2nd International Conference of Young Scientists
“TOPICAL PROBLEMS OF MODERN ELECTROCHEMISTRY AND ELECTROCHEMICAL MATERIALS SCIENCE”

The perspectives on fluoride phosphates cathode materials for metal-ion batteries

Evgeny Antipov

Department of Chemistry, Moscow State University

Outline

- Introduction
- Main types of cathode materials for LIB
- AMPO4F and A_2MPO_4F fluoride-phosphates
- Concluding remarks

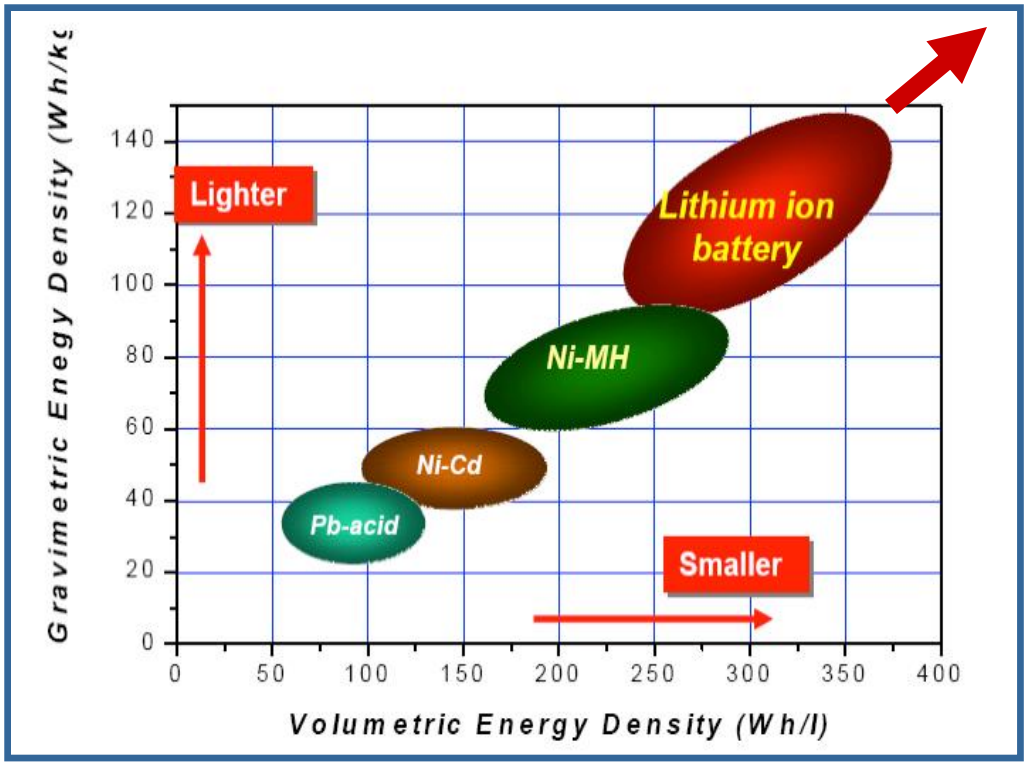
1995: «Advances in battery research are always restricted by chemistry »

R. E. Powers (N.Y. Times)

and Crystallography!

Energy storage systems

up to 250 Wh/kg



Stationary energy storage

HEV, EV

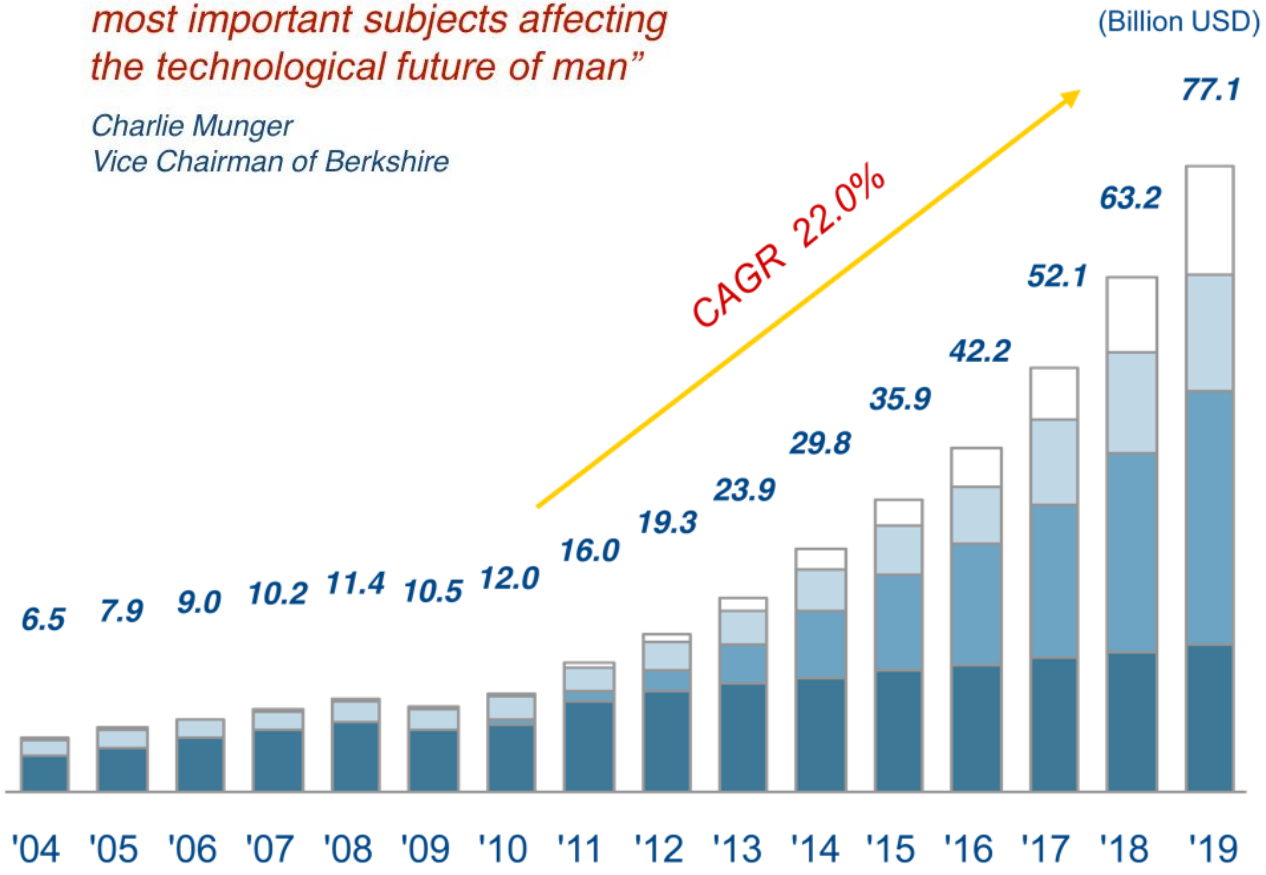
Consumer electronics

Increase of Energy and Power

Perspectives for Li-ion batteries

"Battery technology is one of the most important subjects affecting the technological future of man"

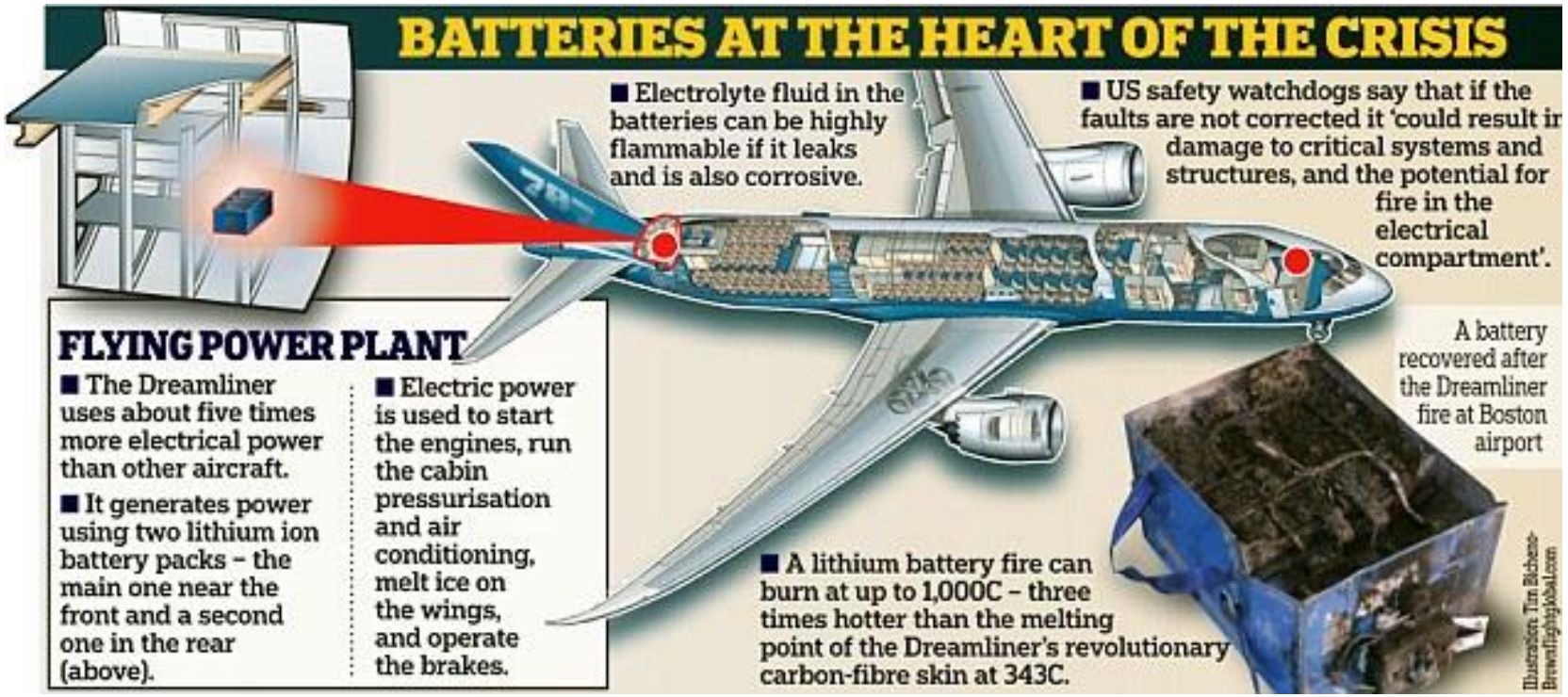
Charlie Munger
Vice Chairman of Berkshire



	Share (’19)	CAGR (’09-’19)
Robot	17.6%	52.4%
Storage	18.5%	18.2%
EV	40.5%	79.8%
IT	23.3%	9.1%

Yunil HWANG, A. D. Little Korea, Korea, "Nano-enhanced Market Perspectives in Solar & Li-ion Battery "OECD workshop on "Nanotechnology for sustainable energy options", 2010

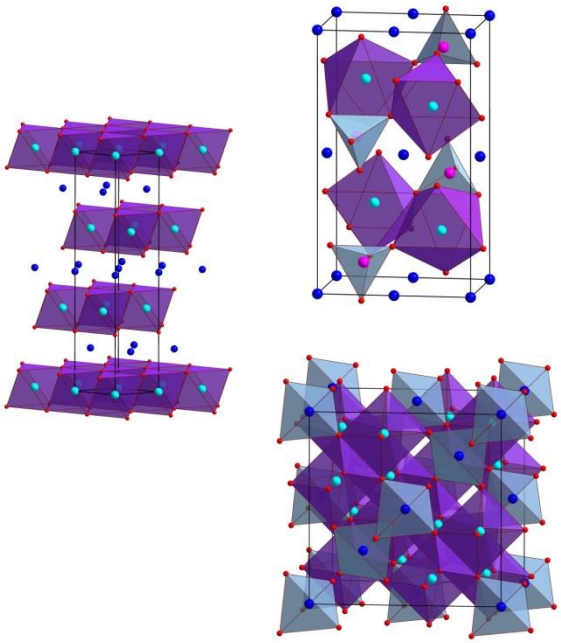
Safety problem



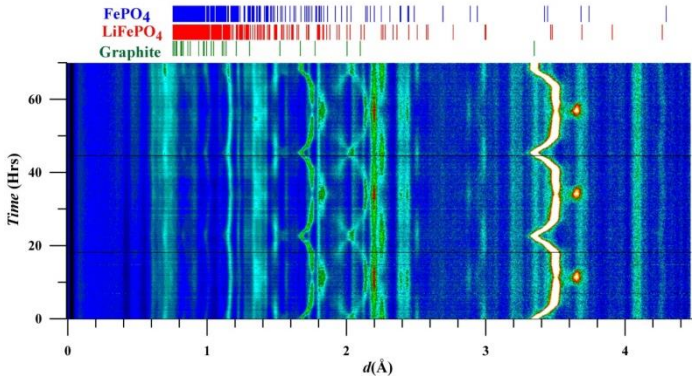
Daily Mail, 20.01.2013

Impact of crystallography

Design of new structures:
- crystal chemistry concepts
- data mining
- *ab initio* structure predictions

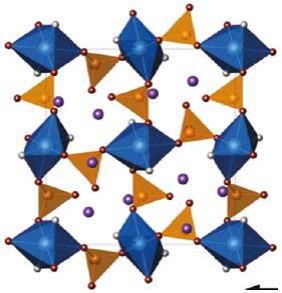


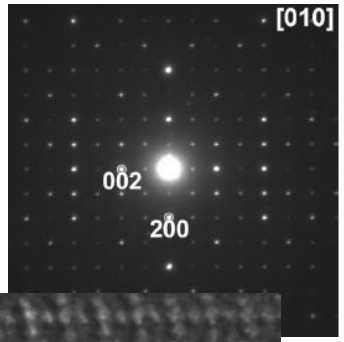
Crystallographic aspects of electrochemical reactions:
- *in situ* and *ex situ* X-ray and neutron diffraction studies
- spectroscopic methods (EXAFS, XPS, XANES etc)
- microstructure evolution

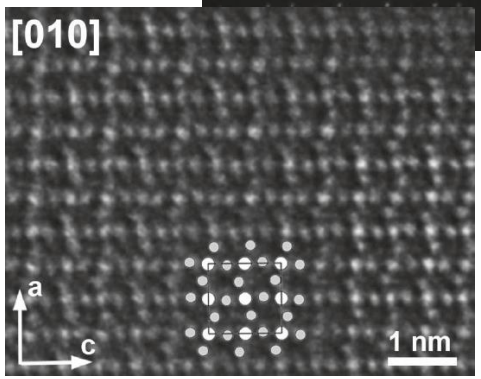


I.A. Bobrikov et al. ,
J. Power Soc.. 258 (2014) 356

Electrochemical processes on atomic scale:
- *ex situ* electron diffraction (PED) studies, atomic resolution TEM imaging and spectroscopy
- *in situ* TEM







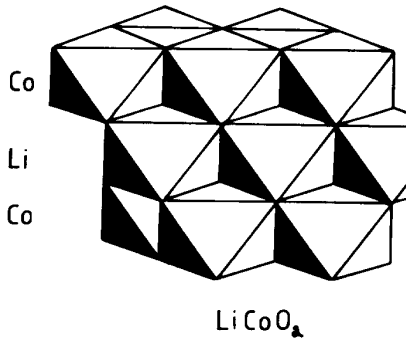
J. Hadermann et al. ,
Chem. Mat. 23 (2011) 3540

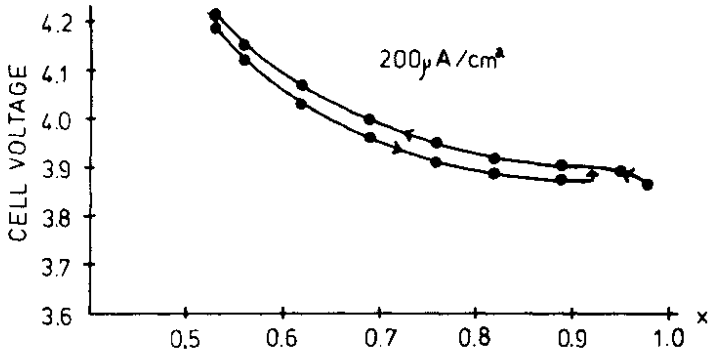
Main discovery

Mat. Res. Bull., Vol. 15, pp. 783-789, 1980. Printed in the USA.
0025-5408/80/060783-07$02.00/0

Li_xCoO_2 ($0<x\leq1$): A NEW CATHODE MATERIAL FOR BATTERIES OF HIGH ENERGY DENSITY

K. Mizushima, P.C. Jones, P.J. Wiseman and J.B. Goodenough
Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR



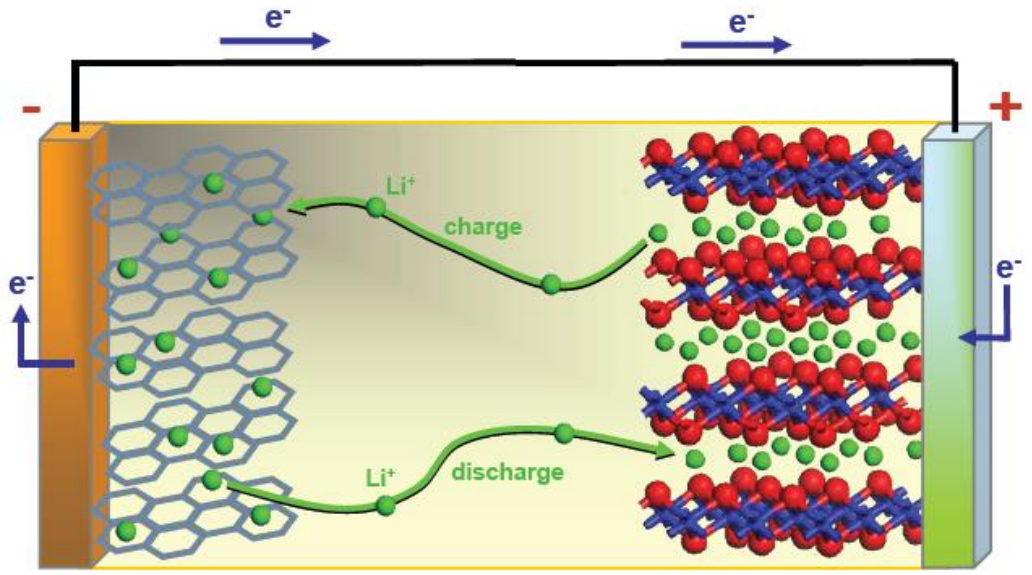


thetic route requires use of a starting high-temperature material that allows low-temperature extraction of lithium. The resultant phase need not necessarily be thermodynamically stable.

