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

Supplementary material for

Lithium tracing in silicon-based electrodes by measuring $^{7}Li/^{6}Li$ isotope ratio: a solid-state NMR approach for battery applications

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1. Calculations of the Lithium mass balance using the electrochemistry data

1.1. Principle

The Li amount (n) in the electrolyte is calculated from the lithium concentration and the electrolyte volume (V):

$$n\ (mol) = C\left(mol \times L^{-1}\right) \times V(L)$$

The Li amount found in the electrode (SEI and particles included) is estimated from of the exchanged capacity (Q), the considered charge (n(e-) =1 for Li^+) and the Faraday constant (F=96485 $C.mol^{-1}$ and 26.80 $A.h.mol^{-1}$). By this calculation, it is implicitly assumed that for each consumed electron a Li^+ ion is found in the electrode, which is an approximation.

$$n\ (mol) = \frac{Q\ (Ah)}{n(e-) * F\ (A \times h \times mol^{-1})}$$

The amount of lithium found in the SEI is estimated from the first cycle coulombic efficiency (Eff_C) and the amount of lithium found in the electrode (n_{elec}). The same approximation is realized.

$$n\ (mol) = \left(1 - Eff_c\right) \times\ n_{élec}\ (mol)$$

1.2. Numerical application for the electrolyte and lithiated electrode prepared with process D (Figure 1D) :

Electrolyte : V=300 µL, C= 1 mol.L^{-1} which gives nLi =0,3 mmol

Lithiated electrode : Q = 25 mAh which gives nLi=0,94 mmol

2. Parameters obtained from deconvolution of ^{7}Li and ^{6}Li MAS NMR spectra

Table S1. Parameters obtained from deconvolution, using DMFIT software,[1] of the ^{7}Li and ^{6}Li MAS NMR spectra shown in Figure 5**.**

Assignement	δ (ppm)	width (Δδ, ppm)	Distribution of the considered isotope in different phases (%)
^{6}Li NMR			
$Li_{12}Si_7$	19.0	7.4	39
SEI	0.96	2.9	26
$Li_{15}Si_4$	6.5	6.4	12
$Li_{13}Si_4$	14.2	10.8	24
^{7}Li NMR			
$Li_{12}Si_7$	19.0	8.7	13
SEI	0.96	6.5	34
$Li_{15}Si_4$	6.5	7.8	15
$Li_{13}Si_4$	14.2	18.8	40

Table S2. Parameters obtained from deconvolution, using DMFIT software,[1] of the ^{7}Li MAS NMR spectra shown in Figure 7									
	Distribution of ^{7}Li in different phases (%)								
	1h00	7h00	13h15	19h30	25h45	32h00	38h15	44h30	50h45
$Li_{12}Si_7$	9	5	3	2	0	0	0	0	0
Li_7Si_3 + $Li_{13}Si_4$	31	34	35	33	34	32	32	34	34
$Li_{15}Si_4$	20	20	20	21	21	22	22	20	20
Electr.	8	8	8	9	9	8	8	8	8
SEI	32	33	34	35	36	38	38	38	38

3. ^{7}Li and ^{6}Li MAS NMR spectra obtained for setups A,B and C.

