Frontier Materials (IFM), Deakin University, 221 Burwood Highway, Burwood, Victoria 3125, Australia

^cFrench Environment and Energy Management Agency 20, avenue du Grésillé- BP 90406 49004 Angers Cedex 01 France

*: corresponding author

Chemical Structure of the Ionic Liquids

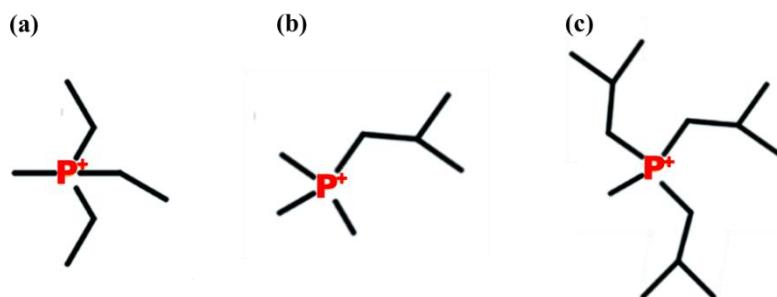


Figure S1. Chemical structure of a) P_{1222}^+ , c) $\text{P}_{111\text{i}4}^+$, and d) $\text{P}_{1\text{i}4\text{i}4\text{i}4}^+$

