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Supplementary Information.

Li/Fe substitution in Li-rich Ni, Co, Mn oxides for enhanced electrochemical performance as cathode materials

Juliette Billaud,*[a] Denis Sheptyakov,[b] Sébastien Sallard,[a,c] Daniela Leanza,[a] Michael Talianker,[d] Judith Grinblat,[e] Hadar Sclar,[e] Doron Aurbach,[e] Petr Novák,[a] and Claire Villevieille*[a]

Table S1 Parameters for the rate capability tests. A potentiostatic step of 30 minutes was applied at the end of each charge, except after the first cycle for which a 3 hours potentiostatic step was employed.

Cycle number	Voltage range	Charging rate	Discharging rate
1	2-4.7 V	C/15	
2-3	2-4.6 V	C/10	
4-6		C/3	
7-9		0.8C	
10-12		0.8C	C
13-15		0.8C	2C
16-19		0.8C	4C
20		C/10	
21-29, … , 61-69		C/3	
30, … , 70		C/10	

Table S2 Refined phase fractions of the monoclinic ($LiMO_2$-type, Space group *C* 2/*m*), rhombohedral (Li_2MO_3-type, Space group *R* -3 *m*). The cationic proportions for the M (transition metals) were assumed to be correct according to the precursors stoichiometry for all phases of the corresponding compounds. Li:Ni intersite exchange allowed. Results from the refinements on neutron powder diffraction data.

Sample		Phase fraction (neutrons) (%)
Reference	monoclinic phase rhombohedral phase spinel impurity	50 (3) 50 (3) 0
$Li_{85}Fe_5$-NCM	monoclinic phase rhombohedral phase spinel impurity	Not measured at HRPT Clearly a lot more in the x-ray data
$Li_{94}Fe_2$-NCM	monoclinic phase rhombohedral phase spinel impurity	49 (2) 38 (2) 12.9 (5)
$Li_{100}Fe_2$-NCM	monoclinic phase rhombohedral phase spinel impurity	45 (3) 55 (3) 0
$Li_{97}Fe_1$-NCM	monoclinic phase rhombohedral phase spinel impurity	56 (2) 36 (2) 7 (1)
$Li_{100}Fe_1$-NCM	monoclinic phase rhombohedral phase spinel impurity	62 (3) 38 (3) 0

Table S3. Refined crystal structure parameters of the monoclinic phase (space group $C2/m$) in the $Li_{94}Fe_2$-NCM compound, a=4.9540(2), b=8.5731(3), c=5.0382(2), β=109.366(2), V=201.87(2) Å^3
Results of the refinement on a neutron powder diffraction data. Parameters given without errors were fixed in the refinements.

Parameter / Atom			values
TM,	*4g* (0,*y*,0)	*Y*	0.169 (1)
		fract. occ. (Ni:Co:Mn:Fe:Li)	0.011 (4):0.117:0.635:0.024:0.213 (4)
		B_{iso} (Å^2)	0.4
Li (Li:Ni),	2b (0,1/2,0)	fract. occ (Li:Ni)	0.574 (8):0.426 (8)
		B_{iso} (Å^2)	1.0
O1	*4g* (*x*,0,*z*)	*x*	0.217 (1)
		z	0.2238 (8)
		B_{iso} (Å^2)	0.86 (2)
O2	*8j* (*x*,y,*z*)	*x*	0.2552 (6)
		y	0.3205 (4)
		z	0.2241 (5)
		B_{iso} (Å^2)	0.86 (2)
Li3	*4h* (0,*y*,1/2)	*y*	0.343 (2)
		B_{iso} (Å^2)	1.0
Li3	*2c* (0,*0*,1/2)	B_{iso} (Å^2)	1.0

Table S4. Refined crystal structure parameters of the rhombohedral phase (space group $R\bar{3}m$) in the $Li_{94}Fe_2$-NCM compound, a=2.8599(1), c=14.265(1). Results of the refinement on a neutron powder diffraction data. Parameters given without errors were fixed in the refinements.

Parameter / Atom			values
TM,	*3a* (0,0,0.5)	fract. occ. (Ni:Co:Mn:Fe:Li)	0.0166 (3):0.117:0.634:0.024:0.058 (3)
		B_{iso} (Å^2)	0.4
Li (Li:Ni),	3a (0,0,0)	fract. occ (Li:Ni)	0.941 (3):0.058 (3)
		B_{iso} (Å^2)	1.0
O1	3a (0,0,*z*)	*z*	0.240
		B_{iso} (Å^2)	0.86 (1)

Table S5. Refined crystal structure parameters of the spinel phase (space group $Fd\bar{3}m$) in the $Li_{94}Fe_2$-NCM compound, a=b=c=8.1576(3). Results of the refinement on a neutron powder diffraction data. Parameters given without errors were fixed in the refinements.