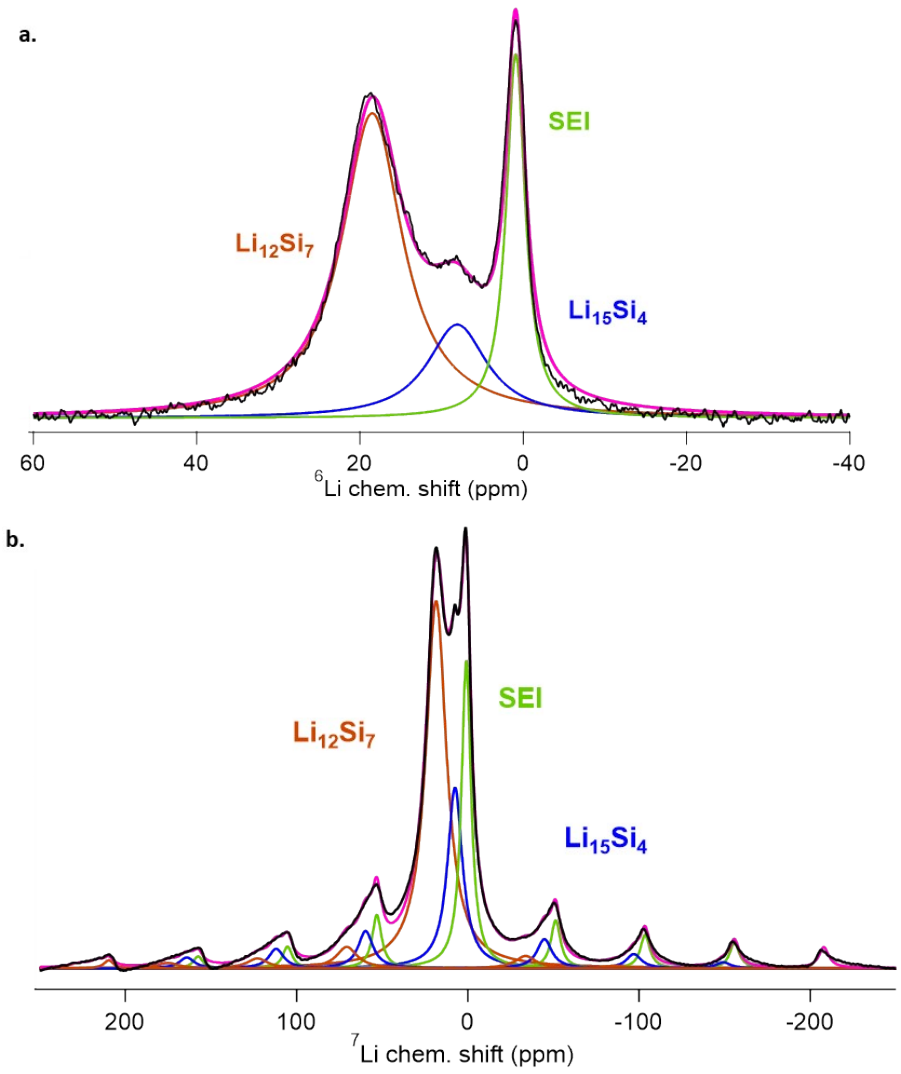

Fig. S1 Li NMR spectra obtained for setup A

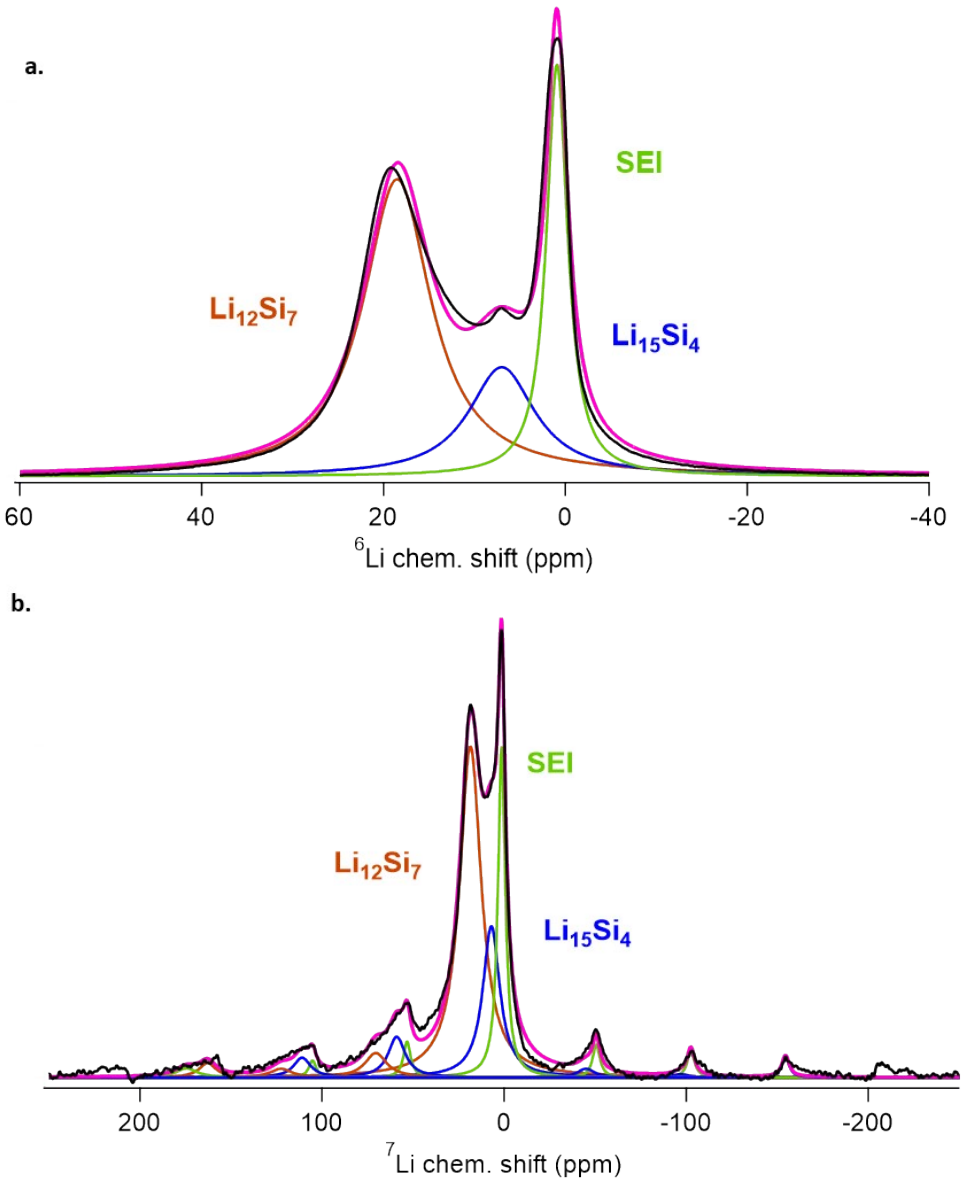

Fig. S2 Li NMR spectra obtained for setup B

