Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

New Insight to Na Intercalation with Li Substitution at Alkali Site and High Performance of O3-type Cathode Material for Sodium Ion Batteries

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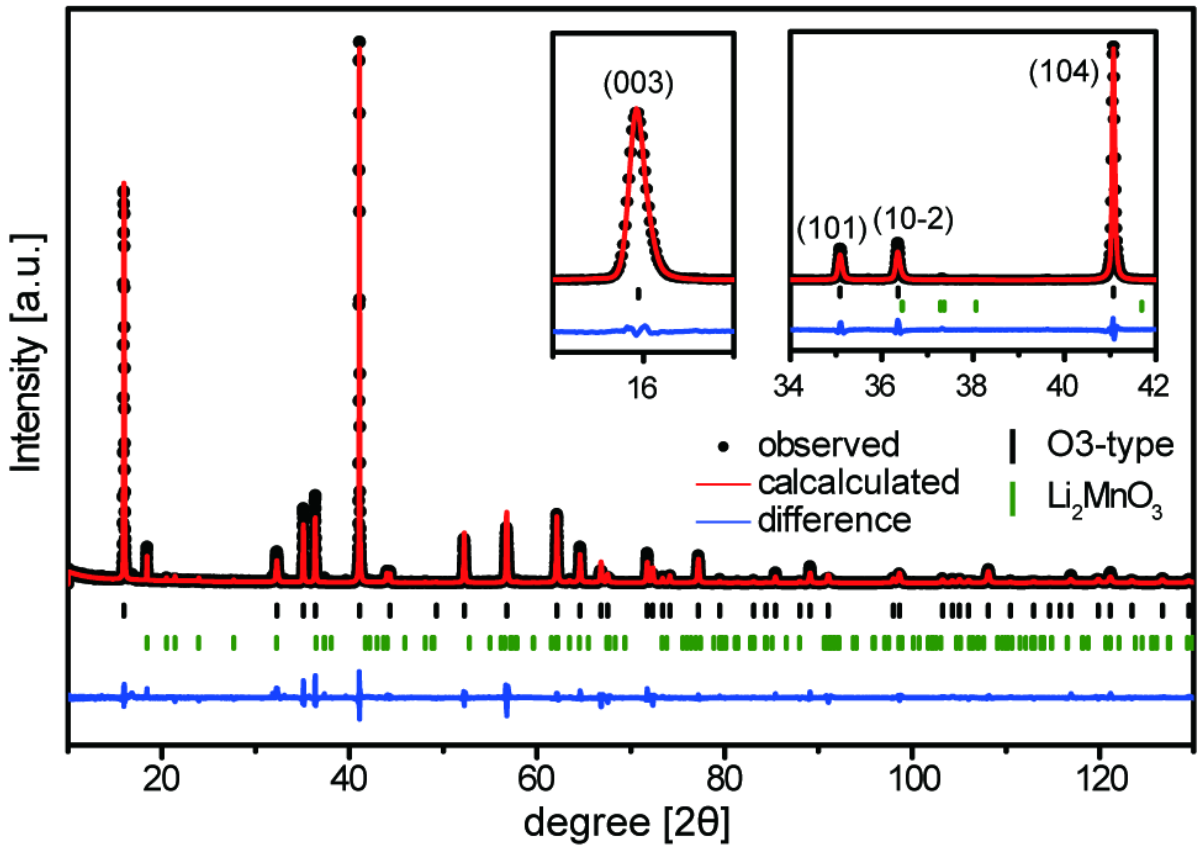

Figure S1. Rietveld refinement result of SPXRD pattern of L2F4M. Diffraction peaks of O3-type layered stucture (space group R -3 m, represented as black bar) and Li_2MnO_3 (represented as green bar) phase are visible. All peaks were matched with either O3-type layere structure or Li_2MnO_3 phase. P2-type layered structure was not found.