Examination of the known Li^+-ion solid

Li-ion battery

Concept (1980) Commersialization: Sony (1990)



LixC6 graphite **Li+- conducting electrolyte** **LiMO2**

$$C_6 + LiCoO_2 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_xC_6 + Li_{1-x}CoO_2 \qquad x \approx 0.5\text{-}0.6\ e^-$$

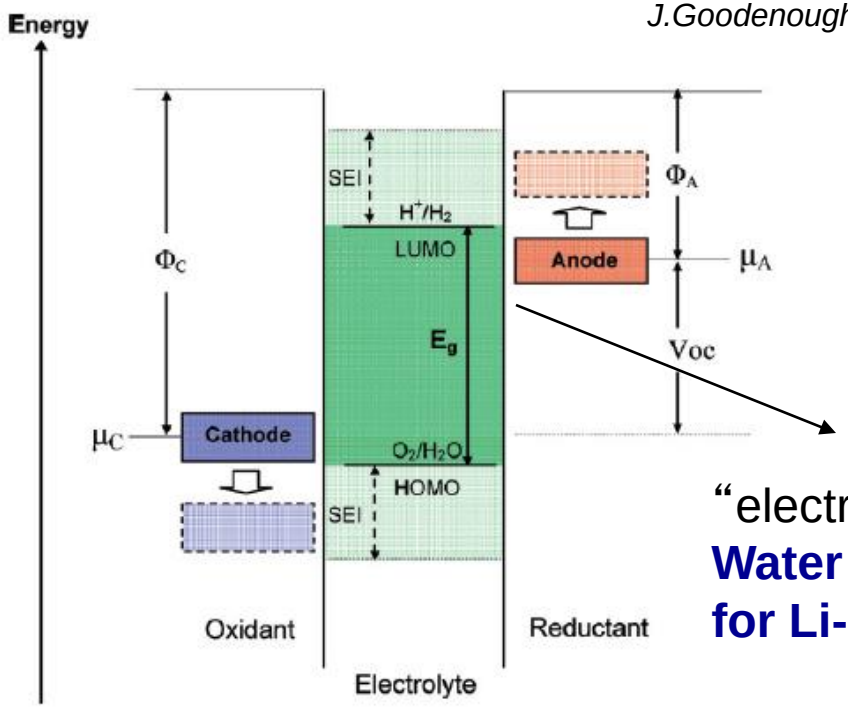
Voltage: 3.6 V **E^o (cathodic) – E^o (anodic) = E^o (cell)**

Electrolyte - salts: $LiPF_6$, $LiBF_4$ ($LiClO_4$, $LiAsF_6$), $LiCF_3SO_3$
- solvents: EC, PC, DMC, DEC **1M $LiPF_6$ in EC/DEC/DMC**

E_g(gravimetric) = **C_g** (charge transferred between two electrodes per unit weight) x **E^0** (cell)

Why Li ?

J.Goodenough & Y.Kim, Chem.Mat. 22 (2010) 587



“electrolyte window”
Water – 1.23 V,
for Li-electrolytes – up to 4 V

1) Larger “electrolyte window” → **higher specific energy**
2) Weak Li-O bonds → **high Li-ion conductivity**
3) Low size → **mechanical stability**

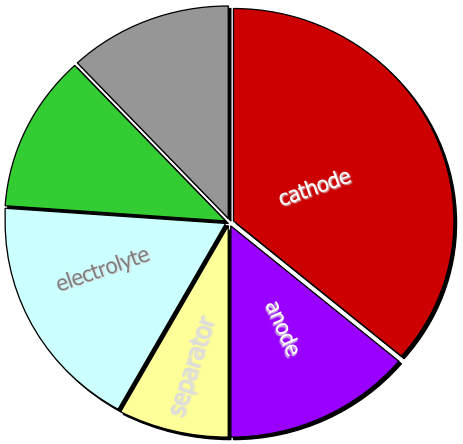
Cathode materials: importance

The energy density of a battery is the product of its capacity and its potential, and is mainly governed by the capacity of the positive electrode. Simple calculations show that an increase in cell energy density of 57 per cent can be achieved by doubling the capacity of the positive electrode, while one needs to increase the capacity of the negative electrode by a factor of 10 to get an overall cell energy density increase of 47 per cent (Tarascon 2002).

Tarascon, J.-M. 2002 *Actualité Chimique* **251**, 130–137.

"Cost of Lithium-Ion Batteries for Vehicles" – ANL Report

Li-ion battery fabrication costs based on a LiCoO2-type cathode:



Component

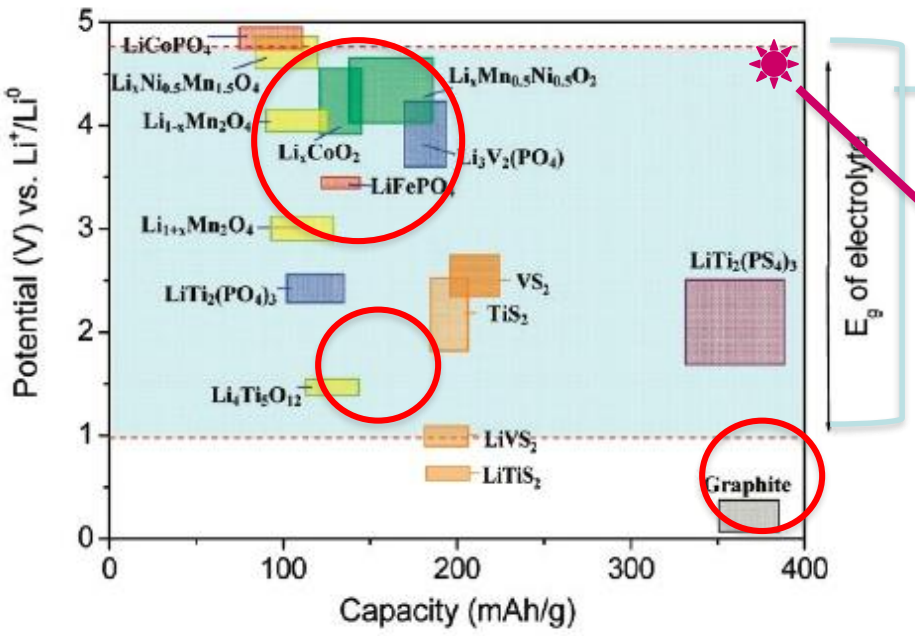
- cathode 36%
- anode 14%
- separator 8%
- electrolyte 18%

Σ "Material": 76%

- labor cost 12%
- overheads 12%

Selection of Electrode Material

J.Goodenough & Y.Kim, Chem.Mat. 22 (2010) 587



H_2O – 1.23 V,
Li-electrolyte – up to 4 V

Electrolyte window

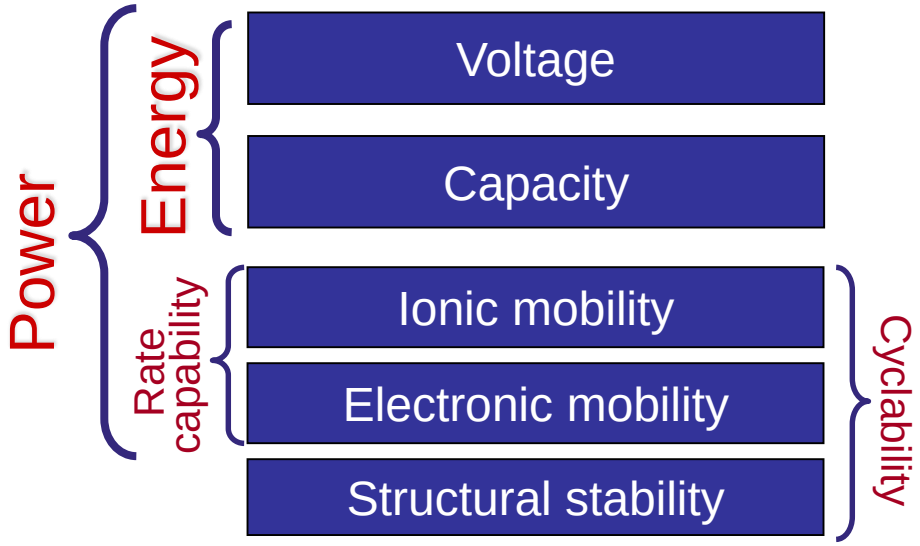
(Oxidation and reduction of electrolyte outside the window)

How to reach this value?

To increase specific energy → to higher cathode potential and capacity

To increase power → to higher Li-ion diffusion rate

Cathode materials: characteristics and requirements



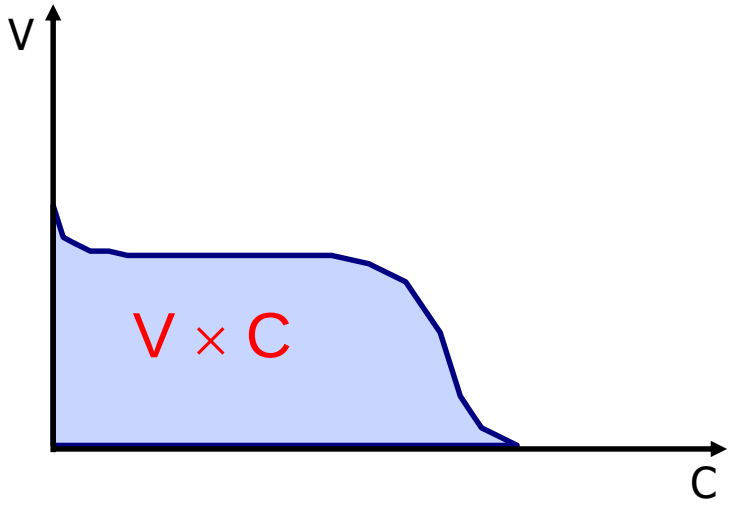
$M^{n+}/M^{(n+1)+}$ redox potential

$$C_T\,(A\,h\,g^{-1}) = \frac{26.8 \times \Delta n}{M}$$

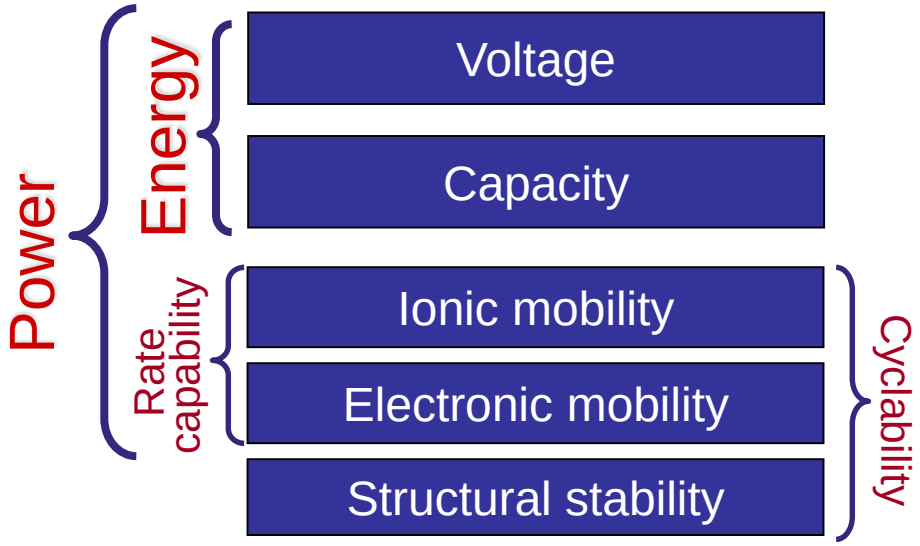
Δn: number of e^- or Li^+

M: Molecular weight (g)

Energy = Voltage x Capacity



Cathode materials: characteristics and requirements



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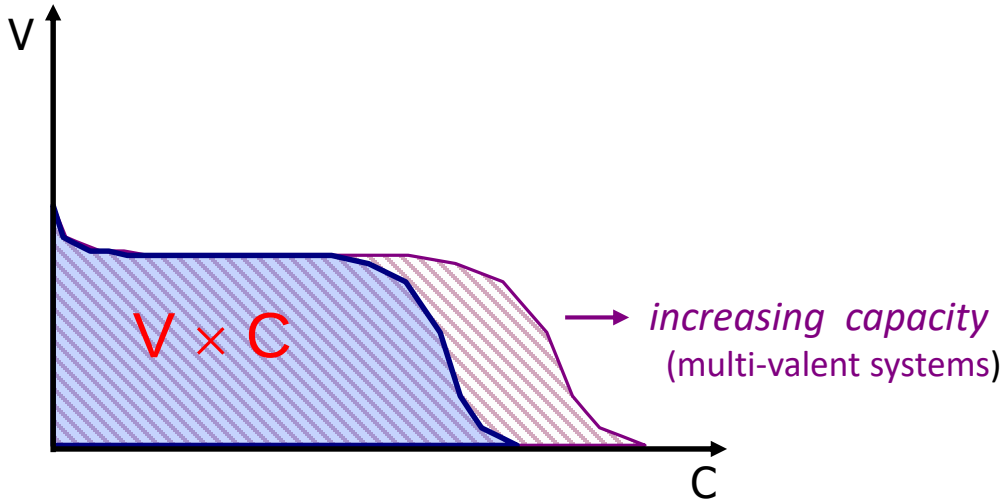

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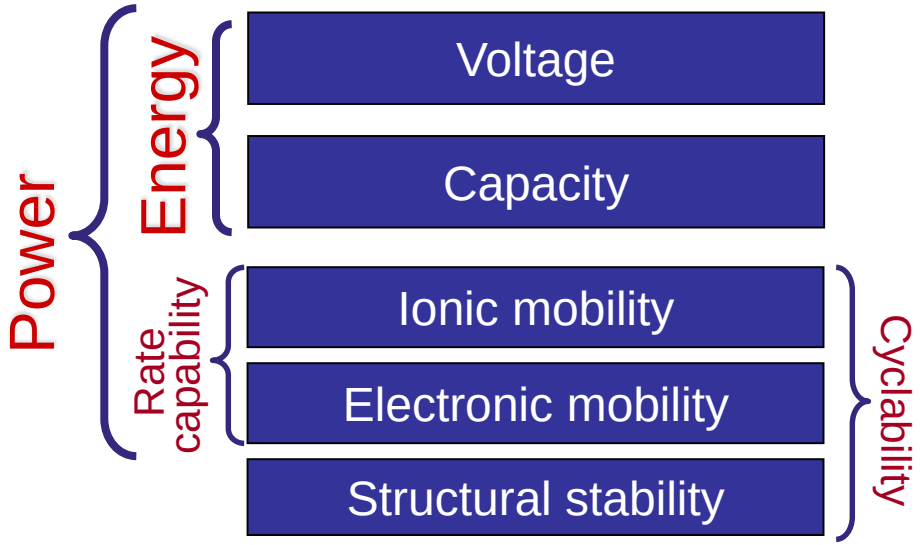