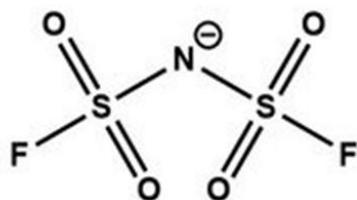


Figure S2. Chemical structure of FSI⁻ anion

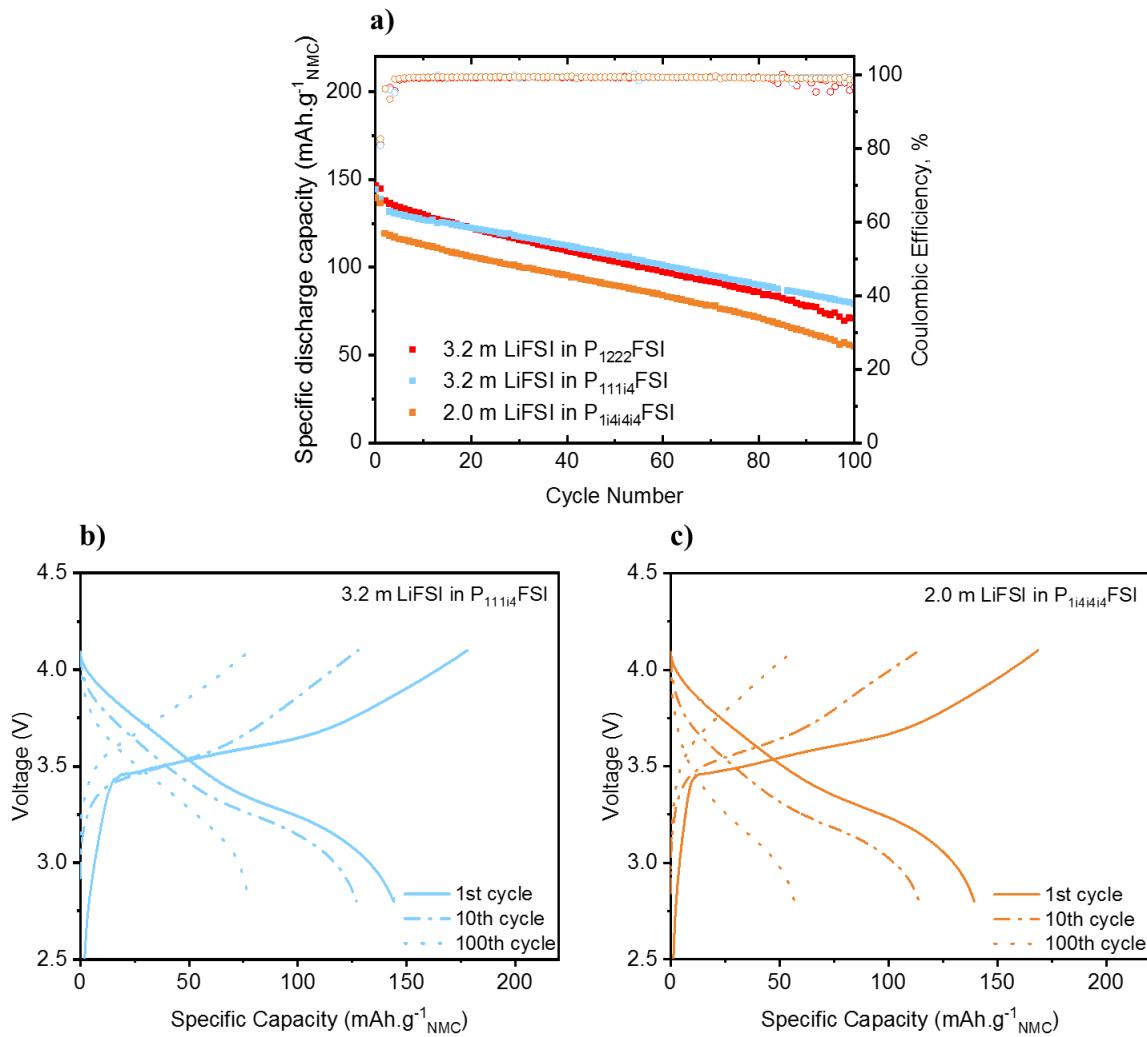


Figure S3. Electrochemical performance of Si/NMC622 cells at 50°C showing the a) Si specific capacity vs. cycle number (Specific capacities are given in mAh per gram of silicon (mAh.g⁻¹ NMC) and b-c) charge-discharge profile of the cells cycled in the superconcentrated IL electrolyte. $P_{1222}\text{FSI}$ -LiFSI (not shown) is very similar to $P_{1114}\text{FSI}$ -LiFSI.

