



# Phase transformations behavior during operation of the phosphate and fluoride phosphate cathode materials for Li(Na)-ion batteries

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## Outline

#### 1. Olivines

1.1 Li(Fe,Mn)PO<sub>4</sub> cathode materials

1.2 Li(Fe,Mn,Co)PO<sub>4</sub> cathode materials

#### 2. Fluoride phosphates

2.1. Na<sub>2</sub>FePO<sub>4</sub>F and (Na,Li)<sub>2</sub>FePO<sub>4</sub>F

2.2 First desodiation of Na<sub>2</sub>FePO<sub>4</sub>F: unexpected behavior in Li-ion and

Na-ion cells

# 1. LiMPO<sub>4</sub> (M = Fe, Mn, Co)



	LiFePO <sub>4</sub>	LiMnPO <sub>4</sub>	LiCoPO <sub>4</sub>
E vs. Li/Li⁺, V	3.4	4.1	4.9
Specific energy density, Wh/kg	580	700	830
Volume change	6.7%	11%	7%

Padhi, A. K. et al, J. Electrochem. Soc., 1997, V. 144, 1188

# 2. LiFe<sub>1-y</sub>Mn<sub>y</sub>PO<sub>4</sub>



D. B. Ravnsbæk, et al., Nano Lett., 2014, V. 14, pp. 1484–1491

N.V. Kosova, et al., Solid State Ionics, 2012, V. 225, pp. 564–569

# 3. Hydrothermal synthesis of Li(Fe,Mn,Co)PO<sub>4</sub>



Composition	a (Å)	b (Å)	c (Å)	V(ų)	EDX (Fe:Mn)
LiFePO <sub>4</sub>	10.301(1)	5.9905(9)	4.6801(5)	288.81(4)	-
$LiFe_{0.9}Mn_{0.1}PO_4$	10.319(1)	6.000(1)	4.6869(8)	290.21(6)	0.91:0.09(2)
LiFe <sub>0.5</sub> Mn <sub>0.5</sub> PO <sub>4</sub>	10.371(2)	6.036(2)	4.7108(9)	294.92(7)	0.54:0.46(2)

# 4. Morphology of the obtained LiFe<sub>1-y</sub>Mn<sub>y</sub>PO<sub>4</sub>



• Smallest direction of the particles corresponds to [010] in s.g. *Pnma* 

• Thickness ≈ 150-200 nm

# 5. GCPL study of Li<sub>1-x</sub>Fe<sub>1-y</sub>Mn<sub>y</sub>PO<sub>4</sub>



 $LiMPO_4$ :C:PVDF = 75:15:10, 1M  $LiPF_6$  in EC:DMC = 1:1

Increasing electrochemical capacity at high discharge rates (10C, 20C) with increasing Mn content

6. GCPL study of Li<sub>1-x</sub>Fe<sub>1-y</sub>Mn<sub>y</sub>PO<sub>4</sub>



More recent results obtained using better synthetic route confirm previous data:  $LiFe_{0.5}Mn_{0.5}PO_4$  exhibits better capacity retention at high rates of discharge

# 7. PITT processing



M. Vorotyntsev et al. J. Electroanal. Chem. 572 (2004) 299–307 Meethong N. et al., Chemistry of Materials, 2008, V. 20 p. 6189–6198

## 8. PITT results



## Total (integral) *f*:

	LiFePO <sub>4</sub>	LiFe <sub>0.9</sub> Mn <sub>0.1</sub> PO <sub>4</sub>	LiFe <sub>0.5</sub> Mn <sub>0.5</sub> PO <sub>4</sub>
$f_{charge}$	0,10	0,19	0,39
$f_{ m discharge}$	0,22	0,25	0,42

# 9. Operando XRPD







a) For  $Li_{1-x}FePO_4$ , almost whole process of is two-phase (LFP and FP)

b) For  $Li_{1-x}Fe_{0.9}Mn_{0.1}PO_4$ , Li-deficient phase exhibits solid solution region  $L_xFMP$  for  $\Delta x$  appr. 0.2-0.3 per f.u.

#### c) For $Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$ , charge:

(two-phase region between LFMP and  $L_xFMP$ )  $\rightarrow$  (solid solution  $L_xFMP$ )  $\rightarrow$  (two-phase region between  $L_xFMP$  and FMP).

#### discharge:

similar picture, but noticeable increase in the extent of the single-phase region is detected

# **10. E-x curves for Li<sub>1-x</sub>Fe<sub>0.5</sub>Mn<sub>0.5</sub>PO<sub>4</sub>**



# 11. Possible explanation of the asymmetry in Li<sub>1-x</sub>Fe<sub>0.5</sub>Mn<sub>0.5</sub>PO<sub>4</sub>

Basis:

a)  $r(Mn^{2+}) > r(Fe^{2+})$  in octahedral coordination (Shannon radii - 0.83 Å vs. 0.78 Å), but  $r(Mn^{3+}) = r(Fe^{3+}) = 0.645$  Å. As a result, for the undoped LiMPO<sub>4</sub>/MPO<sub>4</sub> transitions volume changes: *ca*. 11% for M = Mn and 7% for M = Fe.