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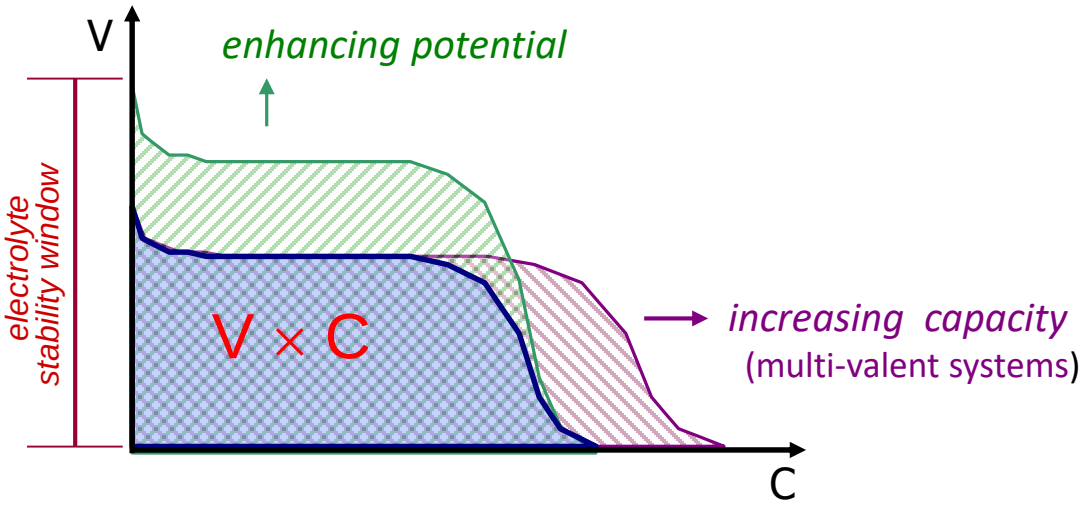
$$C_T\,(A\,h\,g^{-1}) = \frac{26.8 \times \Delta n}{M}$$

Δn: number of e^- or Li^+

M: Molecular weight (g)

Energy = Voltage x Capacity

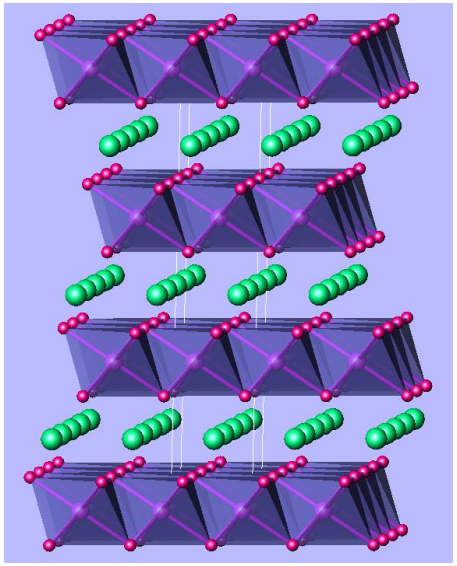
≤ 4.8 V (vs. Li/Li^+)



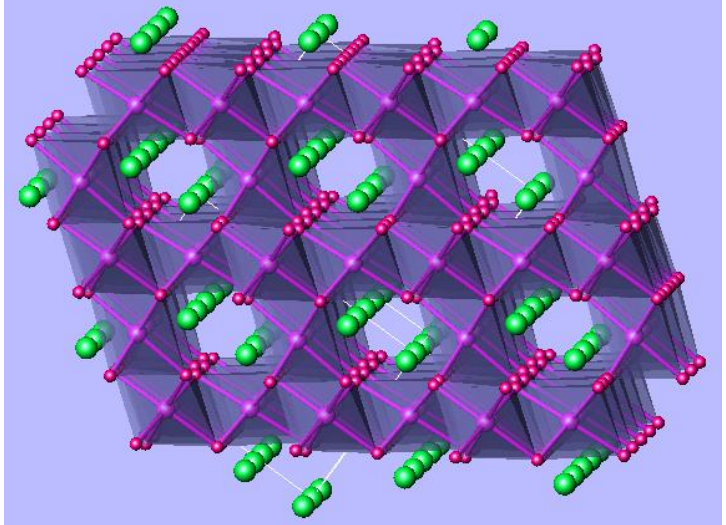
Selection of composition

Main Structure Types

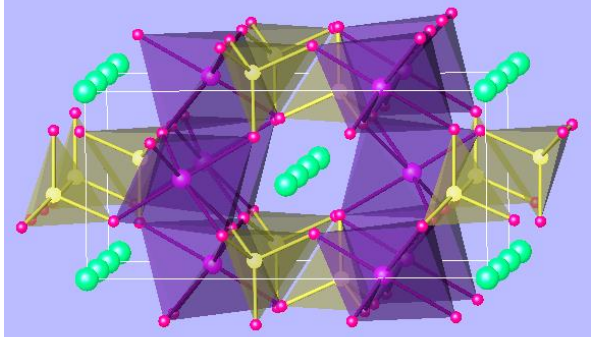
$LiCoO_2$



$LiMn_2O_4$



$LiFePO_4$



Hexagonal close packing

Cubic close packing

C_t	278 mAh/g ($0.5C_t$)	148 mAh/g	170 mAh/g
E_g	556 Wh/kg	592 Wh/kg	583 Wh/kg
σ	10^{-3} S/cm	10^{-5} S/cm	10^{-9} S/cm
D	10^{-9} cm^2/s	10^{-10} cm^2/s	10^{-15} cm^2/s

Polyanion cathodes

Advantages:

-greater chemical and thermal stability, which provides reliable long-term electrochemical cycling and allows them to be used in large-sized batteries

-a rich variety of crystal structures – larger playground for various substitutions

-**the inductive effect**, leading to a significant increase of the redox potential $M^{n+}/ M^{(n-1)+}$

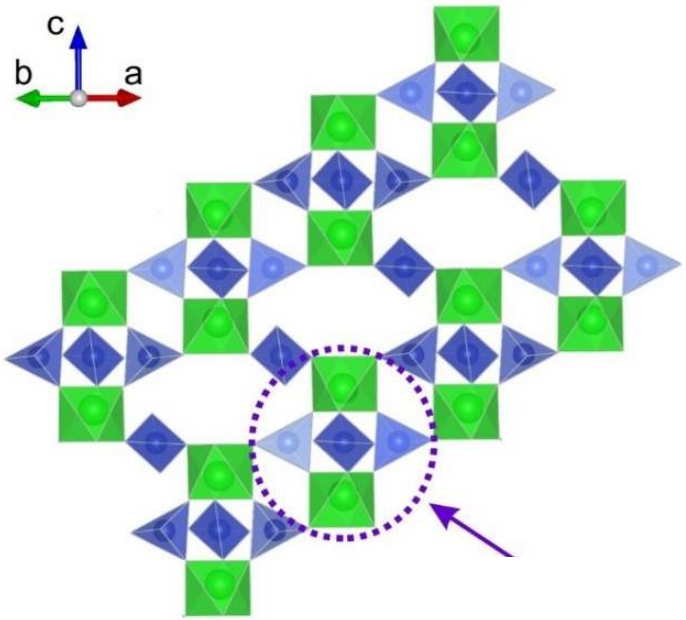
Drawbacks:

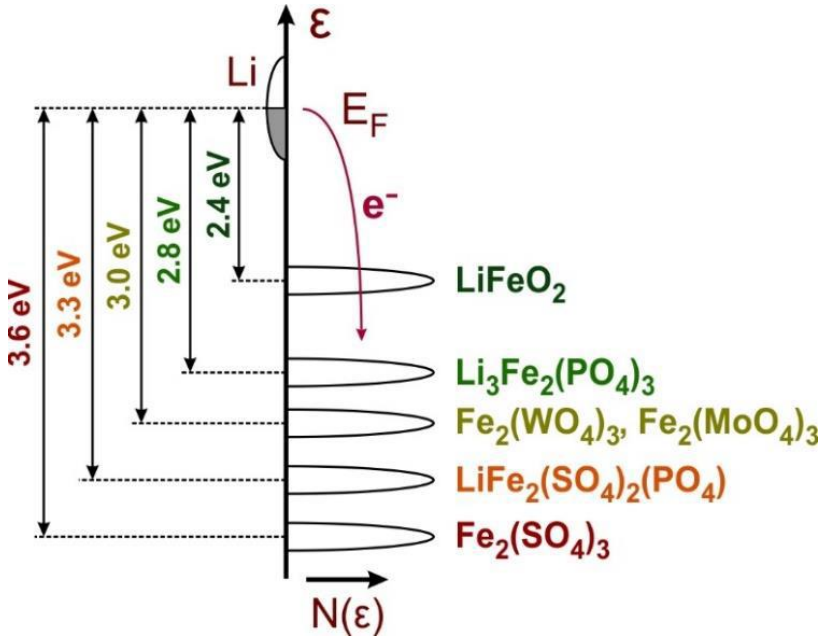
-Larger molecular weight – smaller capacity

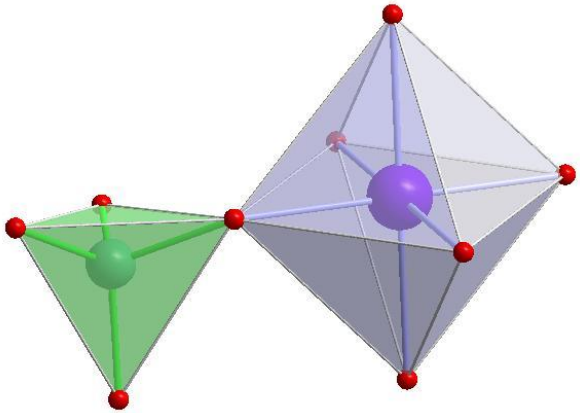
-More sophisticated synthesis

The inductive effect

$A_xMM'(PO4)_3$

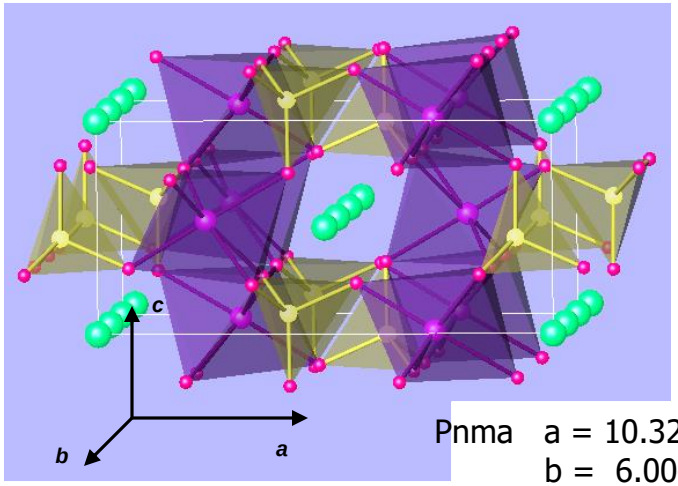






$LiFePO_4$ - olivine

c_t = 170 mAh/g; E ~ 3.5 V



Pnma a = 10.3223(15)Å
b = 6.0047(9) Å
c = 4.6929(7) Å

Advantages:

- stable material (3D structure + PO_4)

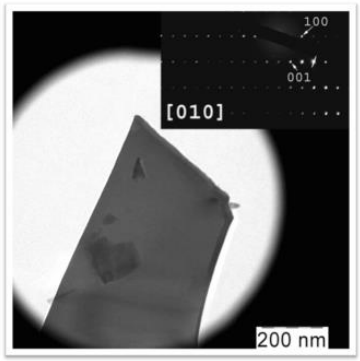
  $LiFePO_4$ ⟷ $FePO_4$ + Li+ + e-

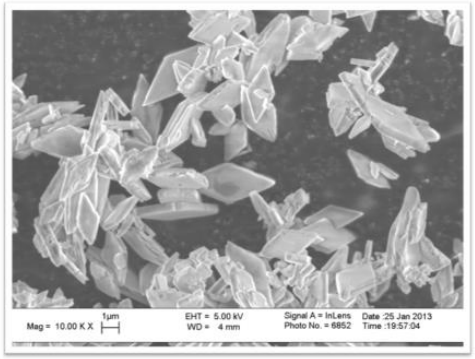
- ecologically friendly
- cheap

Disadvantages:

- low electronic conductivity~ 10^{-9} S/см
- low D~10^{-15} cm^2/s ($t \approx r^2/D$)/ 2-phase mechanism
- low density
- medium potential

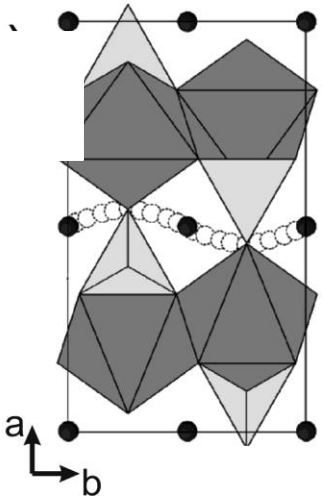
(for phases with Mn = 4.2 V, Co = 4.9 V)



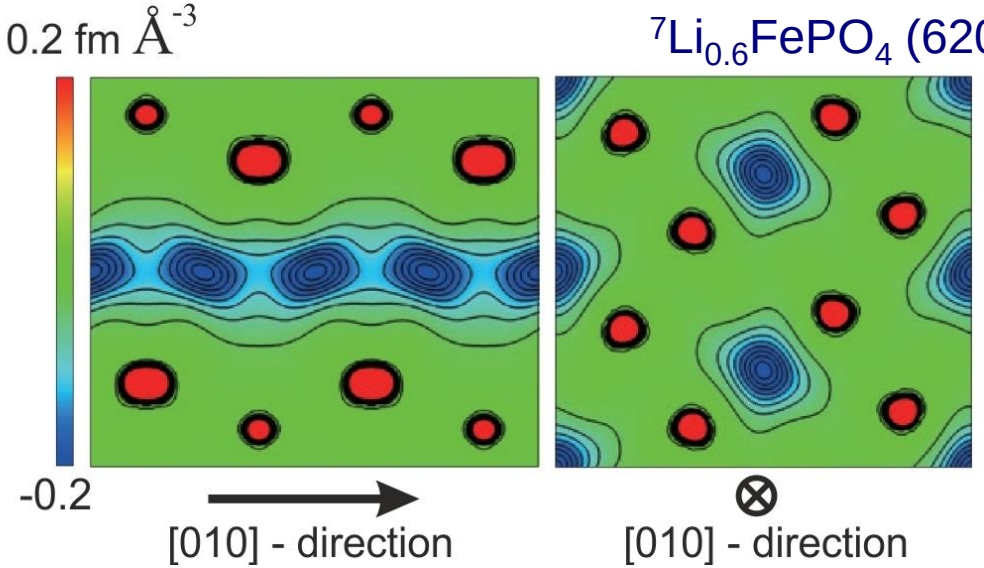


A. K. Padhi, et al., *J. Electrochem. Soc.* 144 (1997) 1609

Li-ion diffusion pathway



MD *(M.S. Islam et al. Chem. Mater. 17 (2005) 5085*



$^{7}Li_{0.6}FePO_4$ (620 K)

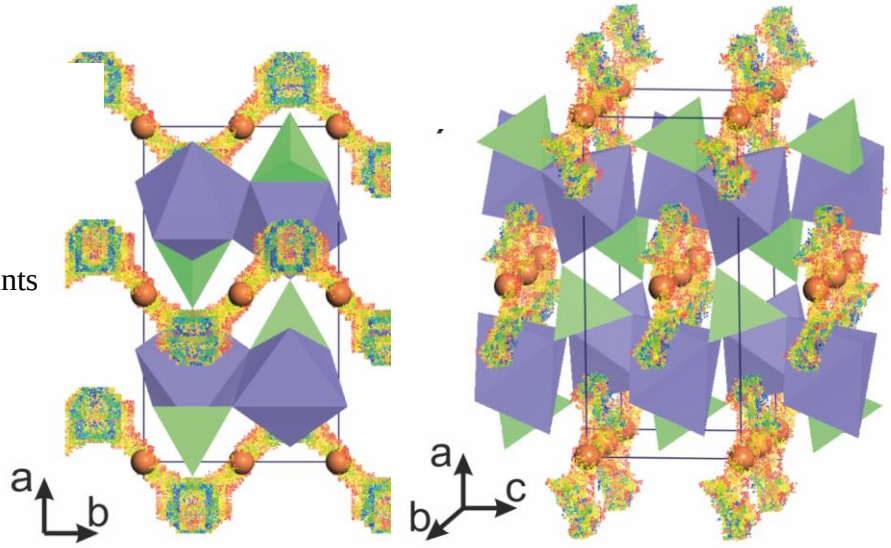
NPD/MEM*: S.I. Nishimura et al. Nature Materials 7 (2008) 707*