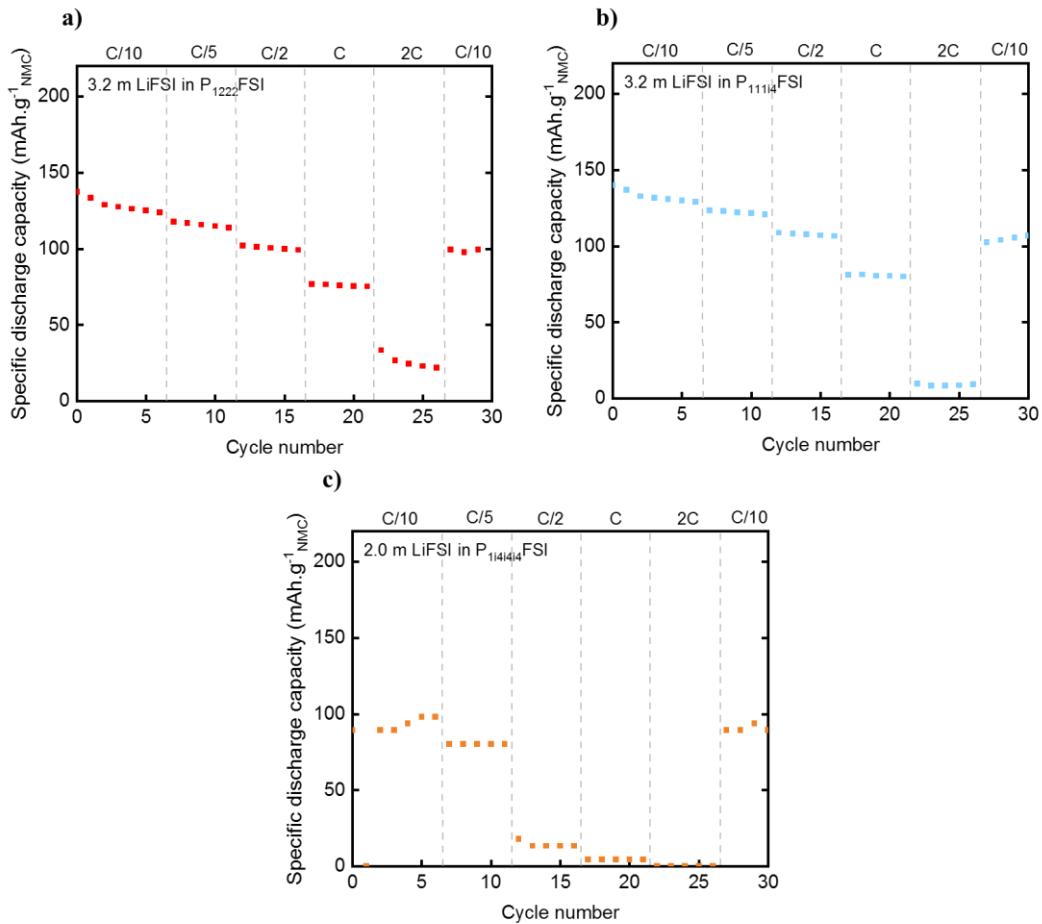


Figure S4. Full-cell rate capability performance of Si negative electrode with NMC622 positive electrode in a) 3.2 m LiFSI in P₁₂₂₂FSI, b) 3.2 m LiFSI in P_{111i4}FSI, and c) 2.0 m LiFSI in P_{1i4i4i4}FSI at 50°C. Specific capacities are given in mAh per gram of NMC (mAh.g⁻¹_{NMC})

