Studies on Electrode Materials for Rechargeable Na Batteries by Synchrotron Radiation

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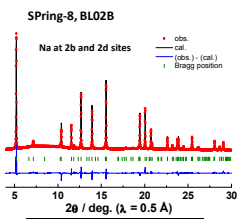
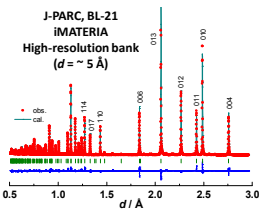
Structural Analysis on P2-Type $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$; X-Ray and Neutron Diffraction

【*Rietveld/MEM Analysis of P2-type $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$*】



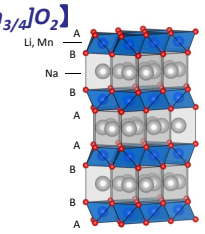


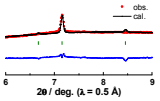
atom	site	g	x	y	z	B (Å²)
Na_1	2b	0.320(1)	0	0	1/4	3.7(1)
Na_2	2d	0.510(1)	1/3	2/3	3/4	2.3(1)
Li	2a	0.24	0	0	0	0.12(1)
Mn	2a	0.76	0	0	0	0.12(1)
O	4f	1.000(1)	1/3	2/3	0.094(1)	0.56(1)

S.G. : $P6_3/mmc$; a = 2.8711(1) Å, c = 11.028(1) Å
R_{wp} = 8.12% R_B = 5.07% R_I = 6.15%

➔ *The results are indicative of self-diffusion of Na ions at different sites.*

Large B-values are also supported by ND.





site	g (Li)	g (Mn)
2a	0.478	0.522
2b	0.121	0.879
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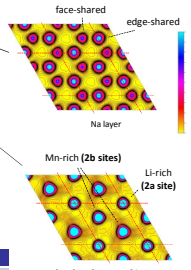
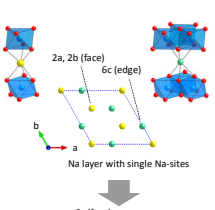
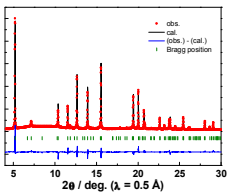


*using space group $P6_3$

➔ ***in-plane "anti-site defects" (and / or stacking faults)***



The results are indicative of self-diffusion of Na ions at different sites.

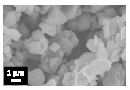


atom	site	g	x	y	z	B (Å²)
Na_1(1)	6c	0.104(1)	0.730(2)	0.397(2)	1/4	0.7
Na_1(2)	6c	0.104(1)	0.064(2)	0.064(2)	1/4	0.7
Na_1(3)	6c	0.104(1)	0.397(2)	0.730(2)	1/4	0.7
Na_1(4)	6c	0.172(1)	0.606(1)	0.606(1)	1/4	0.7
Na_1(5)	6c	0.172(1)	0.728(1)	2/3	1/4	0.7
Na_1(6)	6c	0.172(1)	2/3	0.728(1)	1/4	0.7

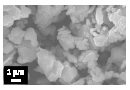
Crystal structures of new layered oxides are resolved by synchrotron XRD and ND, N. Yabuuchi et al., submitted

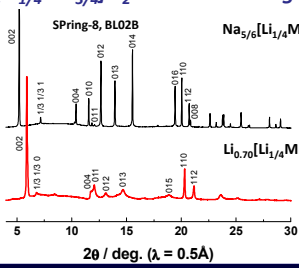
The results are indicative of self-diffusion of Na ions at different sites.

【*P2-Type $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ vs. Ion-Exchanged $Li_{0.7}[Li_{1/4}Mn_{3/4}]O_2$*】

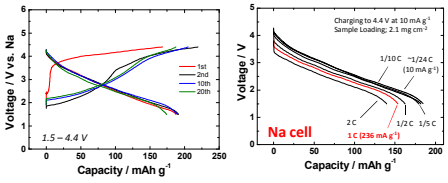


ion-exchange in molten salt



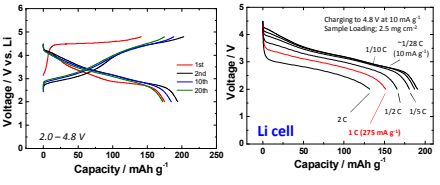


Na cell, P2-type $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$



P2-type $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ in the Na cell shows better rate capability compared with the O2-type phase in the Li cell.

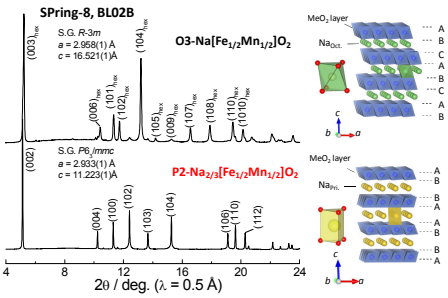
Li cell, O2-type $Li_2[Li_{1/4}Mn_{3/4}]O_2$



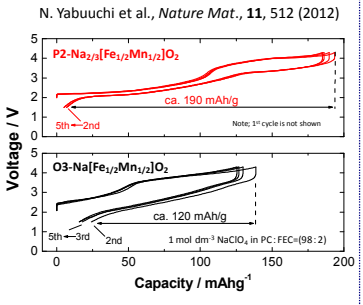
➔ Facilitated diffusion of Na ions in the P2-type phase with a open two-dimensional path.