Parameter / Atom			values
TM,	*16d* (0.5,0.5,0.5)	fract. occ. (Ni:Co:Mn:Fe)	0.449:0.234:1.269:0.047
		B_{iso} (Å^2)	0.4
Li (Li:Ni),	8a (0.125,0.125,0.125)	fract. occ (Li:Ni)	0.85 (1):0.14 (1)
		B_{iso} (Å^2)	1.0
O1	*32e* (*x*,*y*,*z*)	*x,y,z*	0.2585,0.2585,0.2585
		B_{iso} (Å^2)	0.86 (1)

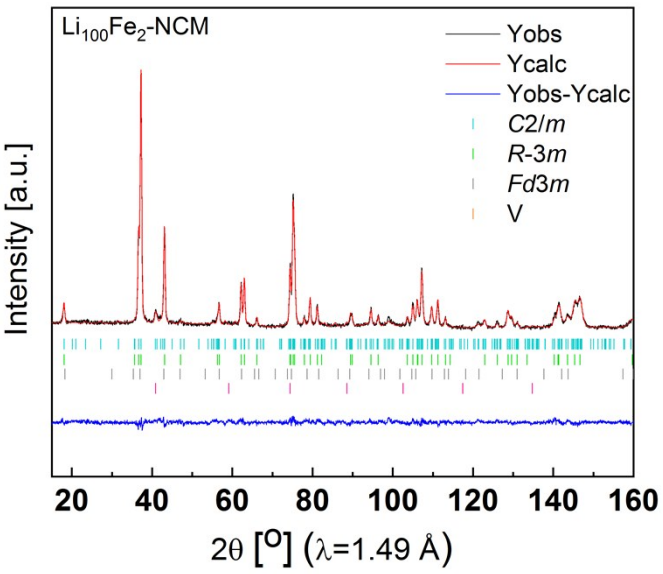

Figure S1. Plot of the Rietveld refinement of the crystal structure parameters based on the neutron powder diffraction data for $Li_{100}Fe_2$-NCM compound. Experimental points, calculated profile and difference curve are shown. The ticks below the graph correspond to the calculated peak positions for the phases (listed from top to bottom): monoclinic *C 2/m*, rhombohedral *R-3m*, spinel impurity and Vanadium of the sample container.

Table S6. Refined crystal structure parameters of the monoclinic phase (space group $C2/m$) in the $Li_{100}Fe_2$-NCM compound, a=4.9608(4), b=8.5657(8), c=5.0330(5), β=109.23(1). Results of the refinement on a neutron powder diffraction data. Parameters given without errors were fixed in the refinements.

Parameter / Atom			values
TM,	*4g* (0,*y*,0)	*y*	0.166 (2)
		fract. occ. (Ni:Co:Mn:Fe:Li)	0.0032 (8):0.117:0.634:0.023:0.192 (8)
		B_{iso} (Å^2)	0.4
Li (Li:Ni),	2b (0,1/2,0)	fract. occ (Li:Ni)	0.308 (8):0.192 (8)
		B_{iso} (Å^2)	1.0
O1	*4i* (*x*,0,*z*)	*x*	0.208 (2)
		z	0.228 (1)
		B_{iso} (Å^2)	0.67 (2)
O2	*8j* (*x*,y,*z*)	*x*	0.255 (1)
		y	0.3191 (6)
		z	0.2270 (9)
		B_{iso} (Å^2)	0.67 (2)
Li3	*4h* (0,*y*,1/2)	*y*	0.339 (3)
		B_{iso} (Å^2)	1.0
Li3	*2c* (0,*0*,1/2)	B_{iso} (Å^2)	1.0

Table S7. Refined crystal structure parameters of the rhombohedral phase (space group $R\bar{3}m$) in the $Li_{100}Fe_2$-NCM compound, a=2.8596(1), c=14.2556(7). Results of the refinement on a neutron powder diffraction data. Parameters given without errors were fixed in the refinements.