Electrochemical Impedance Spectroscopy

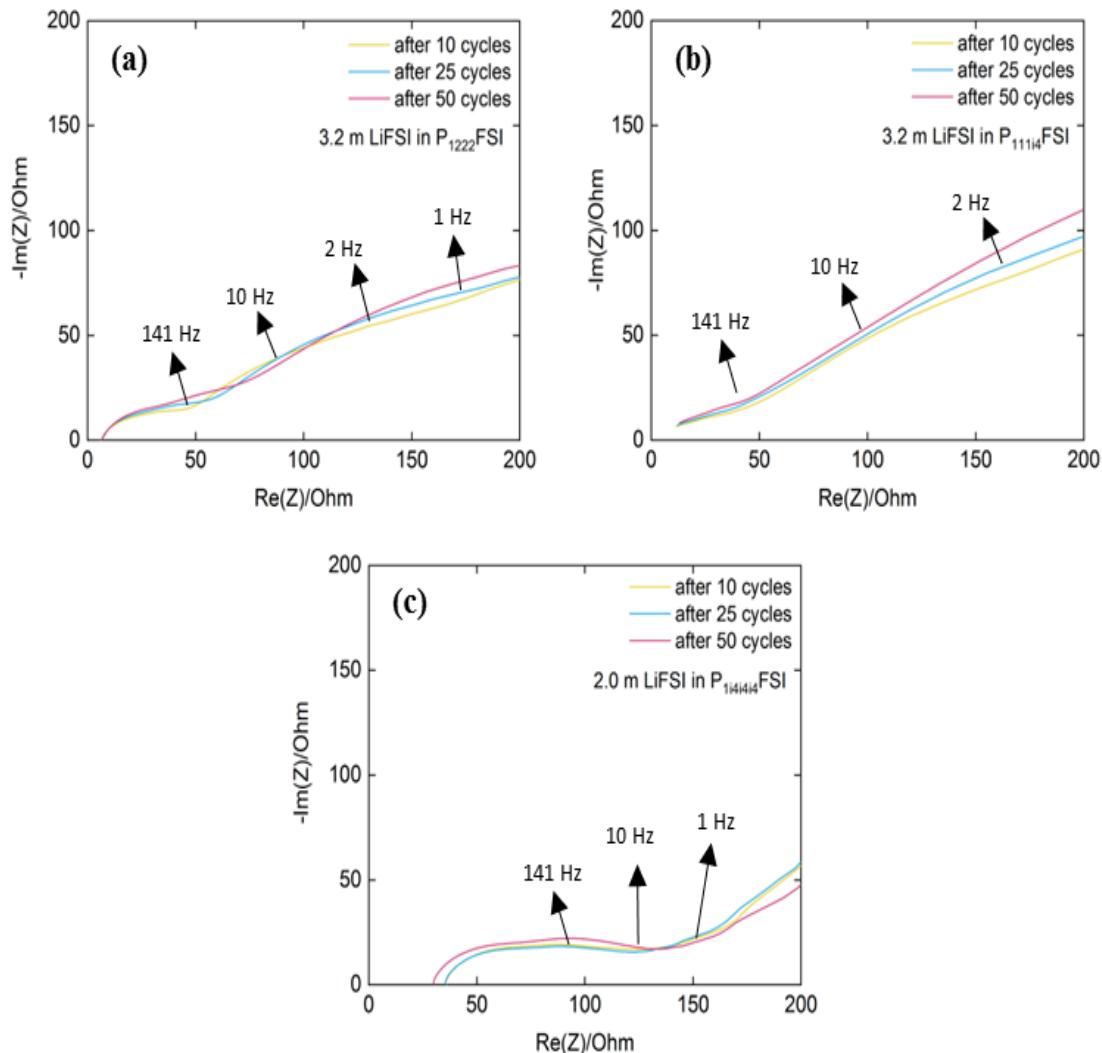


Figure S5. Nyquist plot of the Si/NMC622 cells cycled at 50°C in a) 3.2 m LiFSI in $P_{1222}\text{FSI}$, b) 3.2 m LiFSI in $P_{111i4}\text{FSI}$, c) 2.0 m LiFSI in $P_{1i4i4i4}\text{FSI}$.

Table S1. Estimated cell resistance after 50th delithiation in the IL electrolytes

Electrolyte	$P_{1i4i4i4}\text{FSI-LiFSI}$	$P_{111i4}\text{FSI-LiFSI}$	$P_{1222}\text{FSI-LiFSI}$
$R_{\text{total int.}} (\Omega)$	150	70	120