BVS mapping with 3DBVSMAPPER program

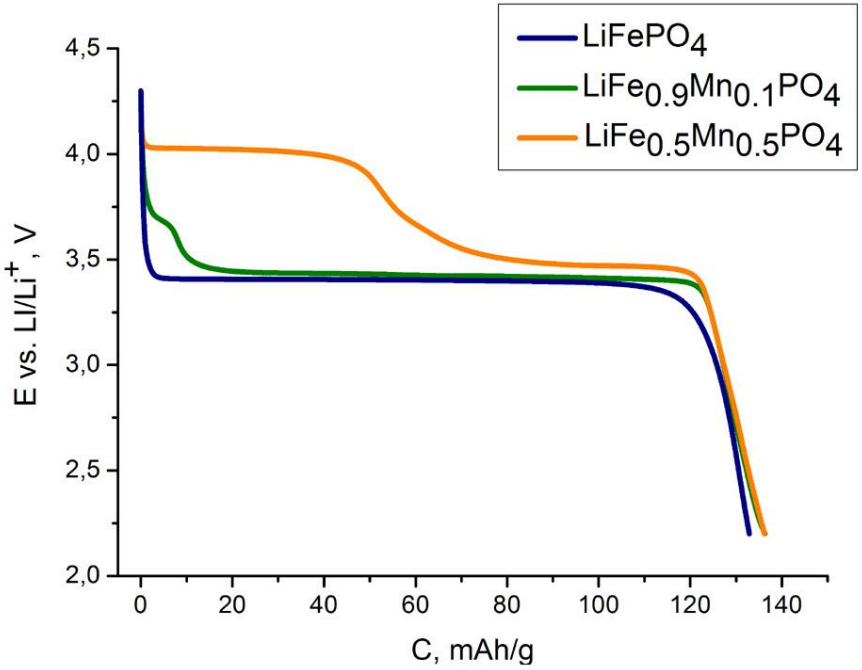
$$BVS = \sum_{j=1}^{N}\left[\exp\left(\frac{R_o - d_j}{b}\right)\right]$$

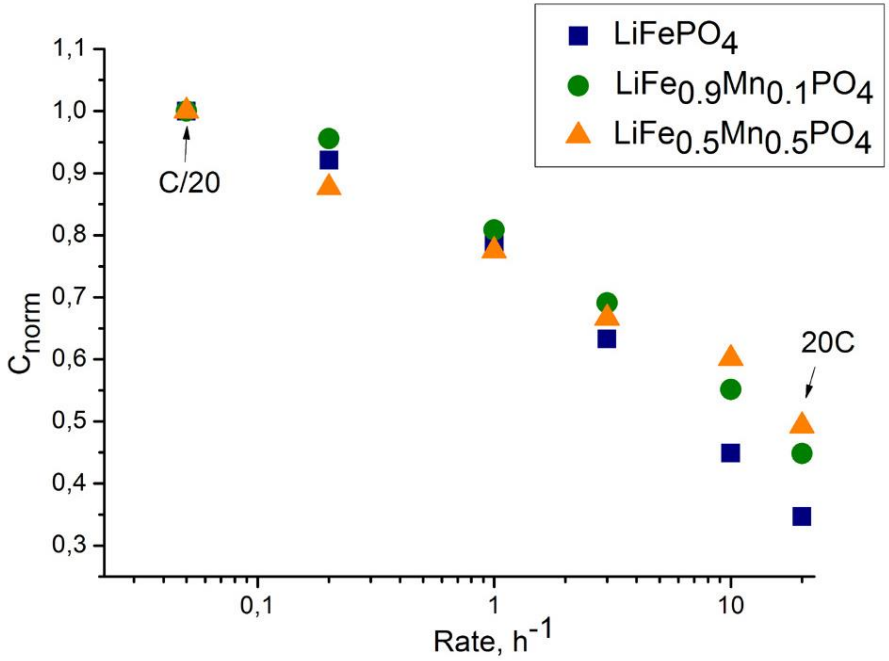
d_j - bond distance,
Ro, *b* – tabular constants

M. Sale, M. Avdeev, *J. Appl. Cryst*. 45(2012),1054



$Li_{1-x}Fe_{1-y}Mn_yPO_4$: influence of cation substitutions

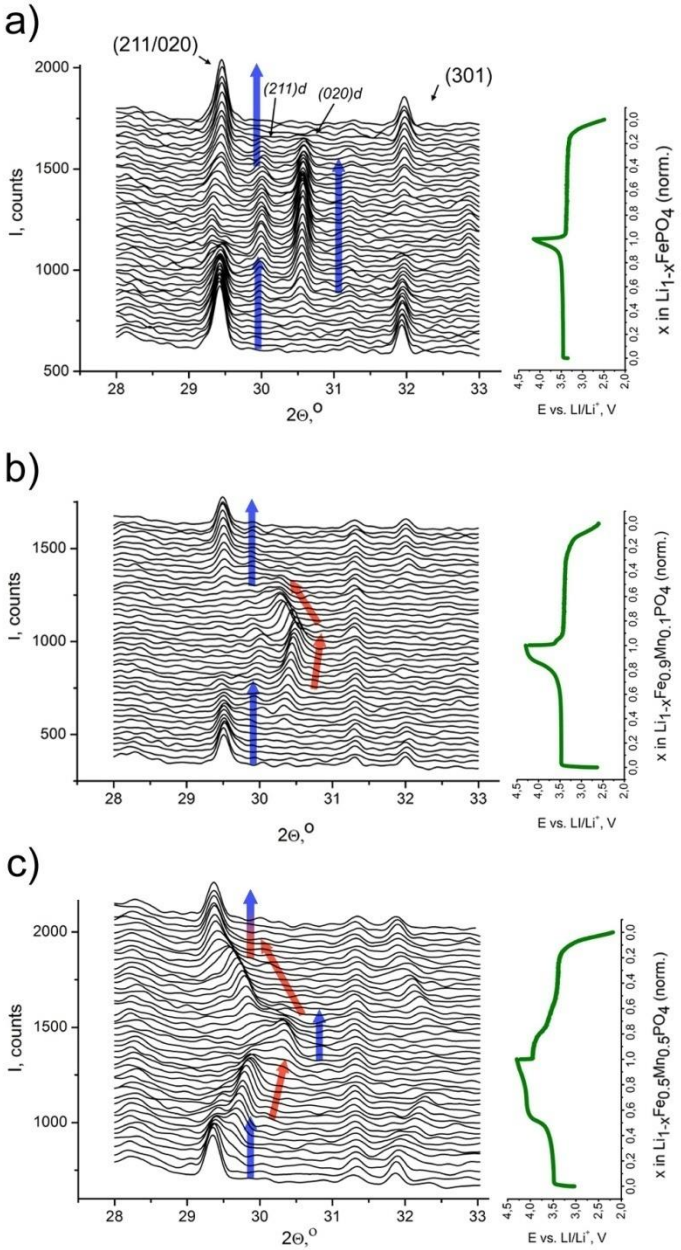


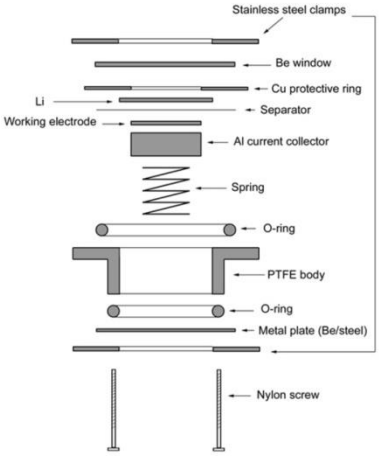


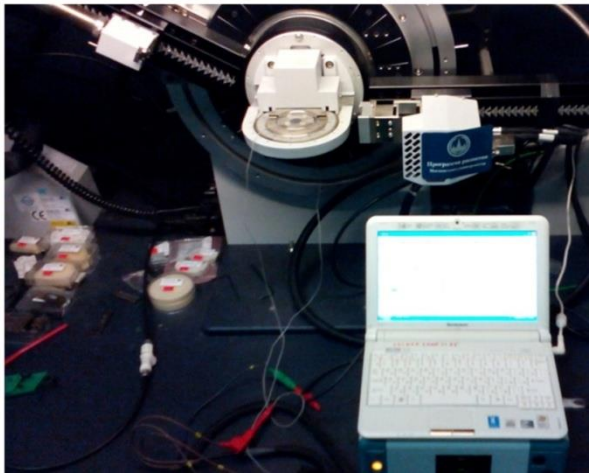
LiMPO4:C:PVDF = 75:15:10, 1M LiPF6 in EC:DMC = 1:1

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

In situ XRPD







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

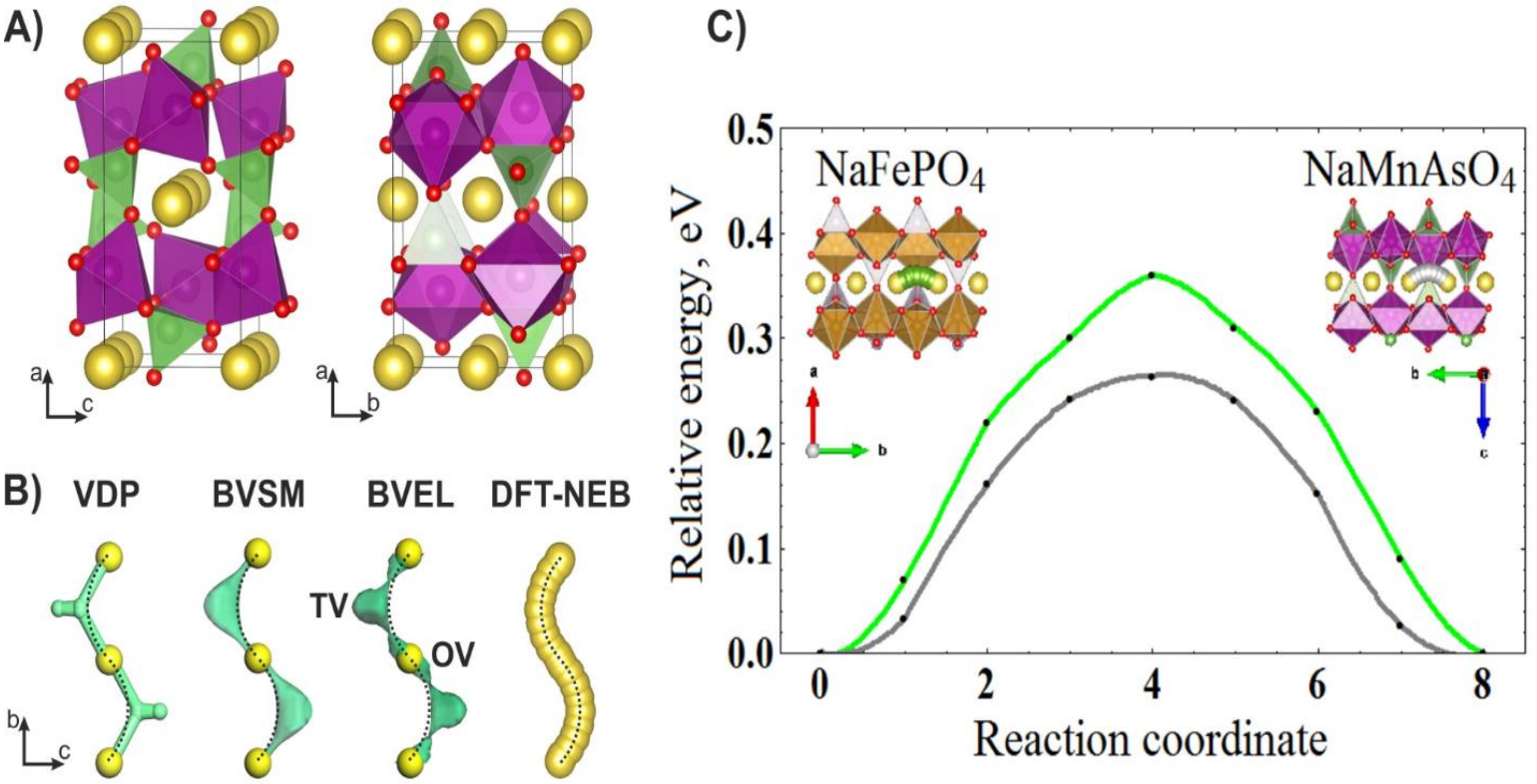
b) For $Li_{1-x}Fe_{0.9}Mn_{0.1}PO_4$, Li-deficient phase exhibits solid solution region LxFMP for Δx appr. 0.2-0.3 per f.u.

c) For $Li_{1-x}Fe_0.5Mn_{0.5}PO_4$, **charge**:
(two-phase region between LFMP and LxFMP) → (solid solution LxFMP) → (two-phase region between LxFMP and FMP).

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

Drozhzhin O.A. et al. Electrochimica Acta 191 (2016) 149

Na-based olivines



E_a for $NaFePO_4$ (maricite) 2.11 eV

Fedotov S.S.. et al. submitted SSI

Crystallochemical tools in search for cathode materials of rechargeable Na-ion batteries and analysis of their transport properties

94.	$Na_3Fe_3(PO_4)_4$		$C2/c$	95532	130	+
95.	$Na_4M_3(PO_4)_2(P_2O_7)$	Fe	$Pn2_1a$	236316	170	+
96.		Co		82116	169	
97.		Mn		92836	172	
98.		Ni		82713	170	
99.	$Na_2MP_2O_7$	Mn	$P1$	187790	194	+
100		Co		71229	193	
101	$Na_2M(SO_4)_2$	Co	$C2/c$	194629	180	+
102		Ni		194630	181	
103	$Na_6Fe_2(SO_4)(CO_3)_4$		$Fd\bar{3}$	20169	183	
104	$Na_3V[(PO_3)_3N]$		$P2_13$	188671	145	+
105	$Na_4NiP_2O_7F_2$		$Imma$	251666	148	+

Fedotov S.S.. et al. submitted SSI

Table 4. Calculated BVS mismatch values and activation energies for some selected and reference materials.

Material	CC	Theoretical capacity, mAh/g	BVS mismatch (BVSM), ±v.u.	Activation energy, E_a (BVEL), eV	Migration map dimensionality	
					VDP	BV
$NaFePO_4$ maricite*	85671	154	1.32	8.94	-	2D
$NaFePO_4$ olivine	169118	154	0.35	1.25	1D	1D
$NaMnPO_4$ olivine	36249	155	0.30	1.30	1D	1D
$NaMnAsO_4$ olivine	95087	124	0.22	1.22	1D	1D
$NaFeSO_4F$*	290051	138	0.92	5.14	-	1D
O3-$Na_{0.921}CoO_2$*	155498	218	0.67	3.76	2D	2D
P2-$NaCoO_2$	246585	237	0.29	0.72	2D	2D
O3-$Na_{0.667}Mn_{0.5}Fe_{0.5}O_2$*	420380	162	0.47	2.90	2D	2D
P2-$Na_{0.667}Mn_{0.5}Fe_{0.5}O_2$	194731	162	0.11	0.50	2D	2D
$NaNiAsO_4$	63353	122	0.08	0.50	2D	2D
Na_2FeVF_7	401862	188	0.06 (1D) 0.19 (2D)	0.70 (1D) 1.07 (2D)	2D	1D/2D
$NaFeF_3$	68981	197	0.77	3.99	3D	3D
$Na_3NiZr(PO_4)_3$	172807	158	0.23	1.16	3D	3D
$Na_4NiP_2O_7F_2$	251666	148	0.13 (1D) 0.15 (2D) 0.31 (3D)	0.59 (1D) 0.80 (2D) 0.85 (3D)	3D	1D/2D/3D
$Na_3V_2(PO_4)_3$	248140	198	0.32	1.25	3D	3D
$Na_{2+x}Fe_{2-x}(SO_4)_3$	252402	189	0.16	1.46	1D	1D
$Na_3V[(PO_3)_3N]$	188671	145	0.17	1.35	3D	3D
$Na_2O{\cdot}11Al_2O_3$*	67545	–	0.08	0.24	2D	2D

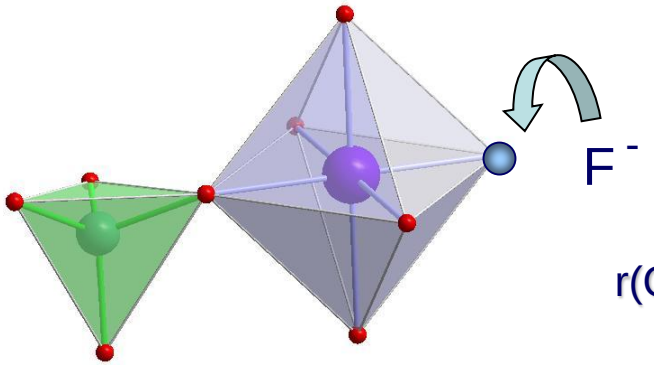
* - reference materials chosen for comparison

Search for new cathode materials: + Fluoride anion

ionicity of the M - L bond

inductive effect: $LiFePO_4$ (J. Goodenough 1997)*

compounds with polyanions $(XO_m)^{n-}$: $(BO_3)^{3-}$, $(SiO_4)^{4-}$, $(PO_4)^{3-}$, $(SO_4)^{2-}$