Reaction Mechanisms on P2-$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$; SXRD and XAS

【Crystal *Structures and Electrode Performance*】

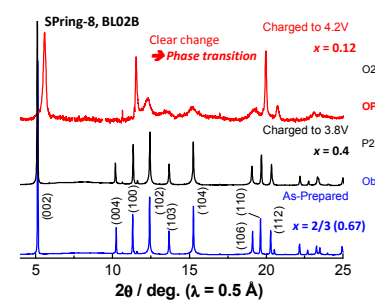


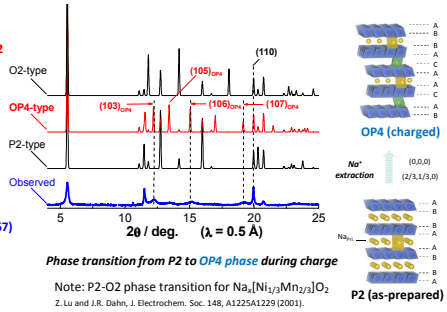
N. Yabuuchi et al., *Nature Mat.*, **11**, 512 (2012)



P2-$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$ shows better electrode performance

【*Phase Transitions on Charge; SXRD*】





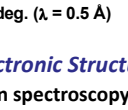
Phase transition from P2 to OP4 phase during charge

Note: P2-O2 phase transition for $Na_x[Ni_{1/3}Mn_{2/3}]O_2$
Z. Lu and J.R. Dahn, J. Electrochem. Soc. 148, A1225A1229 (2001).

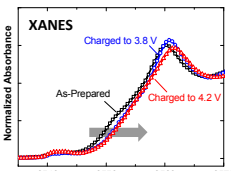
【*Change in Electronic Structures; XAS*】

X-ray absorption spectroscopy (XAS)

Photon Factory, BL-7C



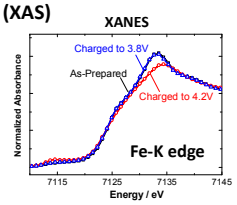
Mn-K edge



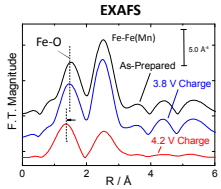
Shift of XANES spectra during charge to 3.8 V, **but NOT from 3.8 to 4.2 V**

➔ ***Mn^{3+}/Mn^{4+} Redox below 3.8V***

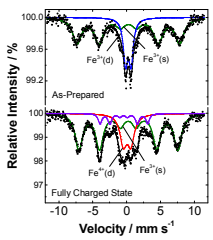
XANES



EXAFS



Mössbauer spectroscopy



Change in the XAFS spectra and shortened Fe-O interatomic distance above 3.8 V
1.99 Å for 3.8 V vs. 1.90 Å for 4.2 V

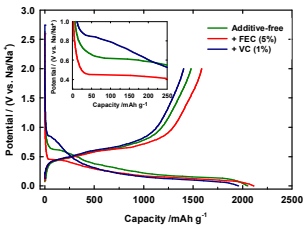
Fe^{3+}/Fe^{4+} Redox at 4 V region.

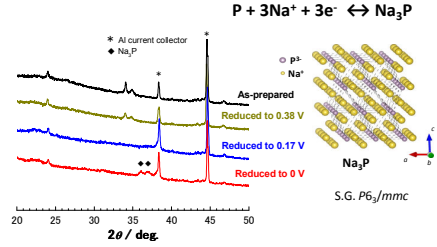
Studies on Surface of Phosphorus Electrodes

【*Charge/Discharge Mechanisms*】

Red phosphorus for Na cells; N. Yabuuchi et al., *ChemElectroChem*, in-press DOI: 10.1002/celc.201300149

$P + 3Na^+ + 3e^- \leftrightarrow Na_3P$



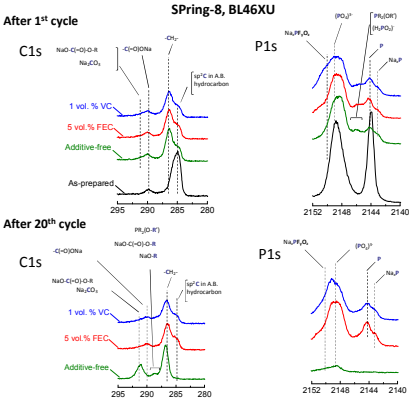


Black Phosphorus is reversibly reduced with a three-electron reaction.

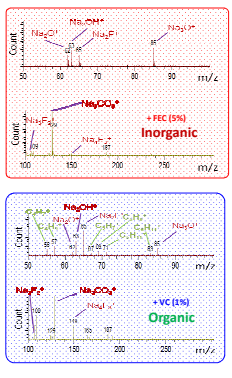
【*Surface Analysis*】

Hard X-ray absorption spectroscopy; HAXPES

SPring-8, BL46XU

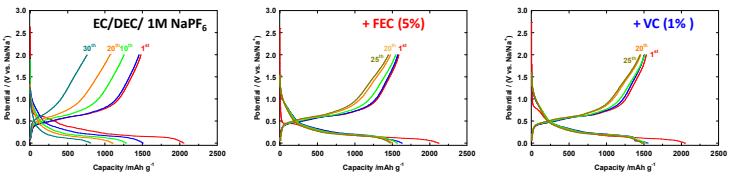


TOF-SIMS



FEC and VC additives effectively stabilize the sufrace films formed on phosphorus and suppress the continuous decomposition of electrolyte and deposition of decomposed products.

【*Cycle Performance*】



FEC and VC additive effectively suppresses the loss of surface chemical species formed on the black Phosphorus, resulting in the good cyclability as electrode materials.

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