Synthesis and Characterization of the Crystal Structure, the Magnetic and the Electrochemical Properties of the New Fluorophosphate $LiNaFe[PO_4]F$

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Received (in XXX, XXX) Xth XXXXXXXXX 2011, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Electronic Supplementary Information (ESI)

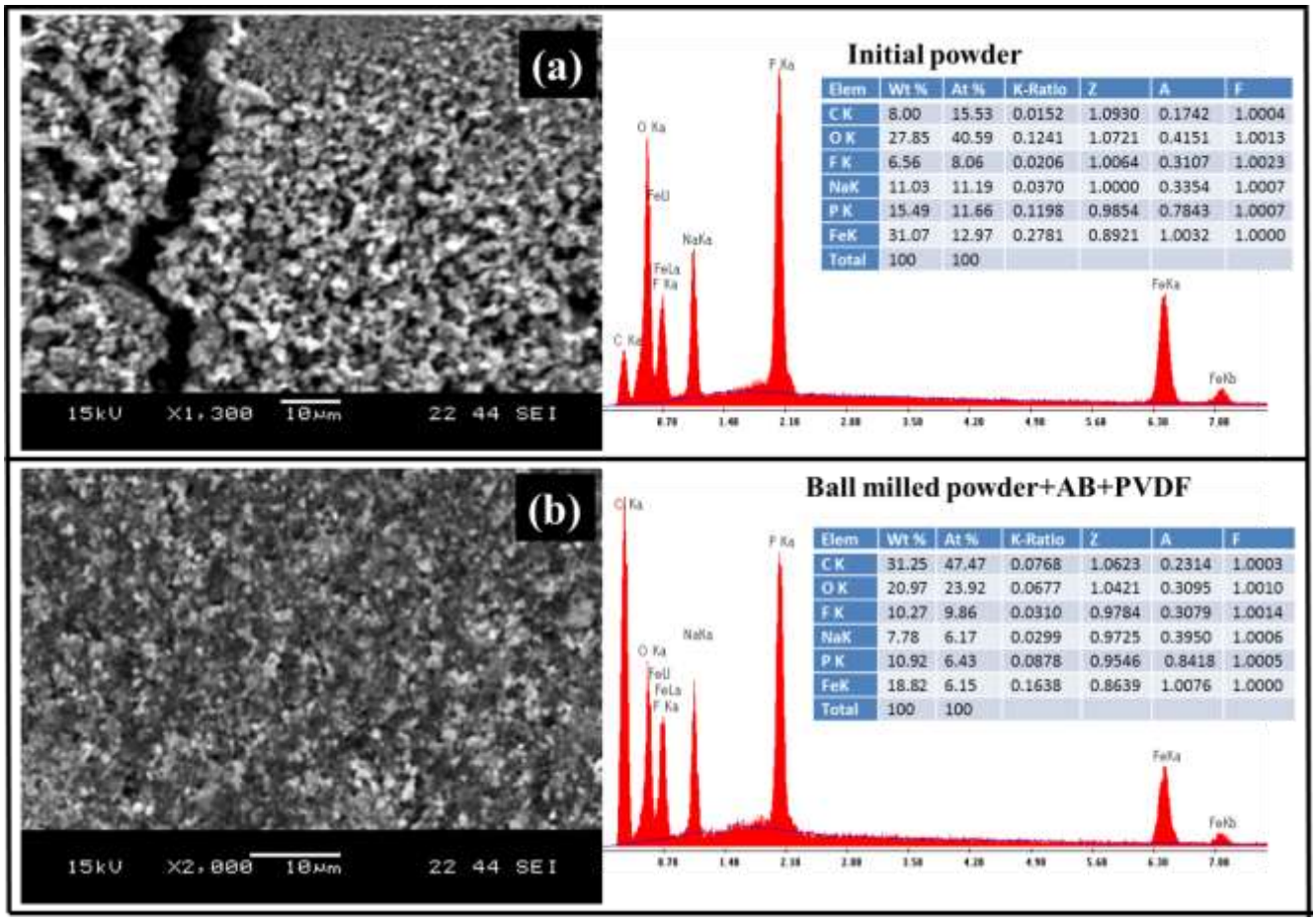

Figure S1. SEM image and EDX analyses of the initial LiNaFe[PO_4]F powder (a), and of the electrode [LiNaFe[PO_4]F+ carbon black (AB) + polyvinylidene fluoride (PVDF)] before cycling (b).