$r(O^{2-}) = 1.21Å \approx r(F^{-}) = 1.15Å$

inductive effect + higher ionicity of the M–F bond → high energy density

difference in formal charges → faster Li^+ transport → high power density

* A.K. Padhi et al. , *J. Electrochem. Soc.* 144 (1997) 1188

Search for new cathode materials: + Fluoride anion

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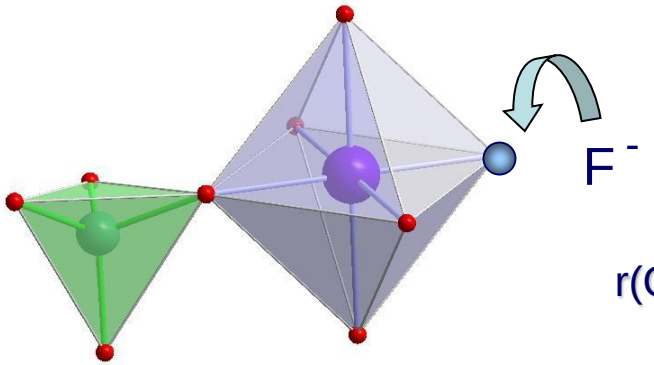


$r(O^{2-}) = 1.21Å \approx r(F^-) = 1.15Å$

inductive effect + higher ionicity of the M–F bond → high energy density

difference in formal charges → faster Li^+ transport → high power density

Compounds with two anions: $(XO_m)^{n-}$ and F^-

$(SO_4)^{2-}$ and F^-

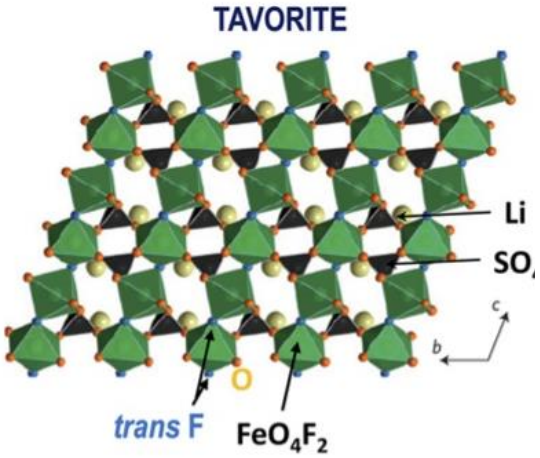
$LiMSO_4F$**

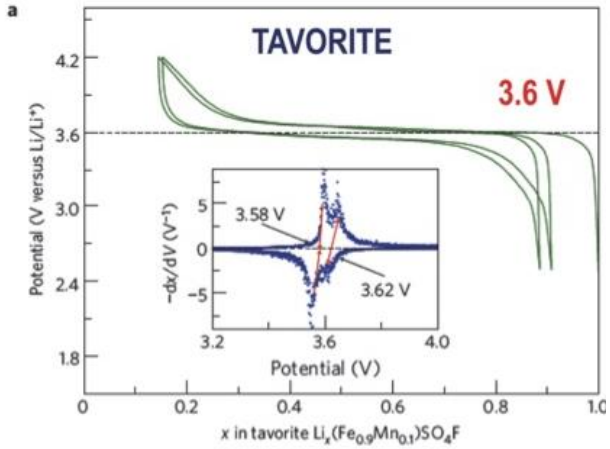
$(PO_4)^{3-}$ and F^-

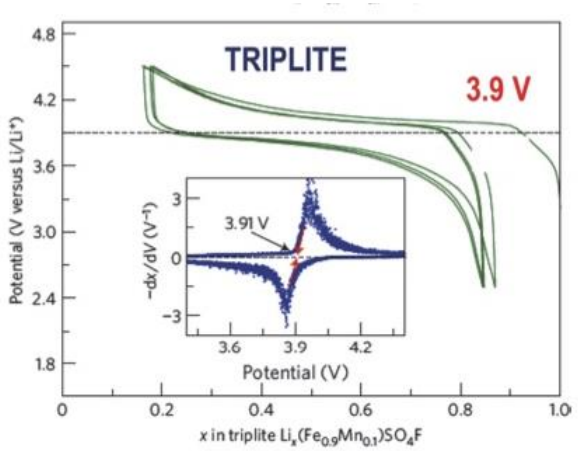
$LiMPO_4F$, Li_2MPO_4F

- A.K. Padhi et al. , *J. Electrochem. Soc.* 144 (1997) 1188

Fluoride-sulphates: $LiFeSO_4F$

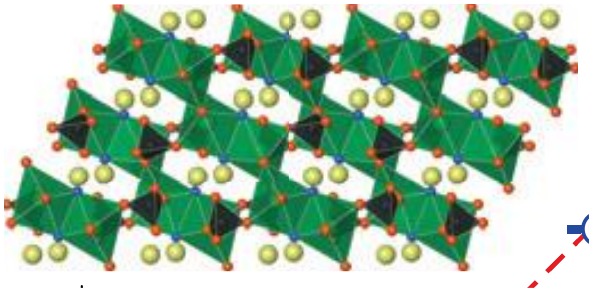




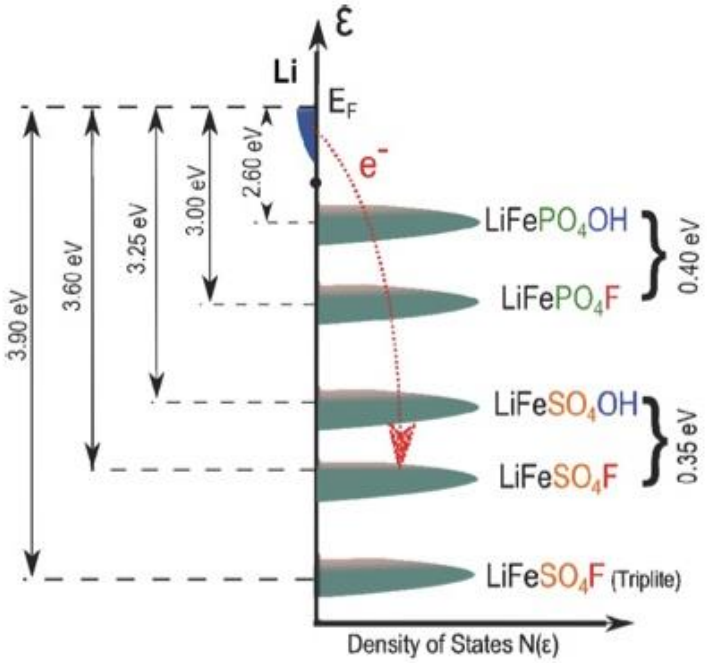


$FeSO_4 * H_2O + LiF \xrightarrow{300^\circ C,\ IL} LiFeSO_4F + H_2O$

tavorite



$LiMn_{0.05}Fe_{0.95}SO_4F$ - triplite



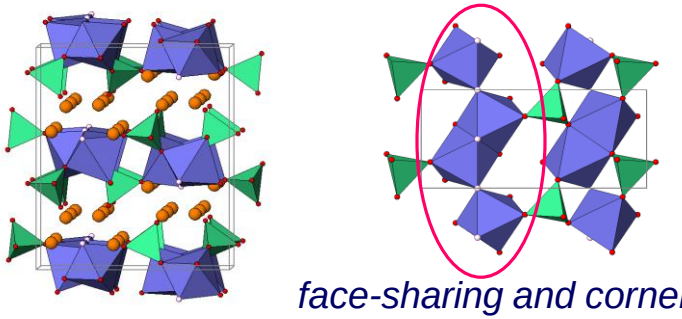
N. Recham et al, Nature Mater.9 (2010) 68

P. Barpanda et al, Nature Mater. 10 (2011) 772

Fluoride-phosphates A_2MPO_4F

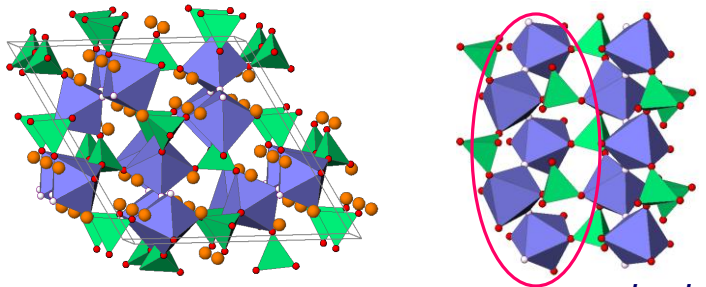
- different conjugation of (MO_4F_2) octahedra
- different transition metal

$(NaLi)_2FePO_4F$ – 2D [1]



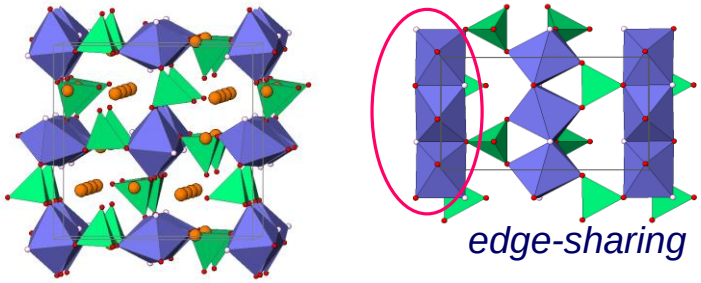
face-sharing and corner-sharing

Na_2MnPO_4F – 3D [2]



corner-sharing

Li_2MPO_4F (M=Ni, Co) – 3D [3,4]



edge-sharing

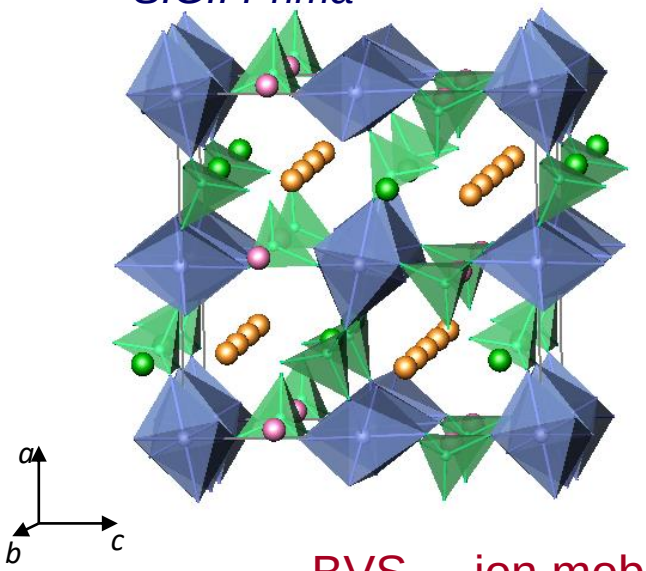
C_T ~ 140 mAh/g for M^{2+}/M^{3+}

C_T ~ 280 mAh/g for M^{2+}/M^{4+}

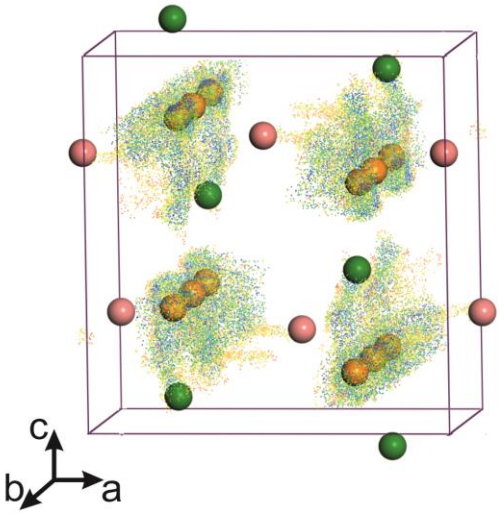
1. B.L.Ellis *et al*., *Nature Mat*. 6 (2007) 749
2. O.V.Yakubovitch *et al*., *Acta Crystallogr.C* 53 (1997) 395
3. M. Dutreilh *et al*., *JSSC* 142 (1999) 1
4. S. Okada *et al*., *J. Power Sources* 146 (2005) 565

3D-Li_2CoPO_4F: crystal structure

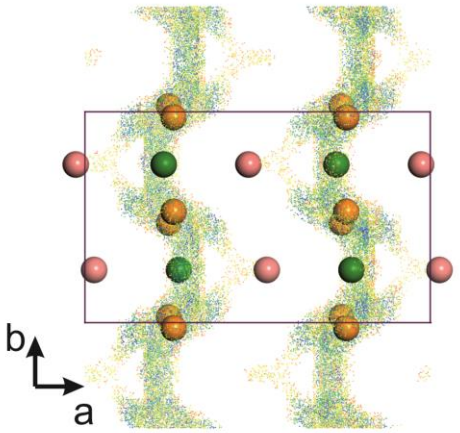
S.G.: Pnma



BVS mapping



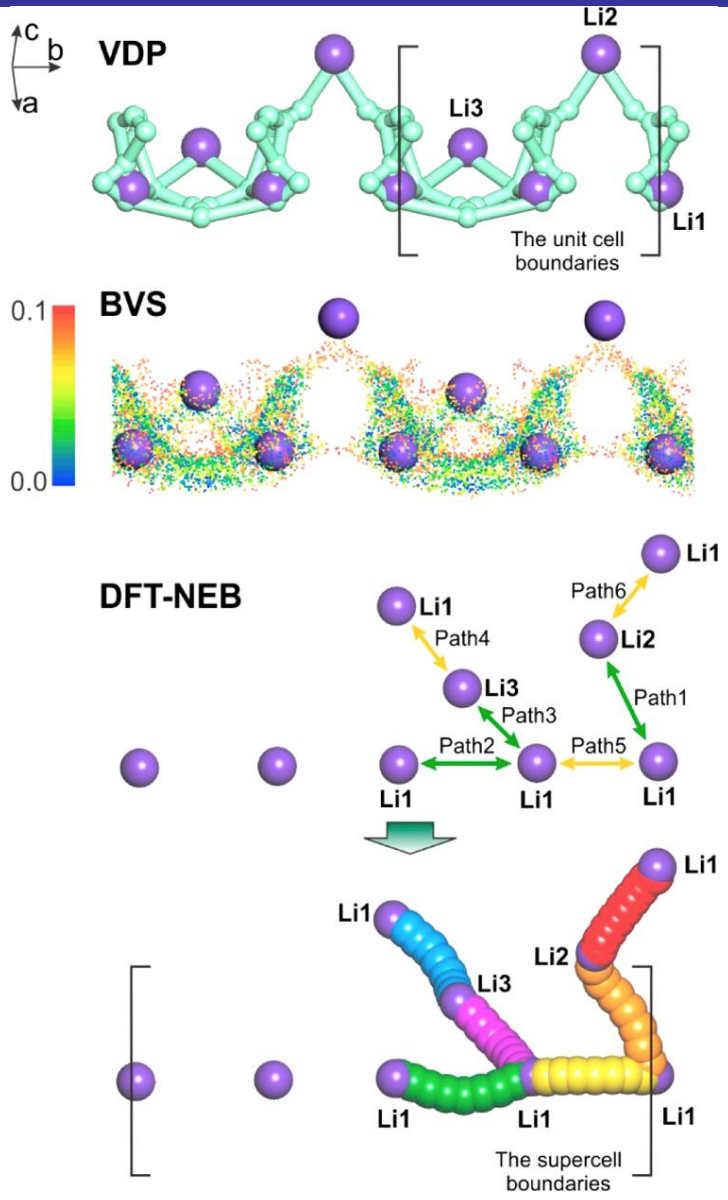
	BVS	ion mobility
● - Li1 (*8d*)	+0.77	+
● - Li2 (*4c*)	+0.98	?
● - Li3 (*4c*)	+1.22	–



- 3D structure (thermal and electrochemical stability)
- 1D Li-ion diffusion pathway
- 3 independent Li-positions,
  Li-ion mobility: Li1 > Li2 > Li3

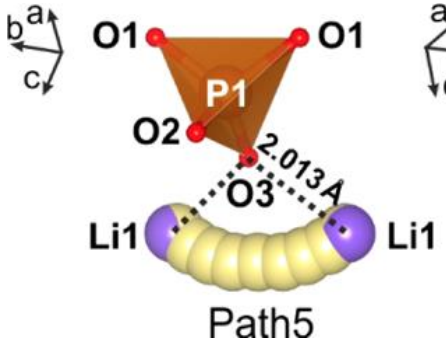
N.R. Khasanova et al., J. of Power Sources 196 (2011) 355