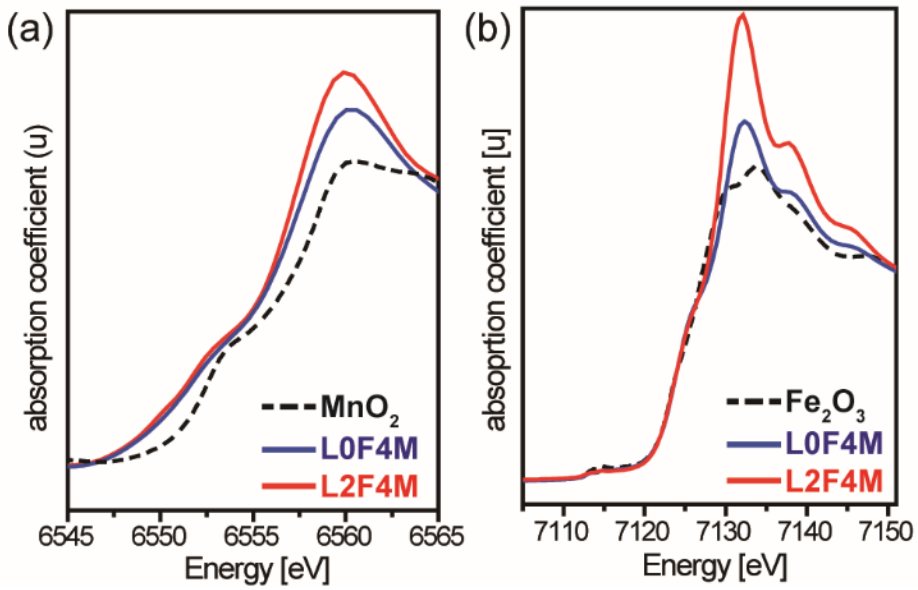

Figure S2. XANES spectra of OCV electrodes of L0F4M and L2F4M at (a) Mn-K absorption edge and (b) Fe-K absorption edge. MnO_2 and Fe_2O_3 spectra are shown as reference oxides.

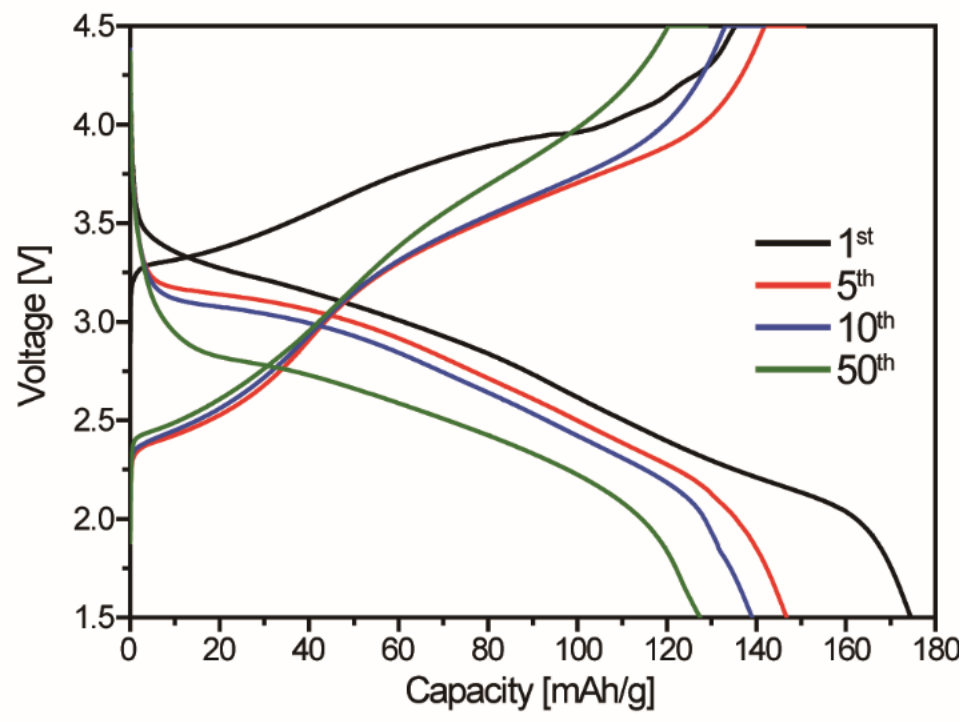

Figure S3. Voltage profile of L1F4M corresponding to the cycle performance shown in Fig. 4a.