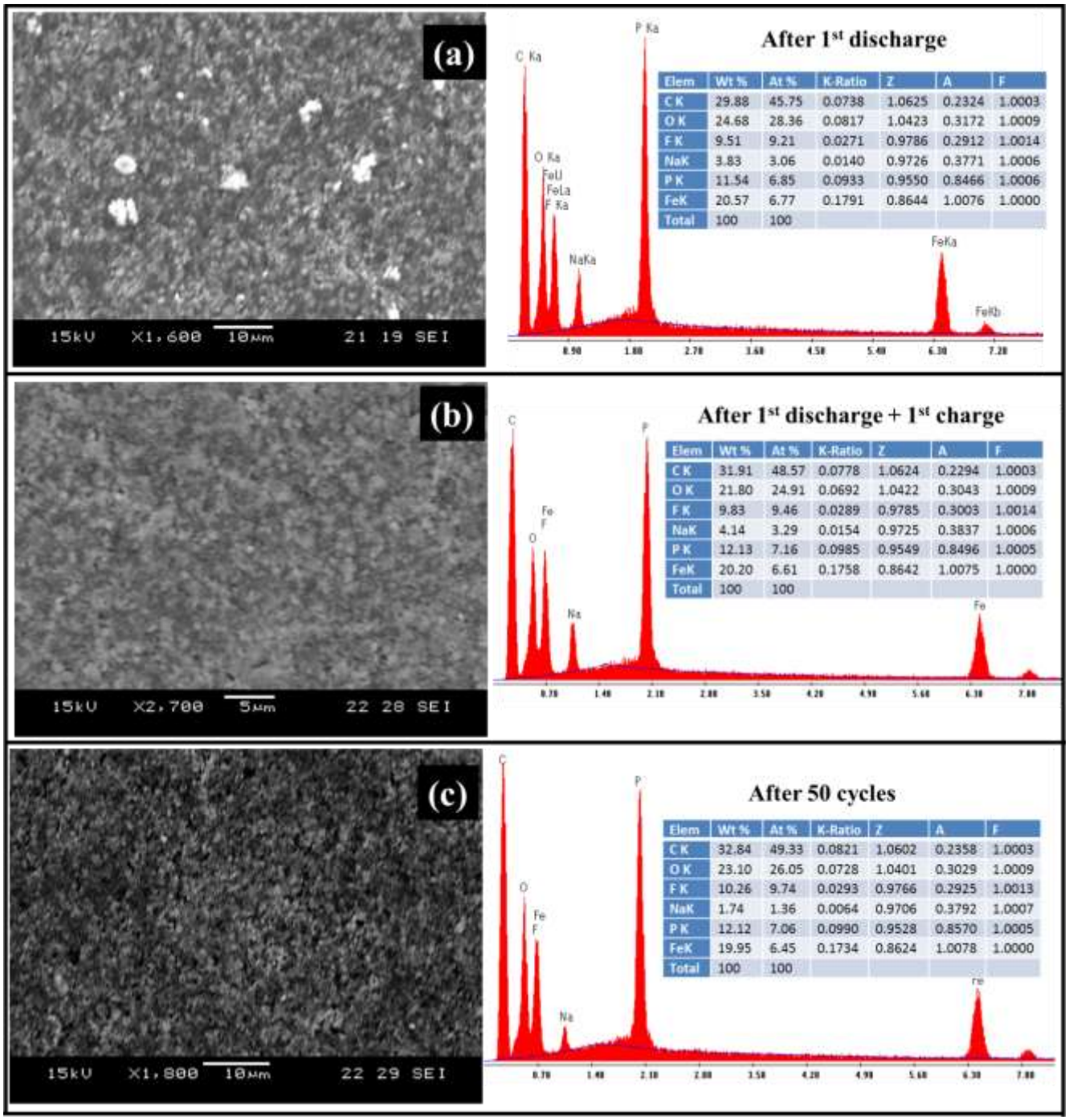

Figure S2. SEM images and EDX analyses of the of the electrode $LiNaFe[PO_4]F$ after the first discharge to 1V(a), after the first charge to 5V (b), and after 50 cycles (c).