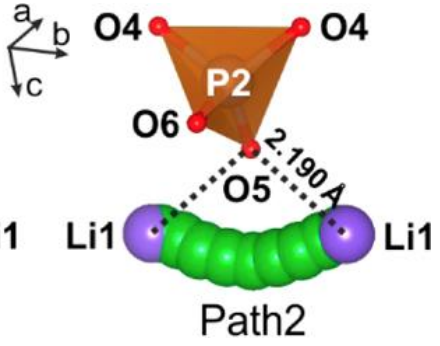
Diffusion pathways



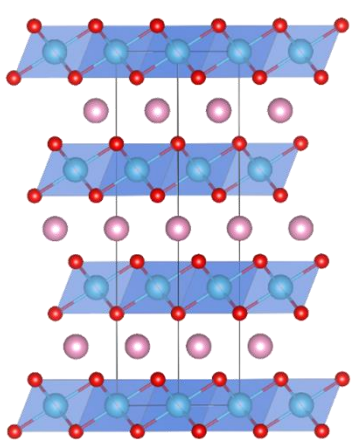
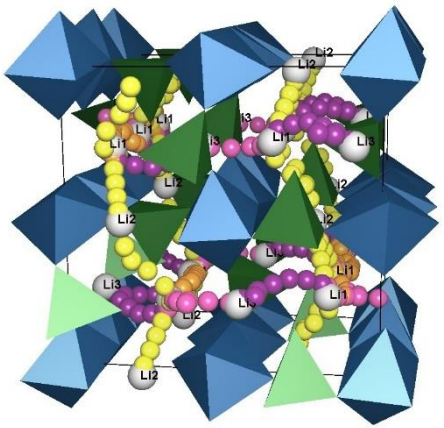
Activation Energies and Migration Path Lengths in Li2 CoPO4 F According to DFT-NEB

N	path length, Å	transition type	E_a, eV
1	3.677	Li1 ➔ Li2	0.35
2	**3.330**	**Li1 ➔ Li1**	**0.12**
3	3.130	Li3 ➔ Li1	0.43
4	3.110	Li3 ➔ Li1	0.34
5	**3.167**	**Li1 ➔ Li1**	**0.41**
6	2.416	Li1 ➔ Li2	0.37





Li-ion transport by DFT-NEB
Li_2CoPO_4F vs $LiCoO_2$

	$LiCoO_2$	Li_2CoPO_4F
Crystal structure, dimensionality of polyhedral framework	2D 	3D 
Average exp. potential vs Li/Li^+, V	3.9	~ 5
Theo. capacity/specific energy, $mAh \cdot g^{-1}$ / $mWh \cdot g^{-1}$	274 / 1068	143 / 715 (1ē) **215 / 1075 (1.5ē)**
Exp. capacity/specific energy, $mAh \cdot g^{-1}$ / $mWh \cdot g^{-1}$	140 / 545	140 / **> 650**
Diffusion barrier, eV	**0.52**	**0.12 – 0.42**

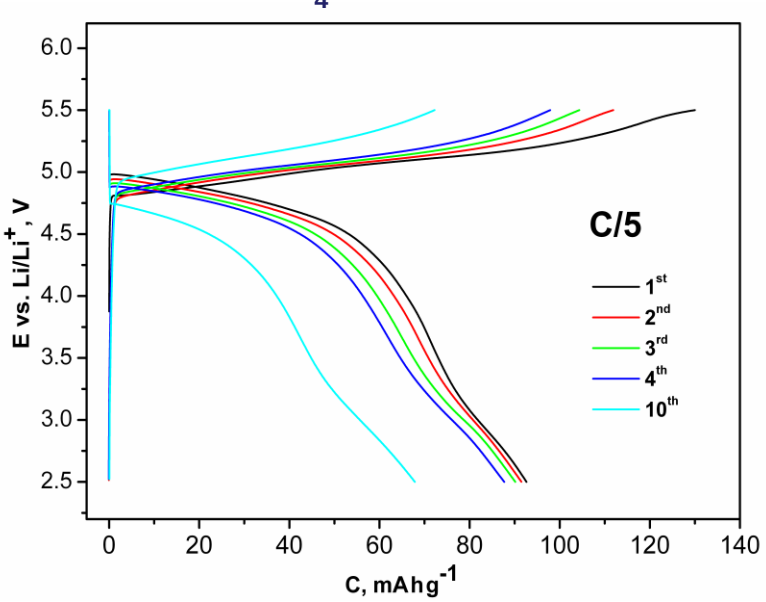
More facile diffusion is anticipated for Li_2CoPO_4F

S.Fedotov et al., Phys.Chem. C 121 (2017) 3194

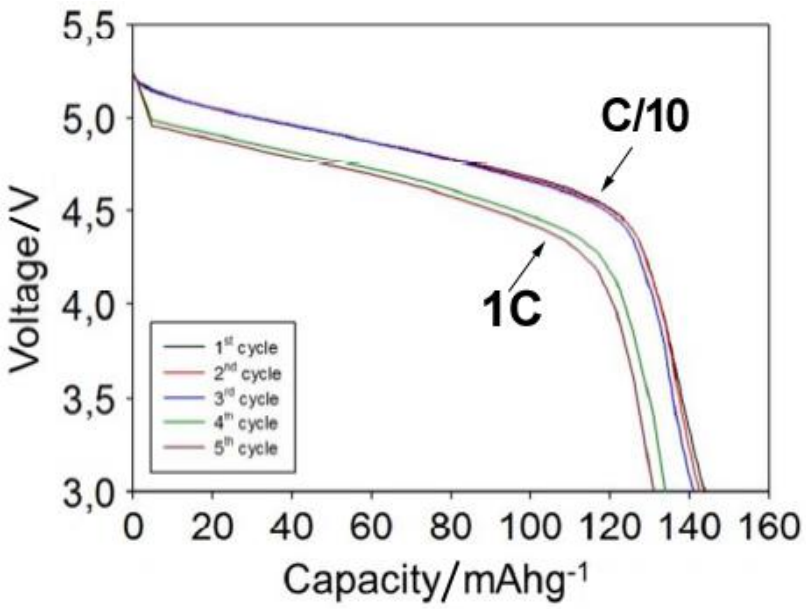
Li_2CoPO_4F: electrochemical properties

high-voltage electrolytes

1M $LiBF_4$ in TMS



1M $LiPF_6$ in FEC/DMC (1/4)



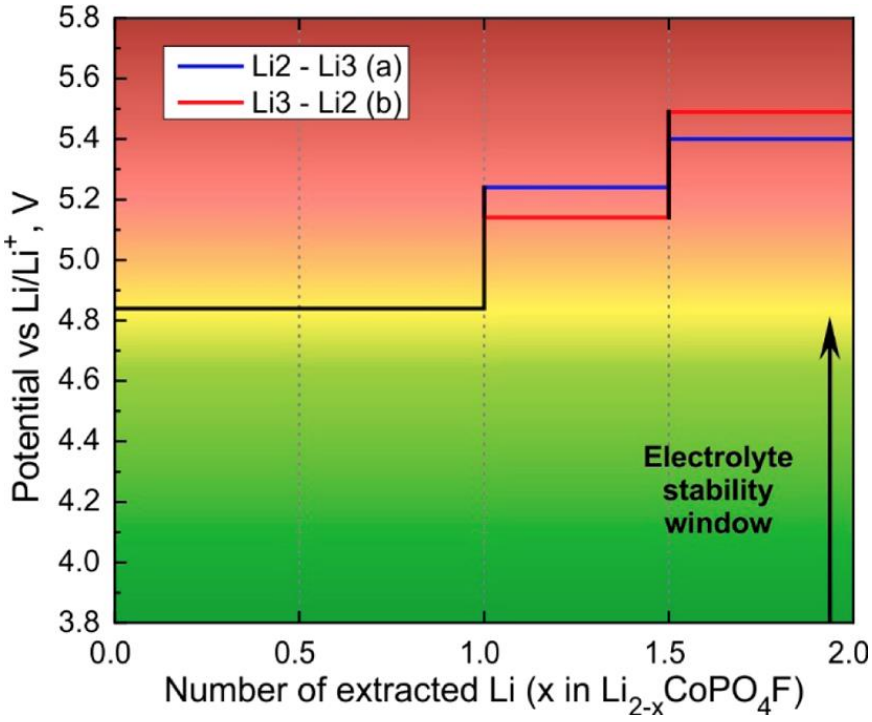
- solid-solution mechanism of Li^+ de/intercalation
- discharge capacity of ~ 140 $mAhg^{-1}$ (~1.0 Li^+)

N.R. Khasanova et al. , *Beilstein Journal of Nanotechnology* (2013) 4, 860

J.Schoiber et al., Cryst.Growth Des. (2016), DOI: 10.1021/acs.cgd.6b00573

Li_2CoPO_4F: electrochemical properties

- Calculated voltage profile (DFT)

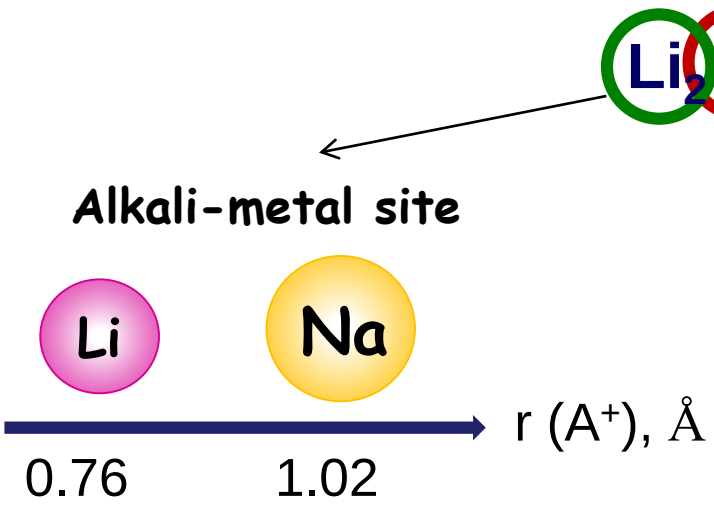


involving of Li2(Li3) in diffusion : extraction of 1.5 Li^+ per f.u. ??? At 5.8 V???

high-voltage electrolyte !
adjusting the working potential !

S.Fedotov et al., Phys.Chem. C 121 (2017) 3194

Li_2MPO_4F system: substitution on metal sites



M	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
r, Å	0.83	0.78	0.74	0.69
E* (M^{2+}/M^{3+}), V	4.1	3.45	> 4.8	>5.2

* for olivine-type materials

"framework elasticity" !

- narrow range of solid solutions !

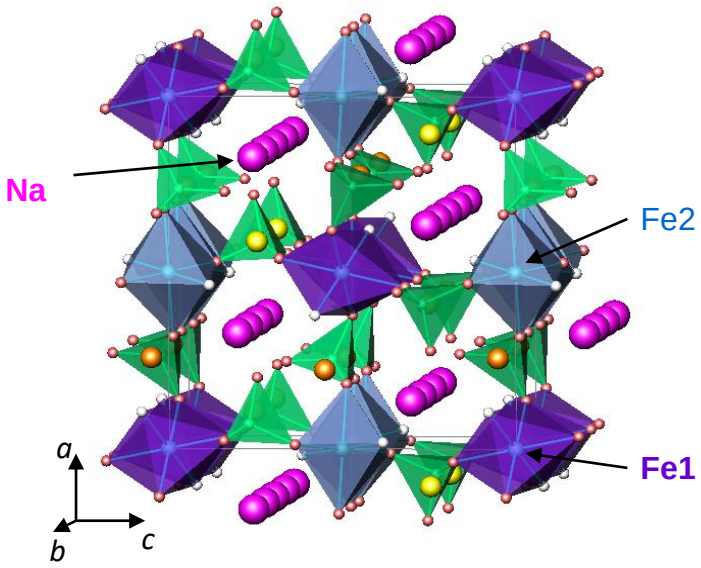
$Li_2(Co_{1-x}Fe_x)PO_4F$ $x \leq 0.3$

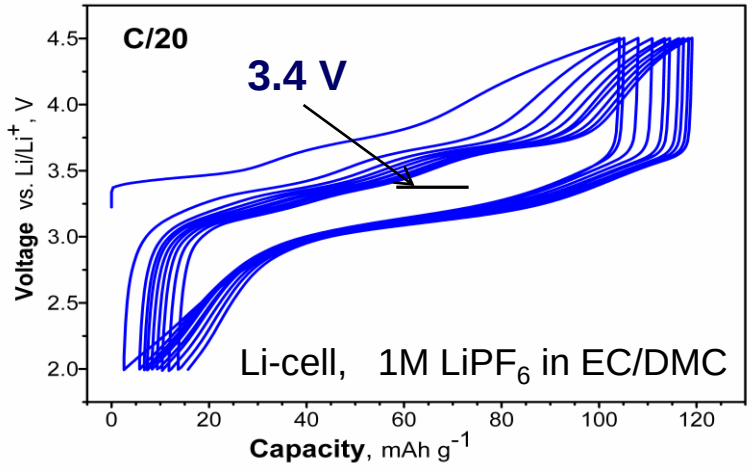
x	Unit cell parameters of $Li_2Co_{1-x}Fe_xPO_4F$			
	a, Å	*b*, Å	*c*, Å	V, Å^3
0	10.455(2)	6.3853(8)	10.8764(2)	726.0(2)
0.1	10.460(2)	6.3907(11)	10.881(2)	727.5(3)
0.3	10.462(2)	6.3971(12)	10.894(2)	729.1(3)

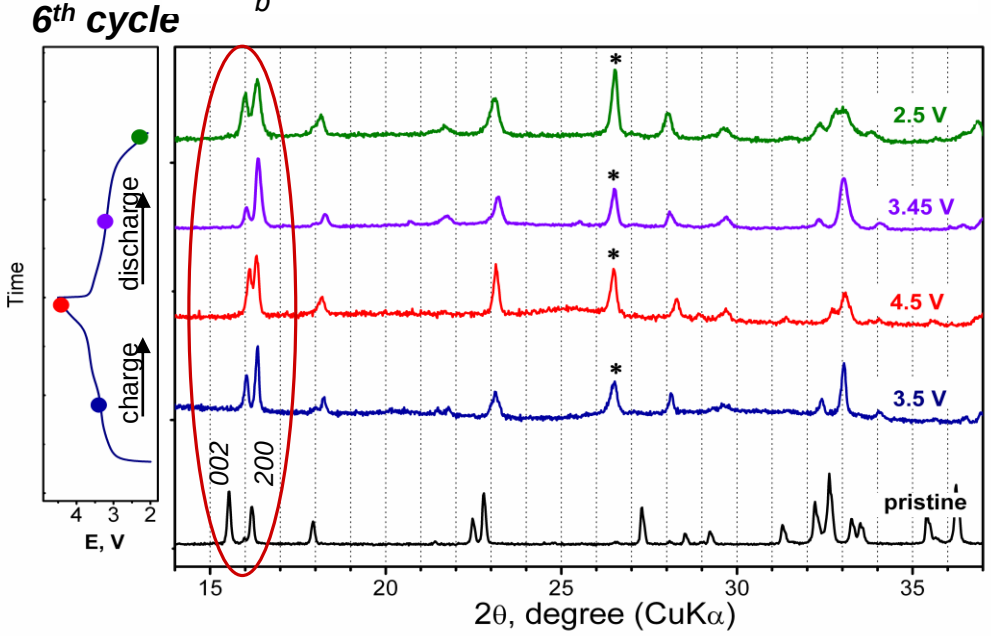
$Li_2(Co_{1-x}Mn_x)PO_4F$ $x \leq 0.1$

x	Unit cell parameters of $Li_2Co_{1-x}Mn_xPO_4F$			
	a, Å	*b*, Å	*c*, Å	V, Å^3
0	10.455(2)	6.3853(8)	10.8764(2)	726.0(2)
0.1	10.465(1)	6.3998(9)	10.8975(14)	729.8(2)

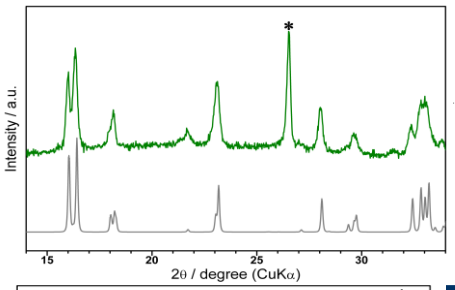
$NaLiFePO_4F$: electrochemical performance

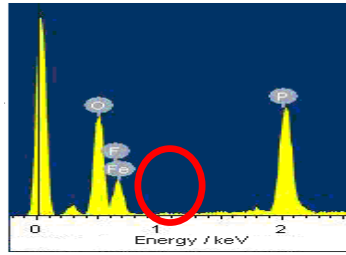


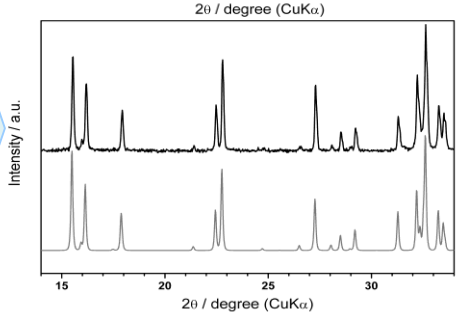


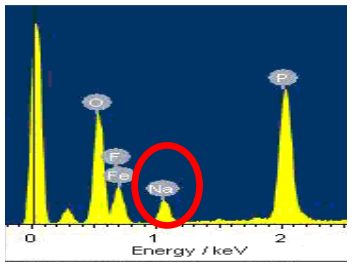


Simulation









formation of 3D- Li_2FePO_4F

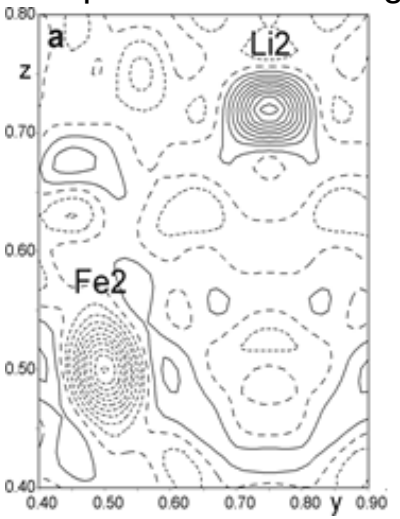
N.R. Khasanova et al., J. Chem. Mat. 24 (2012), 4271.