Parameter / Atom			values
TM,	*3a* (0,0,0.5)	fract. occ. (Ni:Co:Mn:Fe:Li)	0.176 (2):0.117:0.634:0.023:0.048 (2)
		B_{iso} (Å^2)	0.4
Li (Li:Ni),	3a (0,0,0)	fract. occ (Li:Ni)	0.951 (2):0.048 (2)
		B_{iso} (Å^2)	1.0
O1	3a (0,0,*z*)	*z*	0.240
		B_{iso} (Å^2)	0.67 (2)

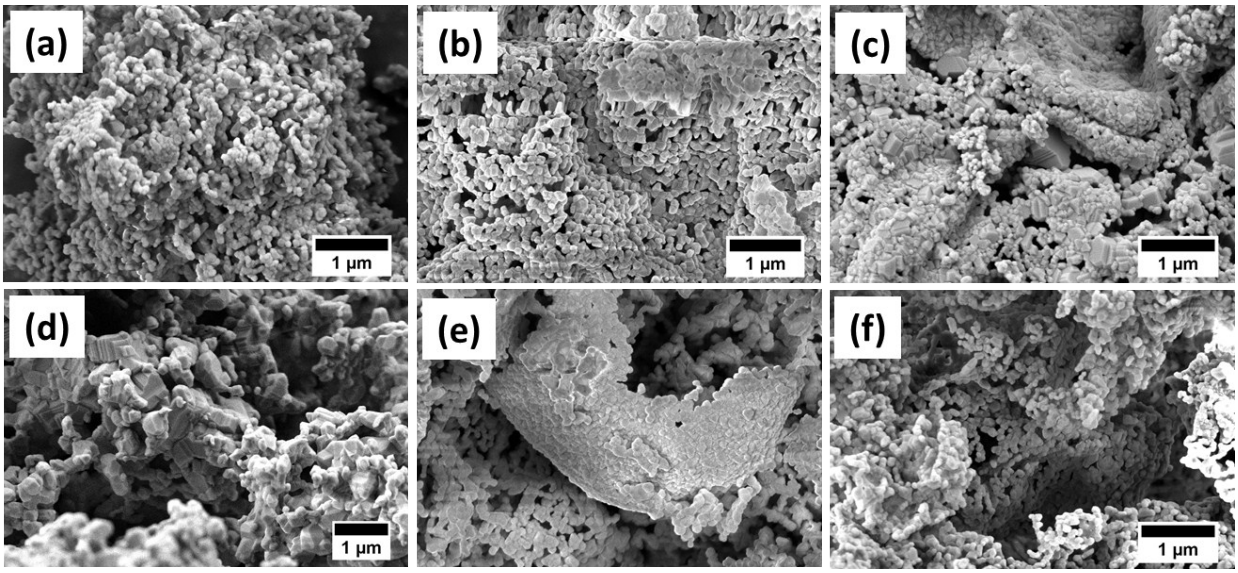

Figure S2. SEM micrographs of: a) Li-rich NCM, b) $Li_{97}Fe_1$-NCM, c) $Li_{94}Fe_2$-NCM, d) $Li_{85}Fe_5$-NCM, e) $Li_{100}Fe_1$-NCMand f) $Li_{100}Fe_2$-NCM, compounds.

Table S8. Evolution of the capacity retention (%) at the 100th cycle after the rate capability experiment

Compound	HE-NCM	$Li_{97}Fe_1$-NCM	$Li_{100}Fe_1$-NCM	$L_{94}Fe_2$-NCM	$Li_{100}Fe_2$-NCM
Capacity retention (%)	84.72	92.73	88.99	94.44	92.99

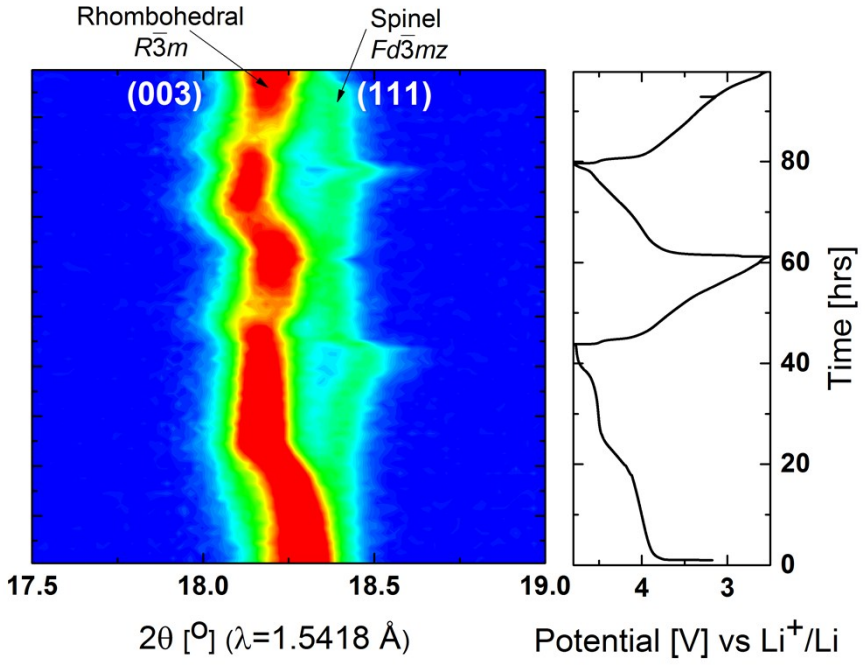

Figure S3. Contour plot representation of the operando XRD measurement at the first and second cycles for the $Li_{85}Fe_5$-NCM compound cycled at C/20. Zoom between 17.5 and 19 degrees (2θ).