Half Cell Performance of Si in IL Electrolytes

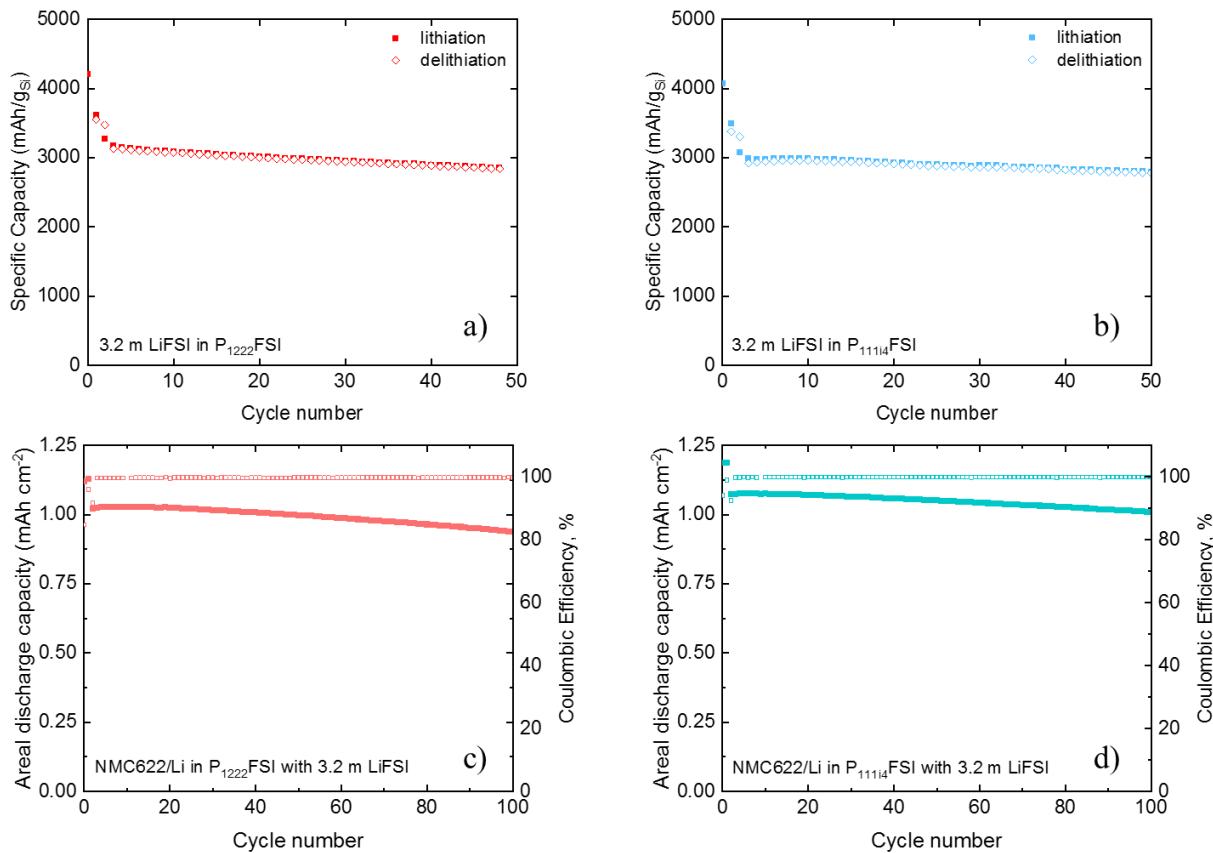


Figure S6. Half-cell electrochemical performance of Si electrode in a) P₁₂₂₂FSI with 3.2 m LiFSI and b) P₁₁₁₄FSI with 3.2 m LiFSI at 50°C at a rate of C/5; Half-cell performance of NMC622 at 50°C in c) in P₁₂₂₂FSI with 3.2 m LiFSI and d) in P₁₁₁₄FSI with 3.2 m LiFSI

Cyclic Voltammetry

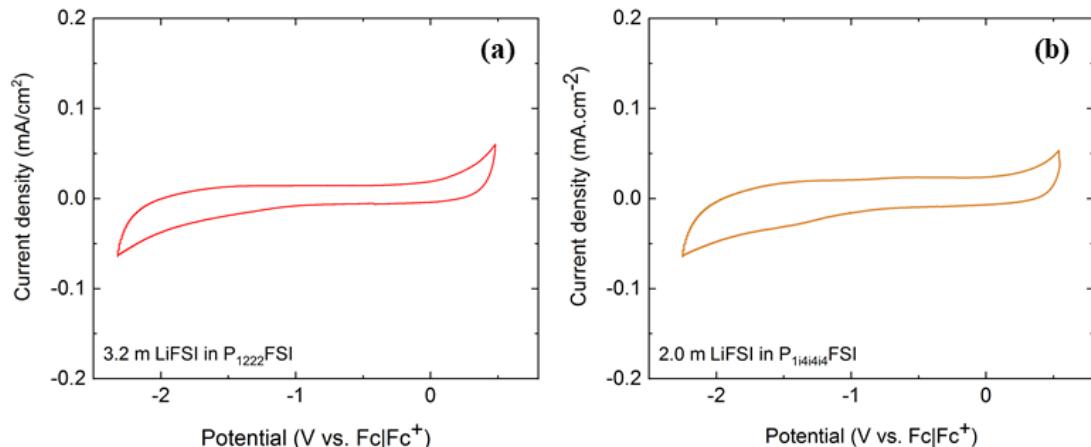


Figure S7. Cyclic voltammetry curves of a) 3.2 m LiFSI in P₁₂₂₂FSI and b) 2.0 m LiFSI in P₁₁₁₄FSI measured at 55°C

TEM-EDX

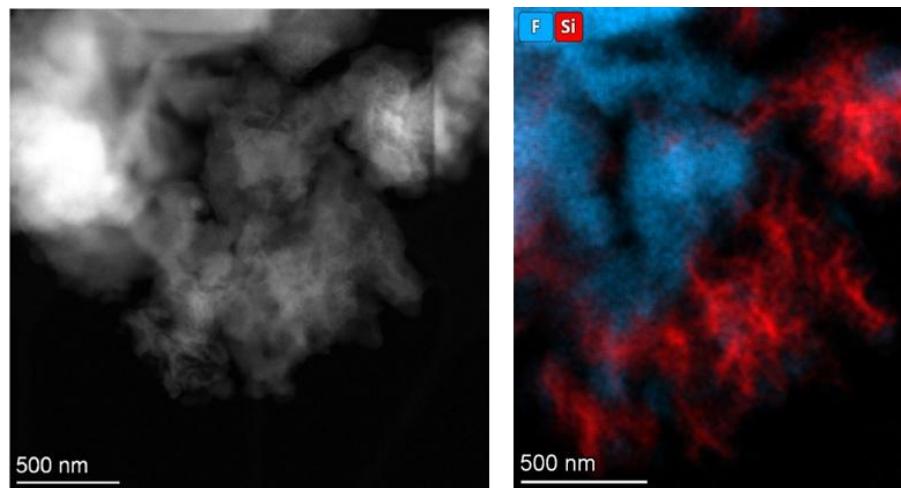


Figure S8. STEM-EDX images of Si particles after 100 cycles, in half-cell configuration (vs Li) in $P_{1222}FSI$ with 3.2 m LiFSI

Table S2. Ratio of the elemental composition of the compounds derived from FSI anion found in the Si electrode cycled in the IL electrolytes after 100th delithiation.