Li_2FePO_4F: ex-situ structure refinement after cycling at 75° C

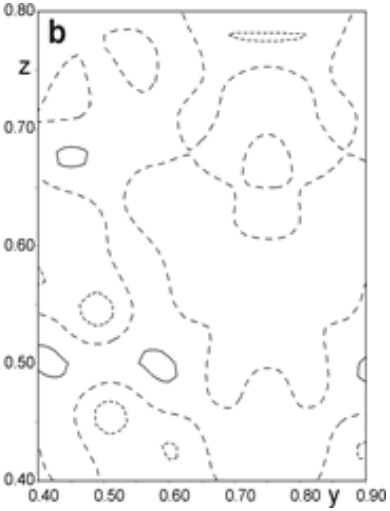
electron diffraction tomography

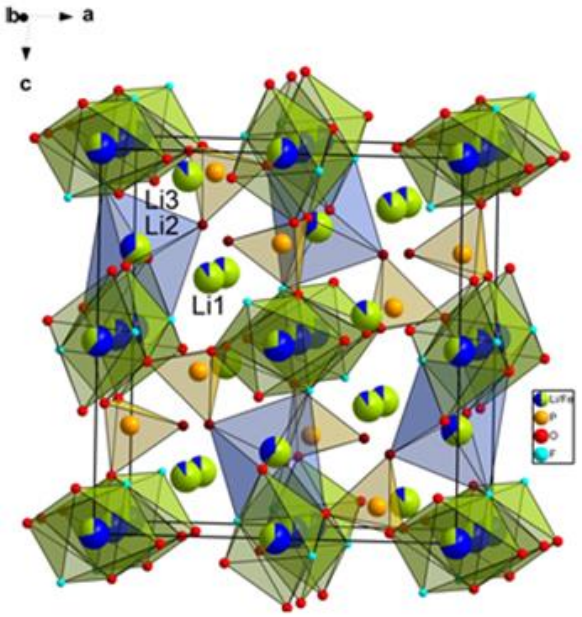
difference Fourier map:

complete Li/Fe ordering



antisite Li/Fe disorder

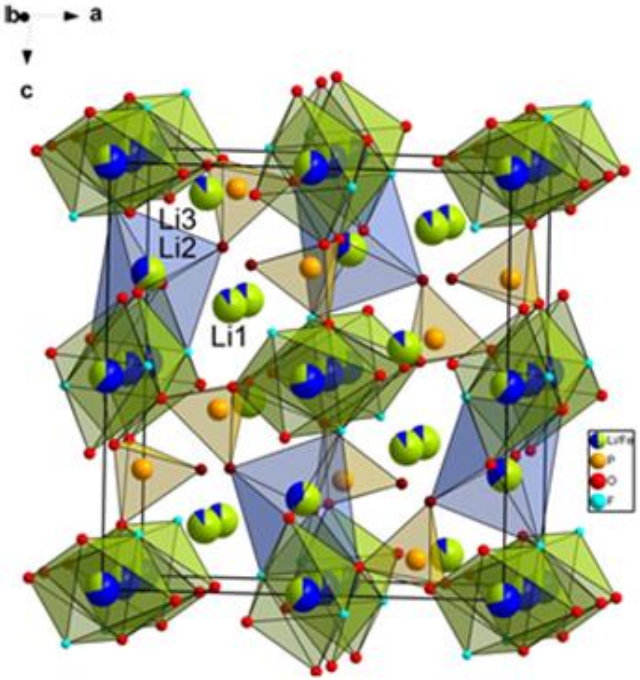


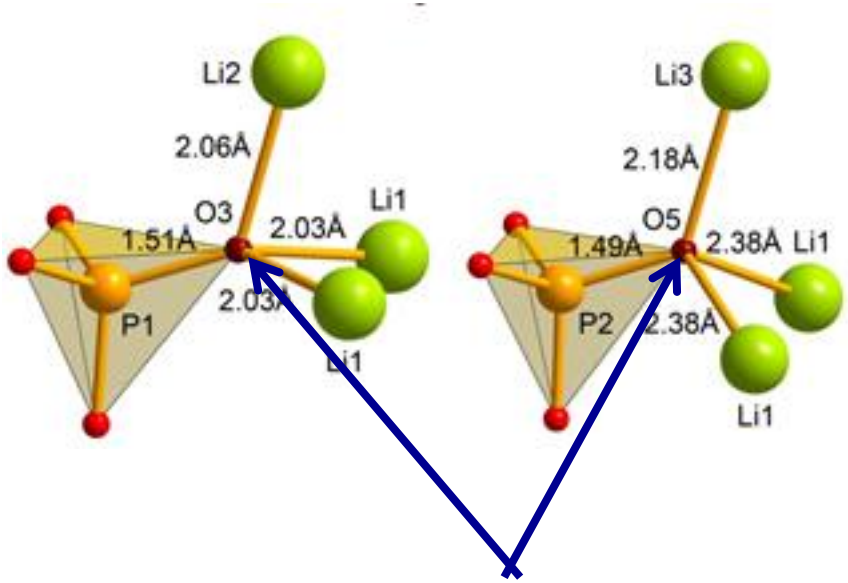


Atom	Position	Occupancy	x/a	y/b	z/c	U_{iso}, Å^2
Li1	8d	0.902(7)Li 0.098(7)Fe	0.748(1)	0.960(2)	0.652(1)	0.0200(7)
Li2	4c	0.64(1)Li 0.36(1)Fe	0.9726(8)	3/4	0.7156(7)	0.0200(7)
Li3	4c	0.88(1)Li 0.12(1)Fe	0.282(1)	1/4	0.575(1)	0.0200(7)
Fe1	4a	0.71(2)Fe 0.29(2)Li	0	0	0	0.0200(7)
Fe2	4b	0.61(1)Fe 0.39(1)Li	0	0	1/2	0.0200(7)

O. Karakulina et al. Chemistry of Materials 28 (2016) 7578

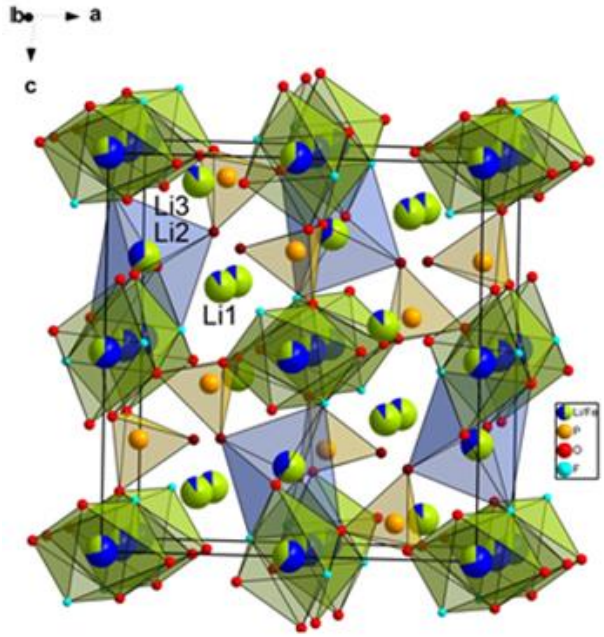
Li_2FePO_4F: antisite disorder

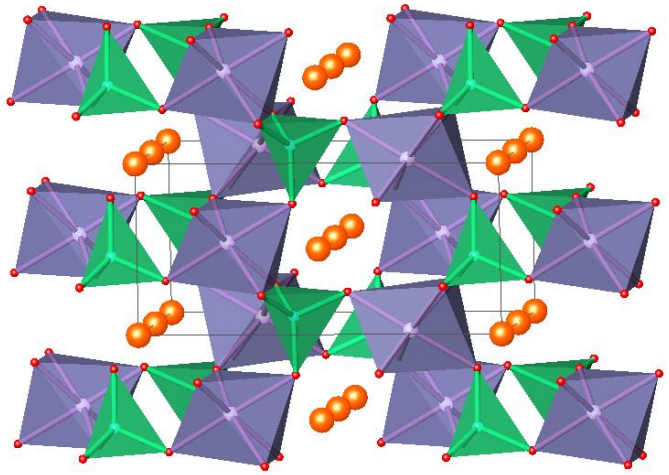


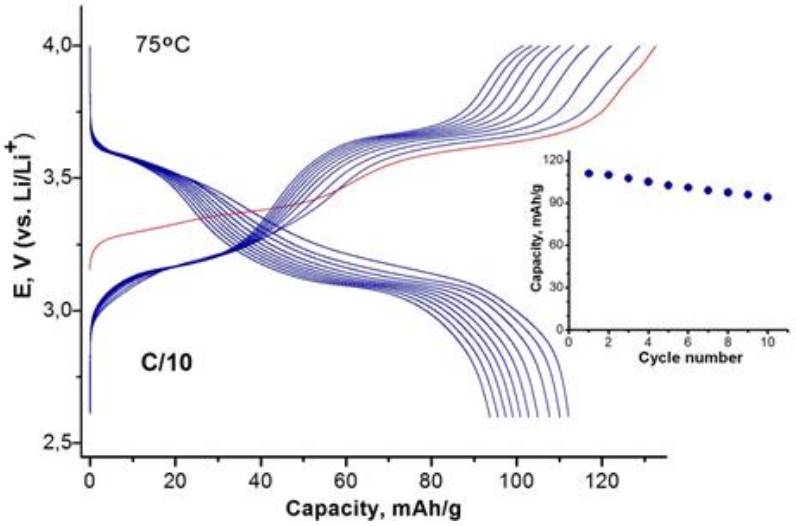


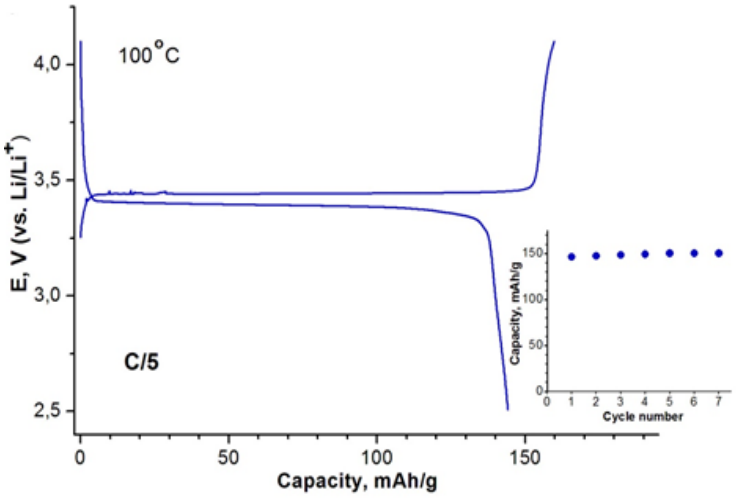
Heavily underbonded after Li1 deintercalation

Li_2FePO_4F: antisite disorder

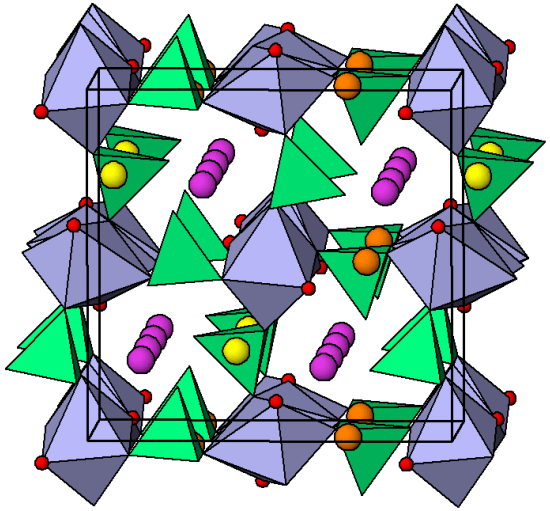






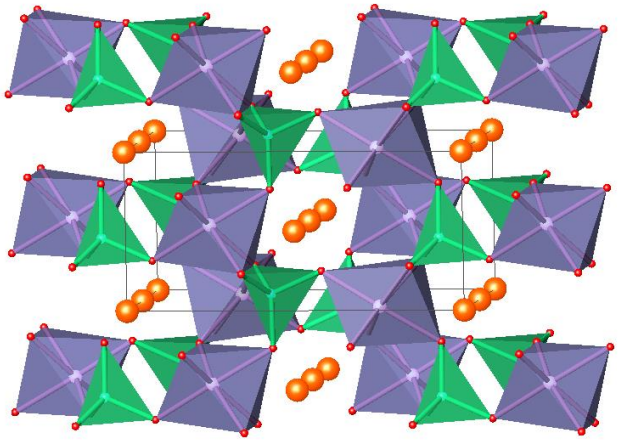


Comparison: Li_2MPO_4F vs. $LiFePO_4$



solid solution

$D_{chem} \approx 10^{-10}$ cm^2/s



2-phase mechanism

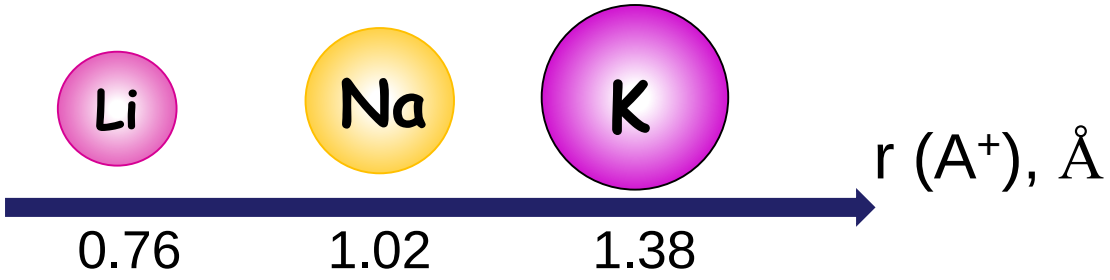
$\approx 10^{-15}$ cm^2/s

	Co	Fe	
Volume change (%)	~ 4.5 %	1.7%	6.7%
E_g for 1Li (Wh/kg)	**730**	496	583
E_g for 1.5 Li (Wh/kg)	**1095**	**744**	-

Possibility of Fe^{2+}/Fe^{4+} ? Ab initio study for Li_2FePO_4F: **Fe3+/Fe4+ possible at potentials ~ 5.1 V vs. Li/Li+**

F. Yang et al., RSC Adv., 2014,4, 50195-50201

$AMPO_4F$: new cathode materials



Background:

1)$Li_{1+x}VPO_4F$ (tavorite structure): 2-electron redox-transition:

~ 4.2 V(vs. Li^+/Li) (cathode) ~1.8 V(vs. Li^+/Li) (anode)

J.Barker et al. JES (2003)150, A1394

2)$Li_{1+x}FePO_4F$ (tavorite structure)

~ 2.8 V(vs. Li^+/Li)

N. Recham et al. Chem. Mater. 22 (2010)1142

3)$LiFeSO_4F$ (tavorite structure)

~ 3.6 V (vs. Li^+/Li)

N. Recham et al, Nature Mater.9 (2010) 68

4)$KFeSO_4F$ **(KTP structure)**

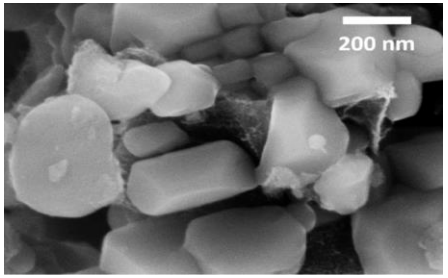
~ 3.7 V (vs. Li^+/Li)