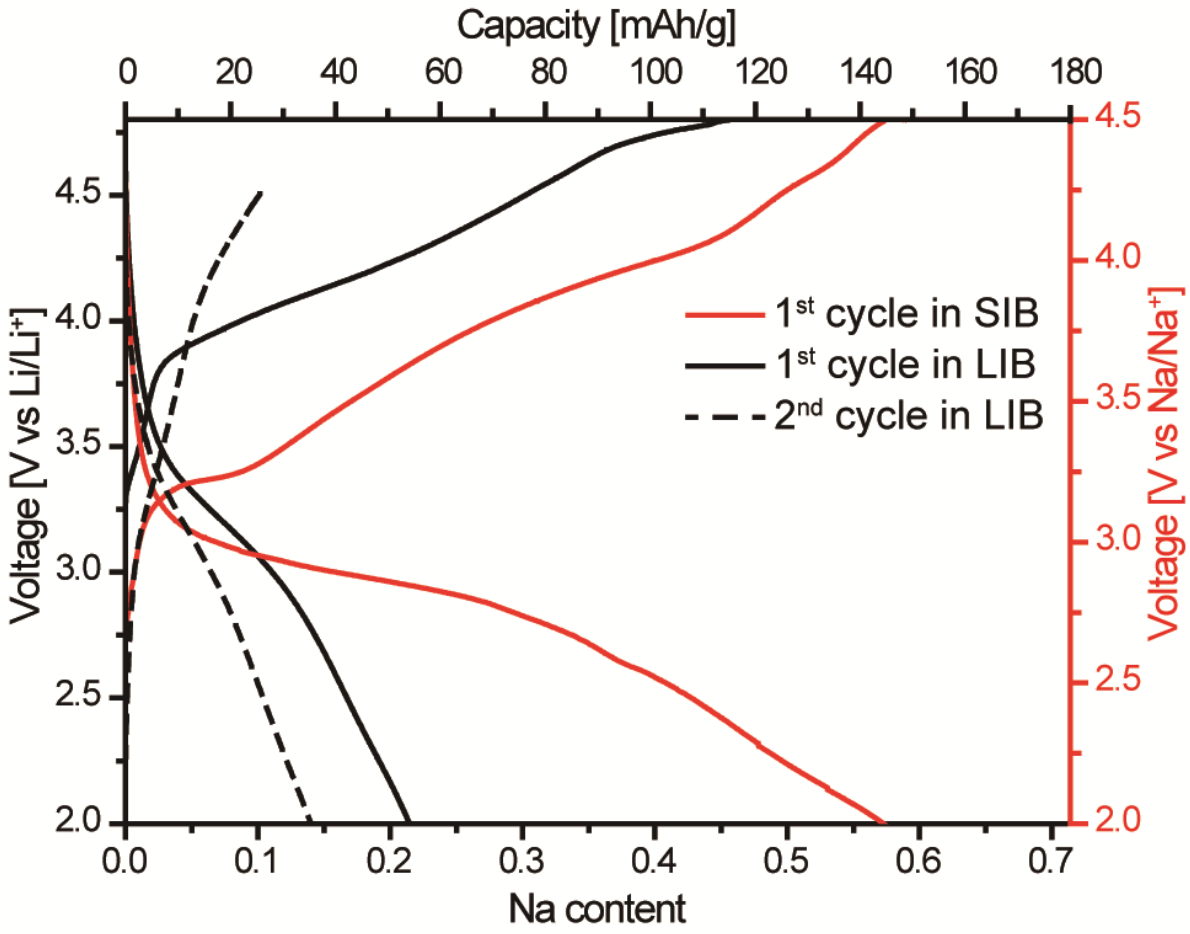

Figure S4. Voltage profile of L2F4M sample in SIB system and LIB system during first and second cycle. Voltage profile in SIB system corresponds with the voltage profile of first cycle that is shows in Figure 4. Low initial discharge capacity of L2F4M in LIB system compared to SIB system shows that the structure is not favorable for Li intercalation.