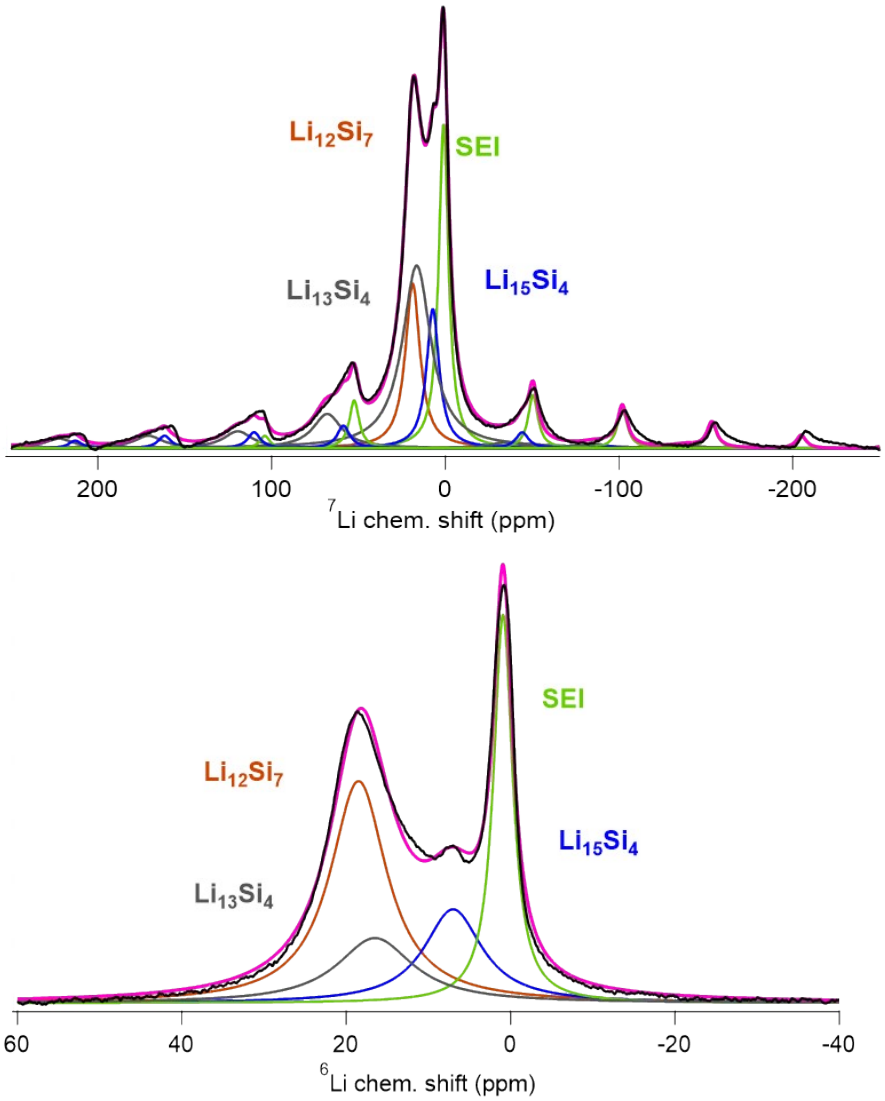

Fig. S3: Li NMR spectra obtained for setup C

REFERENCES

(1) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling One- and Two-Dimensional Solid-State NMR