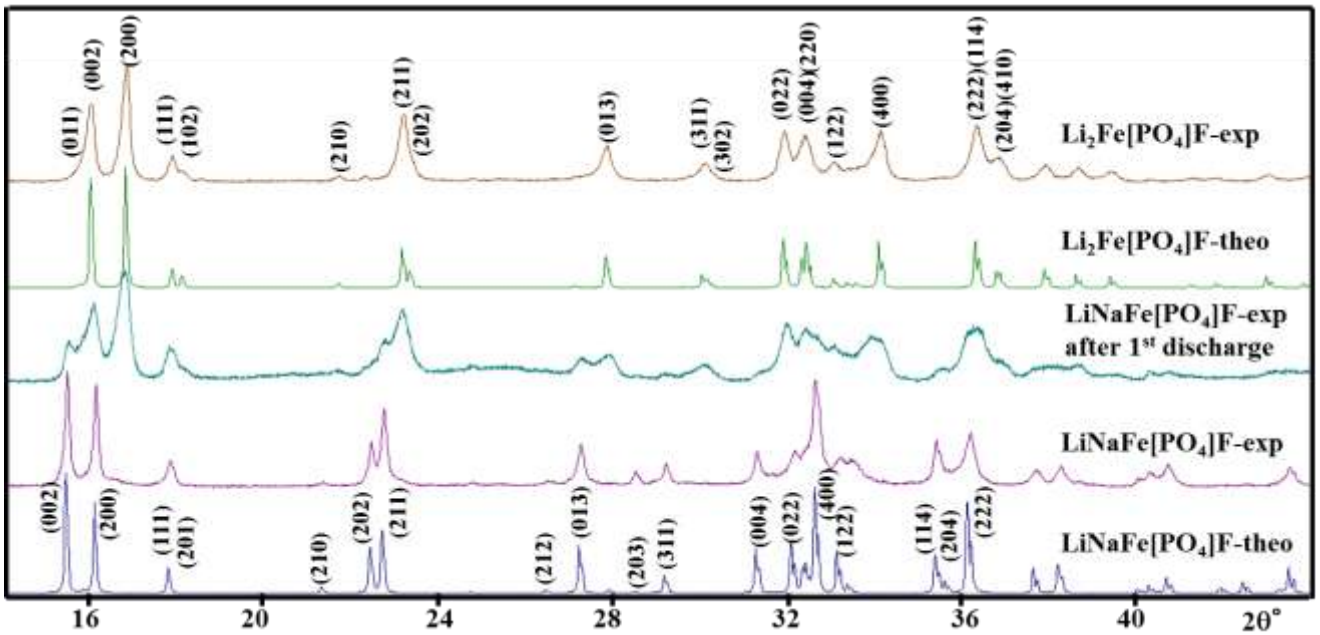

Figure S3. XRD powder patterns of $Li_2Fe[PO_4]F$, $LiNaFe[PO_4]F$ after the first discharge to 1V , and $LiNaFe[PO_4]F$.

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Table S1. Basis vectors for the 4*a*(0,0,0) and 4*b*(0,0,1/2) sites of the *Pnma* space group and the propagation vector k=[0,0,0]. The atomic positions are Fe11 (0,0,0); Fe12 (1/2,0,1/2); Fe13 (0,1/2,0), Fe14 (1/2,1/2,1/2) and Fe21(0,0,1/2), Fe22(1/2,0,0), Fe23(0,1/2,1/2), Fe24(1/2,1/2,0), respectively. The ordering modes are F(+ + + +), C(+ + - -), G(+ - + -), A(+ - - +).

IR	Basis vectors	Shubnikov group
Γ_1	Ax Gy Cz	Pnma
Γ_3	Gx Ay Fz	Pn'm'a
Γ_5	Cx Fy Az	Pn'ma'
Γ_7	Fx Cy Gz	Pnm'a'

Table S2. Atom positions and isotopic displacement parameters for $LiNaFe[PO_4]F$ from the neutron powder diffraction data at 3K.

Atom		*x*	*y*	*z*
Fe1	4*a*	0.0	0.0	0.0
Fe2	4*b*	0.0	0.0	1/2
P1	4*c*	0.0381(13)	1/4	0.7392(15)
P2	4*c*	0.2438(17)	1/4	0.0741(13)
Na1	8*d*	0.2313(14)	0.006(3)	0.3444(11)
Li2	4*c*	0.273(4)	1/4	0.560(3)
Li3	4*c*	0.439(4)	1/4	0.214(4)
O1	8*d*	0.1777(8)	0.0504(13)	0.0369(7)
O2	4*c*	0.2689(12)	1/4	0.2070(10)
O3	4*c*	0.1785(13)	1/4	0.7451(15)
O4	4*c*	0.3765(11)	1/4	0.0146(11)
O5	4*c*	0.4889(13)	1/4	0.6316(11)
O6	8*d*	0.0061(10)	0.5507(12)	0.3194(7)
F1	4*c*	0.1322(11)	1/4	0.4709(12)
F2	4*c*	0.4392(11)	1/4	0.3986(14)

Overall thermal parameter U_{iso} = 0.0034(11) Å^2.

Table S3. ICP analysis of the starting material $LiNaFe[PO_4]F$

Elements and wave length (Å)	**Average concentration (mg/l or ppm)**	**Standard deviation**	**Number of mole**	**Molar ratio toward Fe**	**Molar ratio toward P**
Fe_2382	20.64	0.081	0.36959441	1	0.995455
Fe_2395	20.8	0.0308	0.37245949	1.007752	1.003171
Fe_2404	21	0.0372	0.37604083	1.017442	1.012817
Fe_2599	20.53	0.0669	0.36762468	0.994671	0.990149
Li_4602	2.665	0.0043	0.38395044	1.038843	1.034121
Li_6103	2.56	0.0075	0.36882294	0.997913	0.993377
Li_6707	^ *****	-----	#VALUE!	#VALUE!	#VALUE!
Na_3302	8.321	0.0177	0.36194359	0.979299	0.974848
Na_5889	^ *****	-----	#VALUE!	#VALUE!	#VALUE!
Na_5895	7.959	0.1502	0.34619746	0.936696	0.932438
Na_8183	8.312	0.0432	0.36155212	0.97824	0.973794
P_1774	11.65	0.0377	0.37612482	1.017669	1.013043
P_1782	11.64	0.0156	0.37580197	1.016796	1.012174
P_1859	11.51	0.0117	0.37160487	1.00544	1.00087
P_2136	11.5	0.0382	0.37128201	1.004566	1
The molar ratio of Li/Na/Fe/P is confirmed to be 1:1:1:1 in the starting material					