Area 1:

FSI Elements	Electrolyte	
	$P_{111i4}FSI$ -LiFSI	$P_{1i4i4i4}FSI$ -LiFSI
N:S:F	1:8:5	1:3:3
O:S	0.7:1	2.4:1

Area 2:

FSI Elements	Electrolyte	
	$P_{111i4}FSI$ -LiFSI	$P_{1i4i4i4}FSI$ -LiFSI
N:S:F	1:7:27	1:3:8
O:S	1.2:1	2:1

Area 3:

FSI Elements	Electrolyte	
	$P_{111i4}FSI$ -LiFSI	$P_{1i4i4i4}FSI$ -LiFSI
N:S:F	1:2:2	1:4:3
O:S	2:1	2:1

The values above correspond to the areas delimited in yellow in Figure 4 (main text).

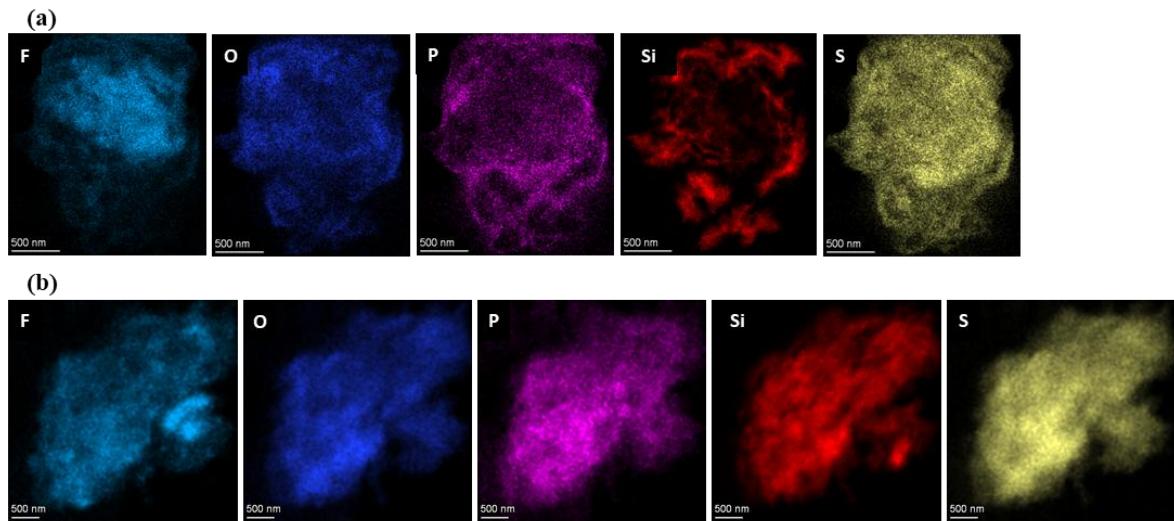


Figure S9. Elemental mapping of the Si electrode cycled in a) $P_{111i4}FSI$ with 3.2 m LiFSI and b) $P_{1i4i4i4}FSI$ with 2.0 m LiFSI after 100th delithiation

MAS NMR: Si Electrode

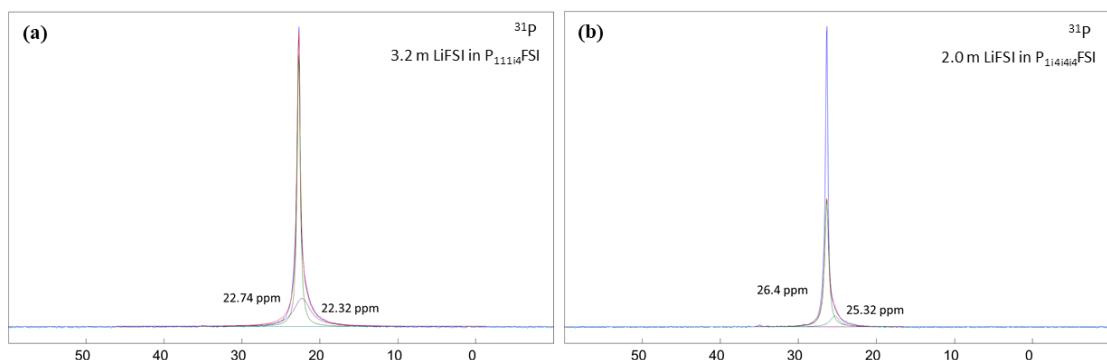


Figure S10. ^{31}P MAS NMR spectra of the Si electrodes after 100th delithiation in a) $P_{111i4}FSI$ with 3.2 m LiFSI and b) $P_{1i4i4i4}FSI$ with 2.0 m LiFSI