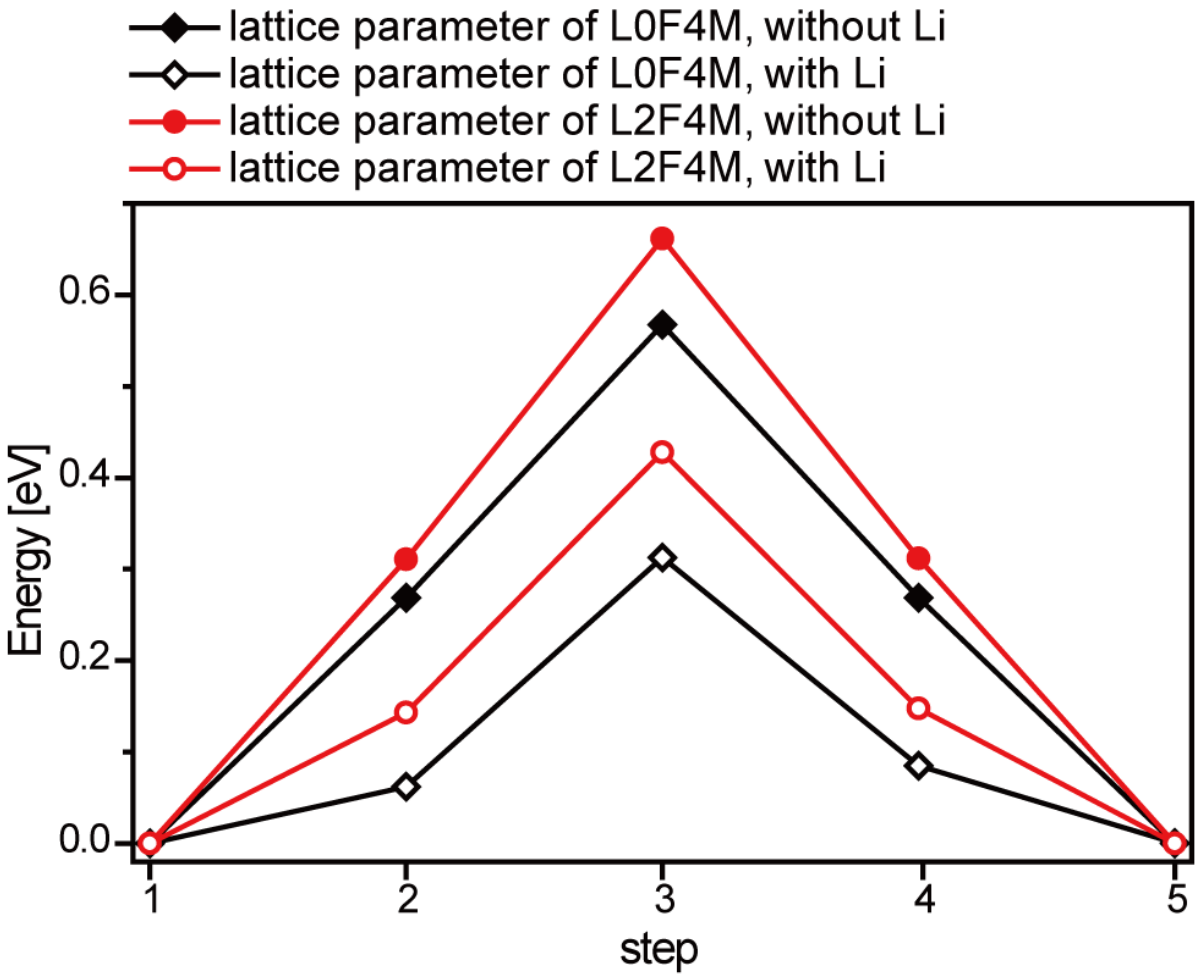

Figure S5. Calculated energy barriers for Na migration to a neighboring Na-vacancy site for L0F4M and L2F4M, which were synthesized without and with Li, respectively. The lattice parameters of L0F4M and L2F4M were obtained from Rietveld refinement of SPXRD patterns and are shown in Table S1. For comparison, we also considered two artificial structures of L0F4M with Li and L2F4M without Li, while keeping the same lattice parameters. For both L0F4M and L2F4M with Li, the substituted Li atom is positioned adjacent to the Na vacancy. The energy barrier calculated with lattice parameter of L0F4M without Li would correspond with L0F4M sample. The energy barrier calculated with lattice parameter of L2F4M with Li would correspond with L2F4M sample. Regardless of the lattice parameter, the energy barrier tends to be lower in the presence of Li. On the other hand, the energy barrier increases as the lattice parameter becomes smaller.

Table S1. Rietveld refinement results obtained from the SPXRD patterns and NRD pattern, shown in Figure 2 and Figure S1. The lattice parameters are for O3-type layered struture. Li_2MnO_3 impurity phase were found in L2F4M and L4F4M. P2-type layered structure was not found in any samples. For Rietveld analysis of NRD pattern, two possible Li coordination, i.e., Li at alkali sites (Li_{Na}) and Li at TM sites (Li_{TM}), were considered and the Li occupancy at each site was refined as well. (§ SPXRD pattern of L0F4M included several impurity peaks. We excluded regions corresponding to main peaks of impurities, thus the impurity phases were not considered during the Rietveld refinement.)

