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New Form of Li₂FePO₄F as Cathode Material for Li-Ion Batteries

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Supporting Information

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i-ion batteries originally developed for portable devices can now be found in applications as diverse as power tools, electric vehicles, and stationary energy storage. To satisfy the need of current and new applications, Li-ion batteries require further improvement in terms of performance properties (energy and power density, safety, and cost). Transition metal compounds containing different polyanion units $(XO_4)^{m-}$ (X = P, S, Si) are considered as the most promising cathode materials for the next generation of Li-ion batteries due to increased redox potential caused by an inductive effect and remarkable electrochemical and thermal stability ascribed to a three-dimensional structure.¹⁻³ Further advances in the polyanion cathodes are related to combining (XO₄)^{m-} and F^- in the anion sublattice, which is expected to enhance the operating voltage due to the higher ionicity of the M-F bond. Indeed, various fluorophosphates (LiVPO₄F, Na₂FePO₄F) and fluorosulphates (LiMSO4F) have been reported to exhibit attractive electrochemical performance.4-8

Among fluorophosphates, compounds of the general formula A_2MPO_4F (A = Na, Li; M = Fe, Mn, Co, Ni) have received particular interest due to their potential to operate on more than one alkali atom per formula unit (f.u.), which would result in higher specific capacity and energy density. The A2MPO4F fluorophosphates crystallize in three different structure types. While the coordination polyhedra of transition metal, MO_4F_2 octahedra, is the same for all three, the means of their conjugation varies from edge-shared in Li_2MPO_4F (M = Ni, Co) and corner-shared in Na₂MnPO₄F to mixed face-shared and corner-shared in Na_2FePO_4F , resulting in different architectures.⁸⁻¹¹ The three-dimensional (3D) Na_2MnPO_4F and the layered Na₂FePO₄F were shown to operate as positive electrode material in Na- and Li-ion cells with reversible capacity of about 120 mAh $g^{-1}~({\sim}0.8$ electron per f.u.). $^{11-13}$ Moreover, the capacity improvement up to ~180 mAhg⁻¹ (~1.46 electrons per f.u.) was observed for nanostructured Na₂FePO₄F cycled at elevated temperature.¹²

Several groups reported on high voltage electrochemical performance of $\text{Li}_2\text{CoPO}_4\text{F}$ and $\text{Li}_2\text{NiPO}_4\text{F}^{.8,14-16}$ These fluorophosphates possess a three-dimensional structure and, by analogy with the olivine phase, are expected to demonstrate good stability and reversibility upon cycling. The complete evaluation of these materials is restrained by the absence of commercial high-voltage electrolytes stable above 4.8 V. The exploration of corresponding Fe- or Mn-based fluorophos-

phates with lower redox potentials might provide an advantage in the energy and power density over the LiFePO₄ cathode materials. So far, these fluorophosphates have not been identified: apparently, the structure framework could not adopt the Fe²⁺ and Mn²⁺ ions, which are larger compared to Co²⁺ and Ni²⁺. In our previous paper, we showed that upon the first charge Li2CoPO4F undergoes structural transformation with the large volume expansion (\sim 5%) demonstrating the framework flexibility.¹⁵ Considering this "structure pliability" we attempted to stabilize Fe-based fluorophosphate by "expanding" the framework through the substitution of Li ions located in the structure voids by larger Na ions; as a result, we succeeded in synthesis of a new NaLiFePO4F phase isostructural to Li₂NiPO₄F (Figure 1). Upon preparing this communication, we have found a short report by Mizuta et al., where electrochemical properties measured on the multiphase NaLiFePO₄F sample were described.¹⁷ Here, we report on the synthesis employed for obtaining the pure NaLiFePO₄F phase, its structure determination, and electrochemical activity. We demonstrate that electrochemical replacement of Na by Li in



Figure 1. X-ray diffraction pattern and Riteveld refinement of NaLiFePO₄F. Inset represents the structure view along the *b* axis: the iron octahedra are shown in blue, and phosphate tetrahedra in green; the alkali sites are distinguished as Na1 in violet, Li2 in yellow, and Li3 in orange.