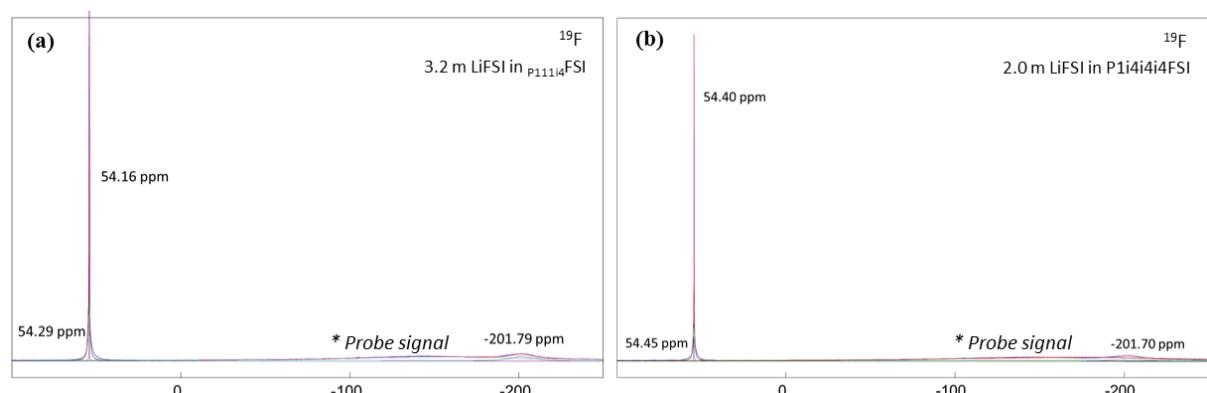


Figure S11. ^{19}F MAS NMR spectra of the Si electrodes after 100th delithiation in a) $P_{111i4}FSI$ with 3.2 m LiFSI and b) $P_{1i4i4i4}FSI$ with 2.0 m LiFSI

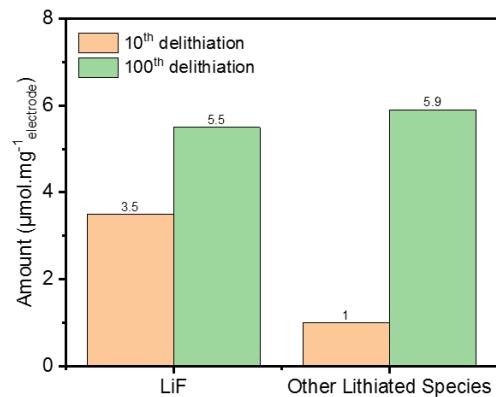


Figure S12. Amount of LiF and other lithiated components on the Si electrodes derived from ¹⁹F NMR and ⁷Li NMR after 10th and 100th delithiation P₁₂₂₂FSI with 3.2 m LiFSI in half-cell configuration, adapted from [1]. Amounts of LiF and other lithiated products are given in μmol per milligram of silicon electrode.

MAS NMR: Positive Electrode

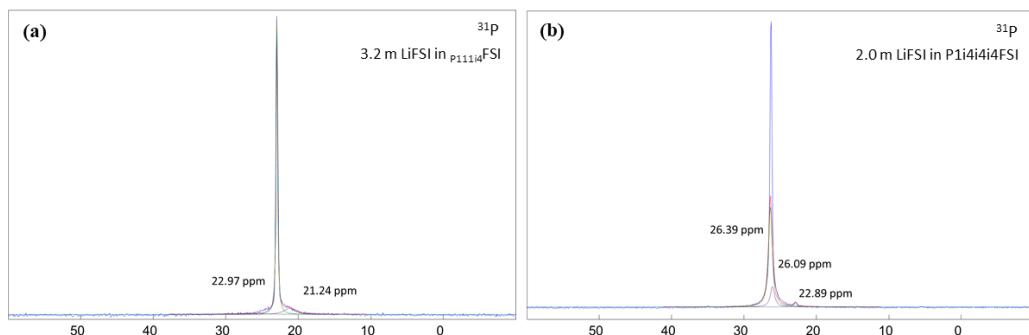


Figure S13. ^{31}P MAS NMR spectra of the NMC622 electrodes after 100th delithiation in a) $\text{P}_{111\text{i4}}\text{FSI}$ with 3.2 m LiFSI and b) $\text{P}_{1\text{i4i4i4}}\text{FSI}$ with 2.0 m LiFSI