b) in the intermediate region of x (approx. 0.4 < x < 0.6) in  $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  reduction and oxidation of both Fe and Mn take place due to the random distribution of the Mn and Fe cations in the lattice



Drozhzhin, O.A. et al., Electrochimica Acta, 2016. v. 191,p. 149-157

## 12. Another examples of the asymmetry between charge/discharge



H. C. Shin et al., Electrochem. Commun. 10 (2008) 536–540 X. Rui et al., J. Power Sources 258 (2014) 19-38

#### 13. Olivine-type Li(Fe<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>)PO<sub>4</sub>: extended solid solution region



## 14. Olivine-type Li(Fe<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>)PO<sub>4</sub>: extended solid solution region

Evolution of (211)/(020) olivine peaks at discharge:



Composition	ΔV	Specific energy	Cyclability
LiFePO <sub>4</sub>	6.7%	560 Wh/kg	Excellent
LiMnPO <sub>4</sub>	11%	700 Wh/kg	Poor; Jan-Teller effect for Mn <sup>2+</sup> /Mn <sup>3+</sup> , large volume change, Mn dissolution
LiCoPO <sub>4</sub>	7%	800 Wh/kg	Very poor; high voltage + antisite defects formation during charge/discharge
LiFe <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> PO <sub>4</sub>	5.3%	680 Wh/kg	<b>Good</b> (high-voltage electrolyte, e.g. 1M LiBF <sub>4</sub> in TMS); under study

#### 15. Operando Mössbauer spectroscopy: LiFePO<sub>4</sub>

LiFePO<sub>4</sub>, C/20 charge/discharge rate. Exposure ~ 30 min



#### 16. Operando Mössbauer spectroscopy: LiFePO<sub>4</sub>



#### 17. Operando Mössbauer spectroscopy: LiFePO<sub>4</sub> vs. LiFe<sub>0.5</sub>Mn<sub>0.5</sub>PO<sub>4</sub>



## 18. Na<sub>2</sub>MPO<sub>4</sub>F

## $Na_2MPO_4F$ (M = Fe, Co): layered crystal structure



- High capacity (124 mAh/g per one alkali cation) and working potential (3–5 V vs.
   Li/Li<sup>+</sup> depending on couple M<sup>+2</sup>/M<sup>+3</sup>)
- May be used in both Li-ion and Na-ion batteries;
- Volume change ~ 4% between Na<sub>2</sub>FePO<sub>4</sub>F and NaFePO<sub>4</sub>F

Ellis, B. L. et al., Nat. Mater., 6 (2007) 749 - 753

## **19.** Na<sub>2</sub>FePO<sub>4</sub>F: solvothermal synthesis



Particle size ~ 100 nm; homogeneous distribution

# 20. (Na,Li)<sub>2</sub>FePO<sub>4</sub>F: Li<sup>+</sup> vs. Na<sup>+</sup> cycling



D<sub>chem</sub> and the single-phase mechanism contribution are higher for the Li<sup>+</sup> (de)intercalation  $\implies$  better rate capability in Li-ion cell

#### 21. Na<sub>2</sub>FePO<sub>4</sub>F: first charge (Na<sup>+</sup> deintercalation) in Li-ion and Na-ion cells



One process – different mechanisms?

#### 22. Na<sub>2</sub>FePO<sub>4</sub>F: first charge (Na<sup>+</sup> deintercalation) by PITT



Li-ion: solid-solution character of the *i-t* transients; Na-ion: two-phase

#### 23. Na<sub>2</sub>FePO<sub>4</sub>F: first charge (Na<sup>+</sup> deintercalation) by operando XRPD

(200)/(133)/(104) peaks (s.g. Pbcn)



## 24. Na<sub>2</sub>FePO<sub>4</sub>F: EDX after charge and soaking in different cells

Sample	Na/(Fe+P) expected from	Na/(Fe+P) from
	the charge passed	EDX, ± 0.05
Initial	1	1.04
Half-charged in Li-ion cell	0.75	0.50
Half-charged in Na-ion cell	0.75	0.77
Charged in Li-ion cell	0.5	0.09
Charged in Na-ion cell	0.5	0.67*
Soaked in 30-fold excess of Li-ion electrolyte for 10 h		0.71
Soaked in 30-fold excess of Li-ion electrolyte for 48 h		0.39
Soaked in 30-fold excess of Li-ion electrolyte for 168 h		0.21

Half of the all Na ions left the phase only at 50% SOC in Li-ion cell: Li<sub>0.5</sub>NaFePO<sub>4</sub>F instead of Na<sub>1.5</sub>FePO<sub>4</sub>F.

Full-charged: almost complete Na<sup>+</sup> removal from the structure,  $Li_{0.91}Na_{0.09}FePO_4F$  instead of NaFePO<sub>4</sub>F. Such deep exchange could not be performed even after soaking the electrodes in 30-fold excess of electrolyte during 1 week.

#### 25. (Na Li)<sub>1.5</sub>FePO<sub>4</sub>F: crystal structure refinement





Switching between electrochemically active alkali metal positions. In the **Na-ion** cell the majority of the Na cations are extracted from the position **Na2**, whereas in the **Li-ion** cell this position remains active only for the chemical Li for Na substitution, but the Na cations are removed from the position **Na1**, which has previously been considered electrochemically inactive

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Thank you for the attention!