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NaLiFePO₄F results in a new Li_2FePO_4F phase with attractive electrochemical properties.

Fluorophosphate NaLiFePO₄F was prepared by annealing a stoichiometric mixture of LiFePO4 and NaF at 650-700 °C for 2 h under Ar-flow. The carbon-containing composite NaLiFePO₄F/C was prepared by adding a carbon black (~5 wt %) to the initial mixture. A full description of synthesis and characterization techniques used in this study can be found in the Supporting Information. The X-ray diffraction (XRD) pattern of the obtained gray powder was fully indexed in the *Pnma* space group with cell parameters a = 10.9823(12) Å, b =6.3607(8) Å and c = 11.439(2) Å (V = 799.1(3) Å³). A considerable increase in cell parameters and volume in comparison with those of Li_2MPO_4F (M = Co, Ni) was observed as a result of the substitution of Na for Li. Chemical composition of the sample was analyzed by an ICP method: the stoichiometry of Na1.01/Li105/Fe0.97/P1.00 was found, and it agreed well with the expected formula. Scanning electron microscopy (SEM) investigation of the NaLiFePO₄F/C composite revealed the crystallite sizes of 0.6–0.8 μ m.

The structure of NaLiFePO4F was determined by Rietveld refinement of the XRD pattern using the structural model of Li₂NiPO₄F as a first approach.⁹ The fractional coordinates and displacement parameters of the atoms were refined along with the occupancy of the three alkali sites. Details of the fitting procedure and the structural and bonding parameters can be found in the Supporting Information. NaLiFePO₄F is isostructural to Li_2MPO_4F (M = Ni, Co); it is built of edgeshared FeO_4F_2 octahedra that run along the [010] direction and are connected to each other by PO_4 tetrahedra (Figure 1). The interconnected polyhedra generate a 3D framework with channels along the [010] and [011] directions that are capable of alkali-ion diffusion. There are three distinct alkali metal positions with different coordination environments: two fivecoordinated sites (A1, A2) and one distorted tetrahedral one (A3). According to Rietveld refinement, the A2 and A3 sites are fully occupied by lithium, while sodium resides in the "most open" A1-position located along the [010] channels. The structural validity of the obtained results was confirmed by bond valence sum calculations (see Supporting Information).

Electrochemical testing on the carbon coated NaLiFePO₄F sample revealed a promising electrode material, which exhibits a sloping profile with an average potential of 3.4 V vs Li. A reversible capacity of about 113 mAh g^{-1} (~ 0.84 Li) was sustained upon cycling between 2.0 and 4.5 V at a rate of C/50 (Figure 2). The first charge process takes place at higher potentials than subsequent ones, while the first and following discharge curves are almost the same. This implies that during the first charge the Na⁺ ions are extracted, and in the following cycles, it seems that only the Li⁺ ions participate in the electrochemical process because lithium substitutes for almost whole sodium in Na1-xLi1+xFePO4F after the first discharge. Upon the first charging, it is more difficult for the larger Na⁺ ions to be taken out from the structure, and this leads to a higher charge voltage. The discharge capacity well sustained upon cycling confirming good reversibility of the electrochemical process (Figure 2). The solid-solution electrochemical behavior, evident from sloping profile of charge/discharge curves, as well as the slight increase of polarization observed upon shifting to higher cycling rates (from C/50 to C/10, Figure S1 in the Supporting Information) suggested good kinetics of this material.



Figure 2. Electrochemical properties of NaLiFePO₄F: charge– discharge curves of the first (red), second (blue), and fifth (green) cycles at the rate C/50 are shown. Inset represents discharge capacity retention data for cycling at different rates.