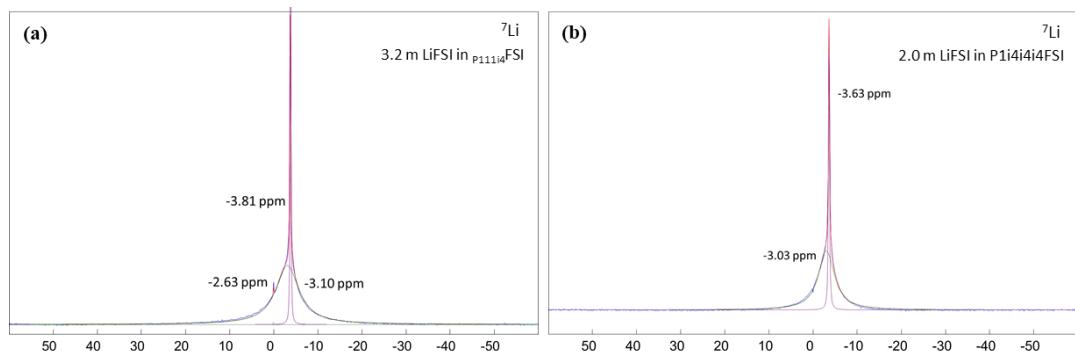


Figure S14. ^7Li MAS NMR spectra of the NMC622 electrodes after 100th delithiation in a) $\text{P}_{111\text{i4}}\text{FSI}$ with 3.2 m LiFSI and b) $\text{P}_{1\text{i4i4i4}}\text{FSI}$ with 2.0 m LiFSI

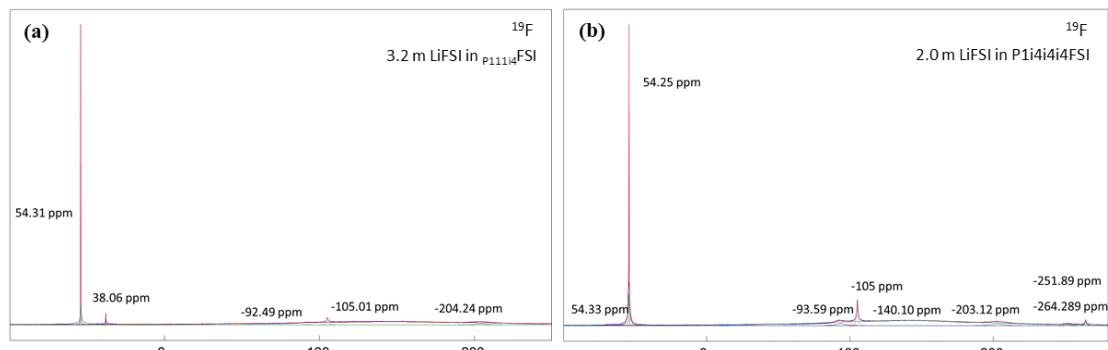


Figure S15. ^{19}F MAS NMR spectra of the NMC622 electrodes after 100th delithiation in a) $\text{P}_{111\text{i4}}\text{FSI}$ with 3.2 m LiFSI and b) $\text{P}_{1\text{i4i4i4}}\text{FSI}$ with 2.0 m LiFSI

References

- [1] K. Arano, S. Begic, F. Chen, D. Rakov, D. Mazouzi, N. Gautier, R. Kerr, B. Lestriez, J. Le Bideau, P.C. Howlett, D. Guyomard, M. Forsyth, N. Dupre, Tuning the Formation and Structure of the Silicon Electrode/Ionic Liquid Electrolyte Interphase in Superconcentrated Ionic Liquids, ACS Appl. Mater. Interfaces. 13 (2021) 28281–28294. <https://doi.org/10.1021/acsami.1c06465>.