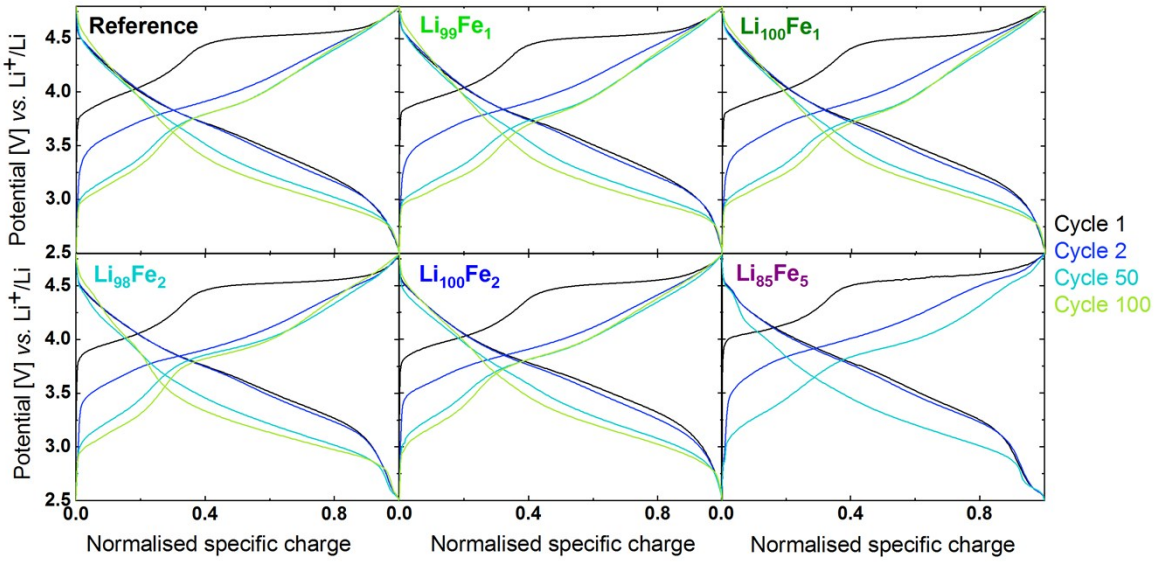

Figure S4. Evolution of the galvanostatic profiles at a rate of C/10.

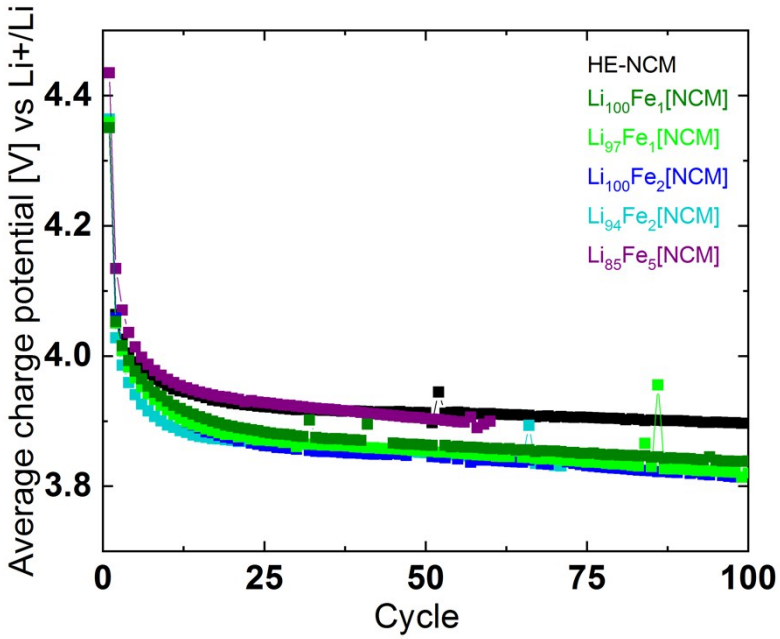

Figure S5. Evolution of the average charge potential as a function of cycle