To examine structural changes upon electrochemical Li de/ intercalation *ex situ*, XRD measurements were performed for the recovered electrode materials: after 5 cycles at a rate of C/ 50, one electrode was charged to 4.5 V, while the second one was charged to 4.5 V and then discharged to 2.0 V. Despite remarkable changes observed on the XRD pattern, the characteristic major peaks of the structure located at $16^{\circ} 2\theta$ and corresponding to the (002) and (200) reflections were still present though shifted to higher angles, with the redistributed intensities (Figure 3). On the assumption that the structure



Figure 3. XRD patterns of the NaLiFePO₄F phase (a) and the electrodes at different stages of cycling at a rate of C/50: (b) before cycling, (c) charged to 4.5 V after 5 cycles, (d) discharged to 2.0 V after 6 cycles. The reflections marked with an asterisk are from graphite.

framework is preserved upon replacing Na^+ by Li^+ , this shift of the reflections corresponds to a decrease in the cell parameters, because the ionic radius for Li^+ is much smaller than that for Na^+ . The XRD patterns of the recovered electrode materials were indexed on the basis of the pristine orthorhombic unit cell with parameters smaller than the initial ones, and the shrink of the unit cell volume by 6.7% was observed (Table 1). The

Table 1. Results of *Ex Situ* XRD Measurements: Cell Parameters of the Tested NaLiFePO₄F Electrodes

electrodes	a, Å	b, Å	<i>c,</i> Å	<i>V</i> , Å ³
initial	10.978(2)	6.3631(12)	11.429(2)	798.4(3)
charged to 4.5 V	10.761(4)	6.246(2)	10.886(4)	731.7(4)
discharged to 2 V	10.775(5)	6.266(3)	11.027(6)	744.5(6)

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quality of the XRD patterns impeded Rietveld refinement for the recovered electrode materials; therefore, to reproduce the observed diffraction pattern, we attempted structure modeling with the Na/Li mixed occupancy of the A1-site. The reverse intensity distribution of the mentioned reflections was obtained by complete substitution of sodium by lithium on the alkali metal site. These results were supported by energy-dispersive X-ray spectroscopy (EDX) analysis, which revealed the absence of sodium in the recovered electrode materials (Figure S2 in the Supporting Information). The observed changes on the XRD patterns along with the results of EDX analysis revealed the compositional transformation of NaLiFePO₄F to Li₂FePO₄F upon electrochemical cycling, and a new polymorph of Li₂FePO₄F with a 3D structure was identified for the first time.

NaLiFePO₄F can be used directly as a cathode material in the Li-cell, and the derived Li₂FePO₄F phase is capable of reversible de/intercalation of 0.84 Li ions with a volume change of 1.7% between charged (V = 731.7(4) Å³) and discharged (V = 744.5(6) $Å^3$) states. The single-phase de/lithiation mechanism in Li₂FePO₄F was verified by the *ex situ* XRD measurements for the electrodes at intermediate states of charge (Figure S3 in the Supporting Information). Stable cycling performance, the small volume change, and the solid-solution electrochemical behavior, which implies the absence of serious kinetic limitations, make this fluorophosphate system very suitable for reversible de/intercalation of Li, especially if its energy density will be enhanced, for example by partial substitution of Mn for Fe. In addition, this fluorophosphate system keeps the possibility of utilizing more than one alkali metal per formula unit, which will be further investigated.

The new Li₂FePO₄F polymorph exhibits several advantages over other iron-based fluorophosphates. Its electrochemical behavior is close to that of the layered Li₂FePO₄F: both deliver reversible capacity in the solid-solution regime at 3.4 V, but its volume change upon redox is two times smaller than that for the layered polymorph (1.7% against 3.7%).⁵ Another fluorophosphate, LiFePO₄F with a tavorite structure, demonstrates complex two-phase electrochemical activity at much lower potential (2.75 V) and with significant volume expansion (7.9%).¹⁸

This study demonstrated that the structure type adopted by fluorophosphates of the general formula A_2MPO_4F (A = Na, Li; M = Fe, Mn, Co, Ni) depends on the size of transition metal and the Li/Na ratio. It allowed to obtain the new NaLiFePO₄F phase, which upon cycling in the Li-cell produces the threedimensional Li₂FePO₄F polymorph with attractive electrochemical properties. This finding provides new opportunities for further exploration of various electrochemically active fluorophosphates.

ASSOCIATED CONTENT

S Supporting Information

Experimental details, results of Rietveld refinement, structural and bonding parameters, electrochemistry data, EDX spectra of tested electrodes. These materials are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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