Synchrotron X-ray diffraction pattern							
	***a* [Å]**	***c* [Å]**	***V* [Å^3]**	**Li_2MnO_3 wt%**	**R_{wp}**	**R_B**	**Reduced χ^2**
§L0F4M	2.93621 (1)	16.6919 (2)	124.627 (1)	0	19.5	11.0	6.77
L1F4M	2.94000 (1)	16.4319 (1)	123.003 (1)	0	15.8	5.91	5.57
L2F4M	2.94291 (1)	16.3927 (1)	122.951 (1)	8.4 (2)	18.3	7.08	5.23
L4F4M	2.94751 (1)	16.5156 (1)	124.262 (1)	26.2 (2)	18.6	6.19	8.19
Neutron diffraction pattern							
	***a* [Å]**	***c* [Å]**	***V* [Å^3]**	***R*$_p$**	***R*$_{wp}$**	**Reduced χ^2**	
	2.93930 (2)	16.4133 (2)	122.804 (2)	2.41	3.21	2.81	
		x	***y***	***z***	**Occupancy**	**U_{iso} ×100**	
L1F4M	**Na**	0	0	0.5	0.657 (3)	1.07 (2)	
	Li_{Na}				0.120 (7)		
	Li_{TM}	0	0	0	0.036 (7)		
	Fe				0.467 (1)		
	Mn				0.537 (3)		
	O	0	0	0.26993 (4)	1.001 (9)		

Table S2. ICP analysis result of as-synthesized powder.

	L0F4M	L1F4M	L2F4M
Na	0.826	0.744	0.781
Li	-	0.116	0.289
Fe	0.490	0.486	0.488
Mn	0.510	0.514	0.512

Table S3. Contents of Na, Li, Fe, and Mn in ex situ electrodes at OCV state, at first charged state, at first discharged state, and second charged state. The values are obtained by ICP-OES analysis.

	as-synthesized powder (OCV)	after 1st charge (4.5V)	after 1st discharge (1.5V)	after 2nd charge (4.5V)	after 20th cycles (3.5V)
Na	0.781	0.130	0.877	0.131	0.493
Li	0.289	0.234	0.265	0.243	0.251
Fe	0.488	0.489	0.493	0.490	0.498
Mn	0.512	0.511	0.507	0.510	0.502