N. Recham et al, Chem. Mater. 24 (2012) 4363

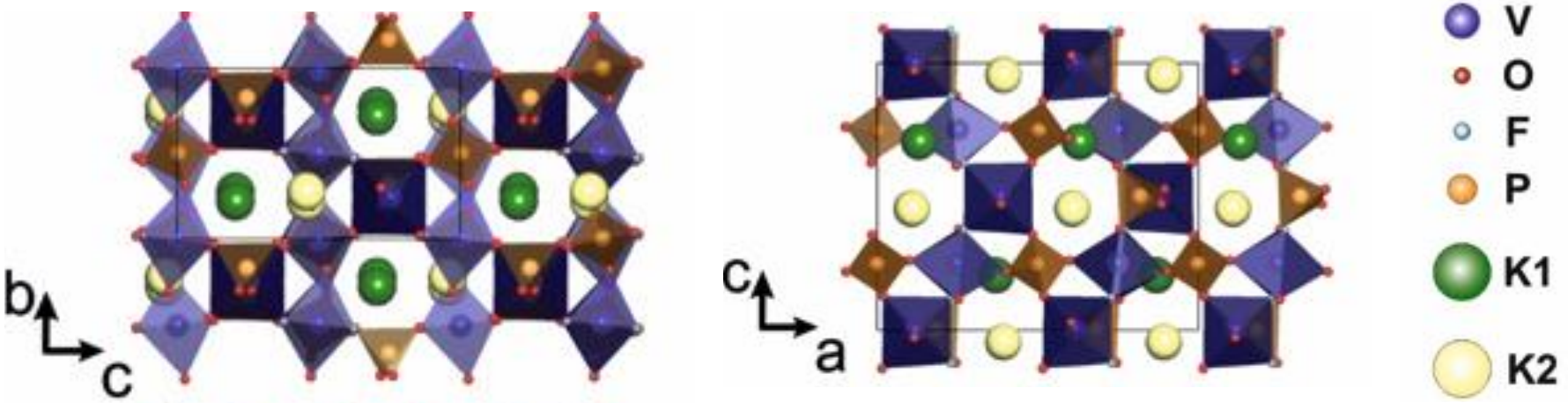
$AMPO_4F$ **with KTP-type structure ???**

$AVPO_4F$ (A = Li, K)

- **Synthesis** at 600˚ C, Ar-flow for 1h
  $VPO_4 + KHF_2 \rightarrow KVPO_4F$

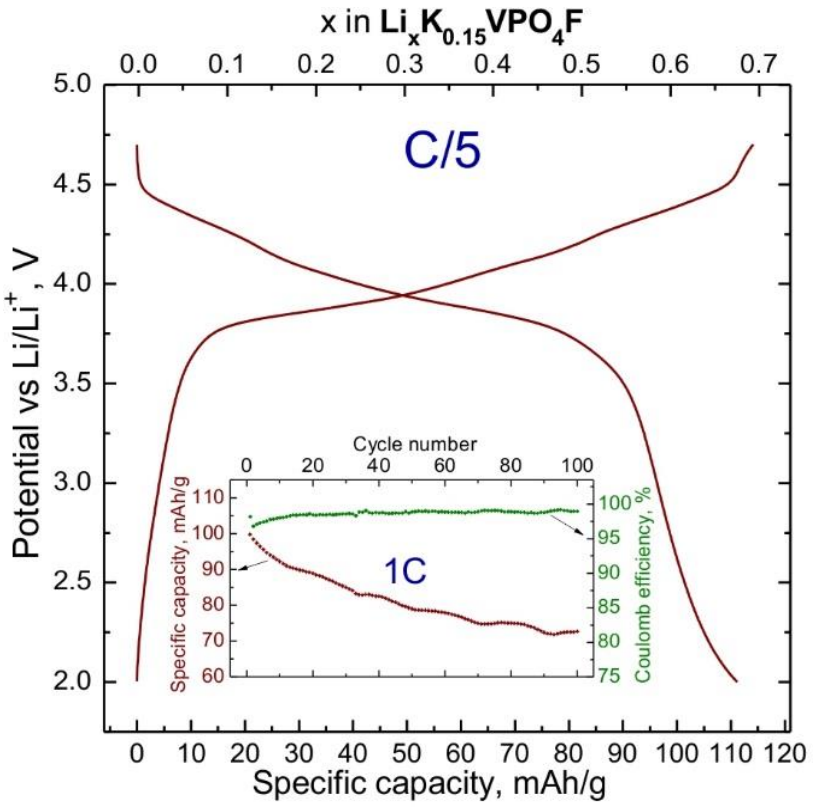


- **Structure**
  S.G. #33 *Pna*2_1, *a* = 12.8200(3) Å, *b* = 6.3952(1) Å, *c* = 10.6115(2) Å

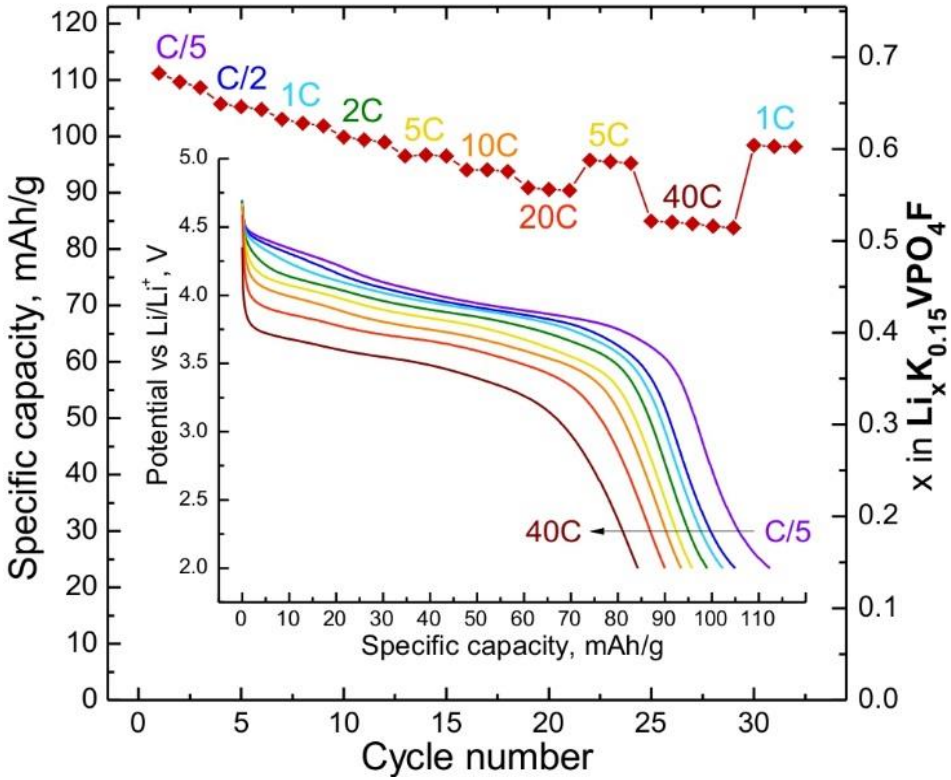


Fedotov S.S. et al, Chem. Mater. 28 (2016) 411

$AVPO_4F$ (A = Li, K): cycling behaviour



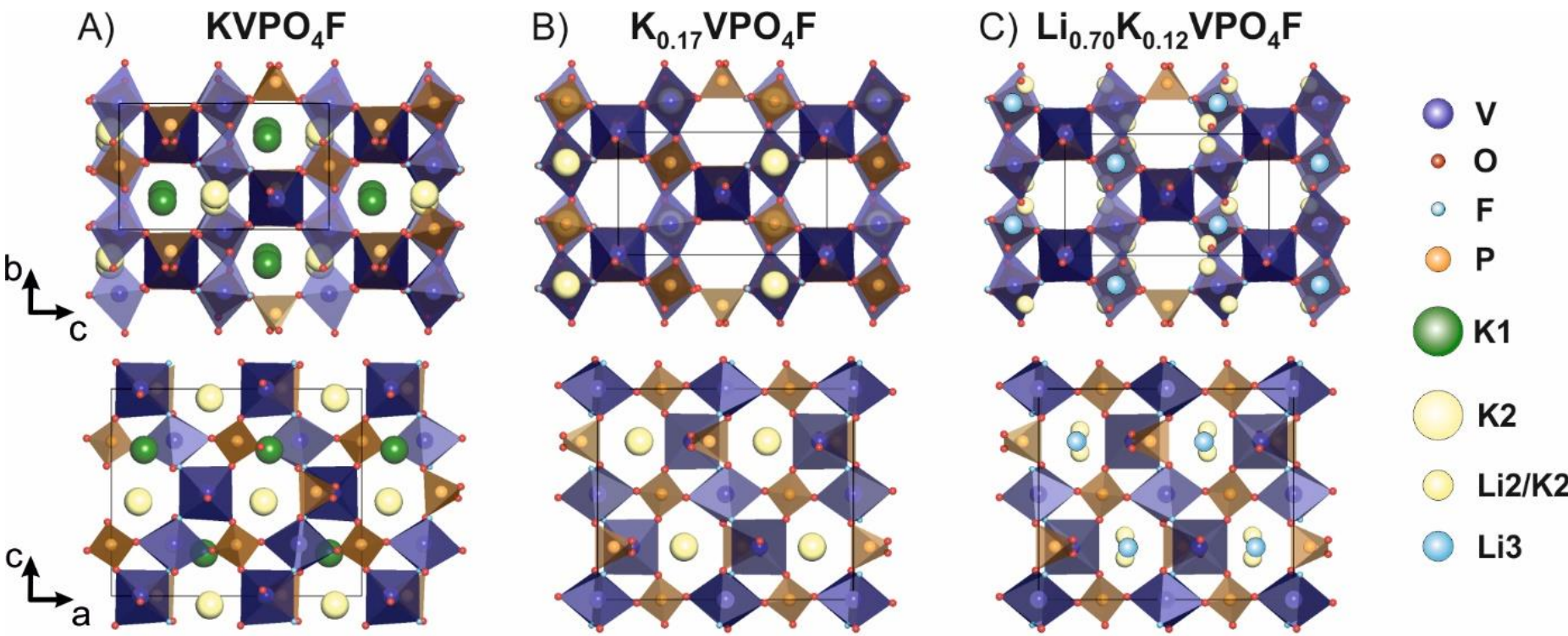
A charge-discharge curve of $Li_xK_{0.15}VPO_4F$ at C/5. The inset - the capacity retention and Coulomb efficiency in the cycling at 1C rate



C-rates capability upon cycling and discharge curves of $Li_xK_{0.15}VPO_4F$

A remarkable capacity retention at 40C maintaining more than 50% of theoretical (156 mAh/g) or 75% of initial specific capacity

Structural transformations: “depotassiated” and lithiated forms

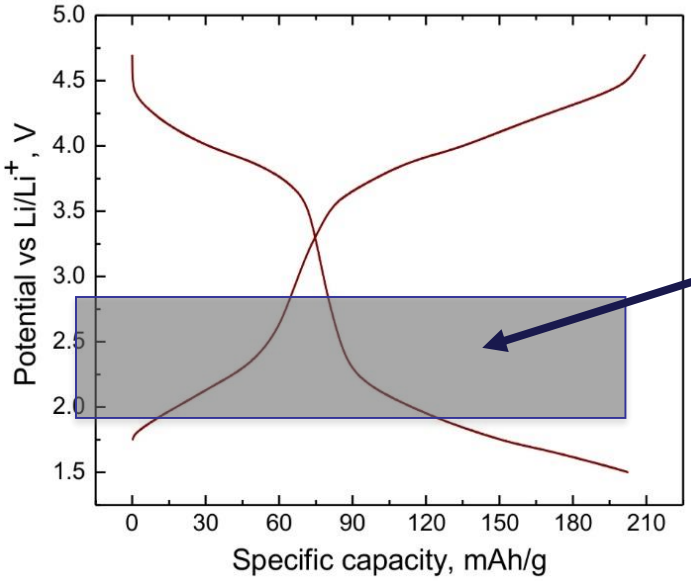


Pna21 **Pnan** **Pnan**

Volume variation among all phases is less than 2.2% !!!

More Li… or what's next?

I. Low-voltage domain:

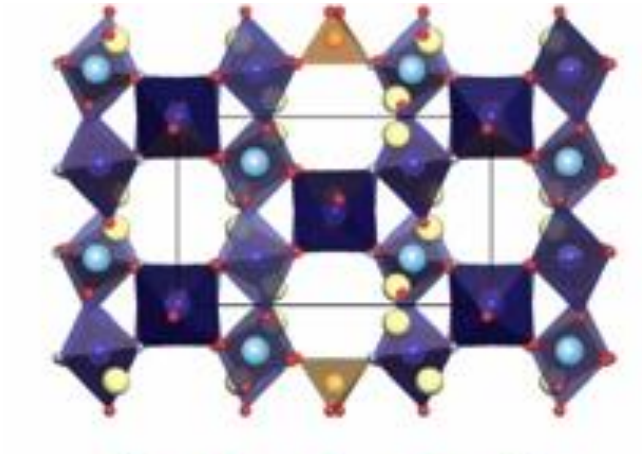


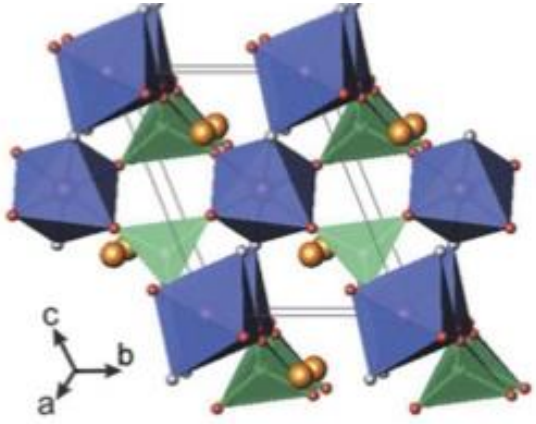
Second Li^+ ?
V^{3+}/V^{2+} ?

Theo. capacity (2 Li^+)
~300 mAh/g !

The goal:
increasing both potential and capacity

$AVPO_4F$ (A = Li, K): comparison of KTP and tavorite structures for LIB





E_g	624 Wh/kg	655 Wh/kg
E_v	~2000 Wh/l	2140 Wh/l
ΔV	~2%	8.5%
Mechanism	Solid solution	Two phase

Perspective cathode material for high-power batteries

Both materials can be used in symmetrical cell

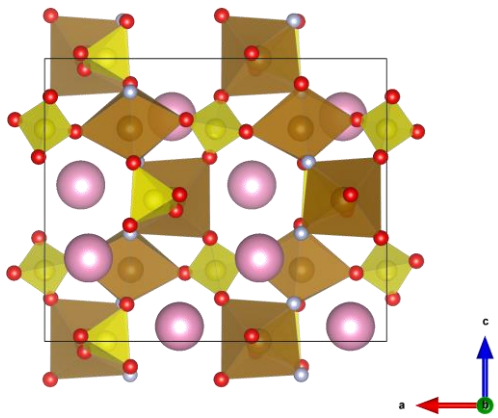
KTP-type fluoride-sulfate framework

Recham, N. et al *Chem. Mater.* 2012, 24, 4363–4370.

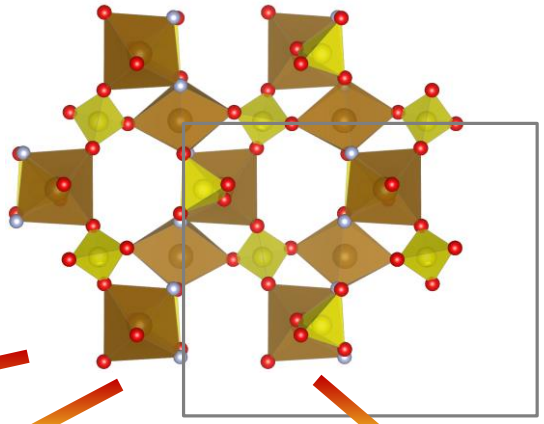
$KFeSO_4F$

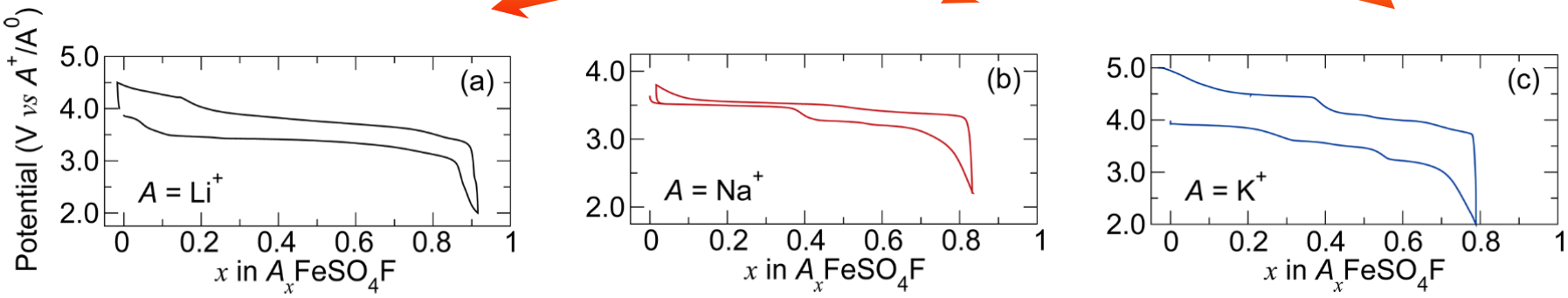
Tarascon's group

$FeSO_4F$



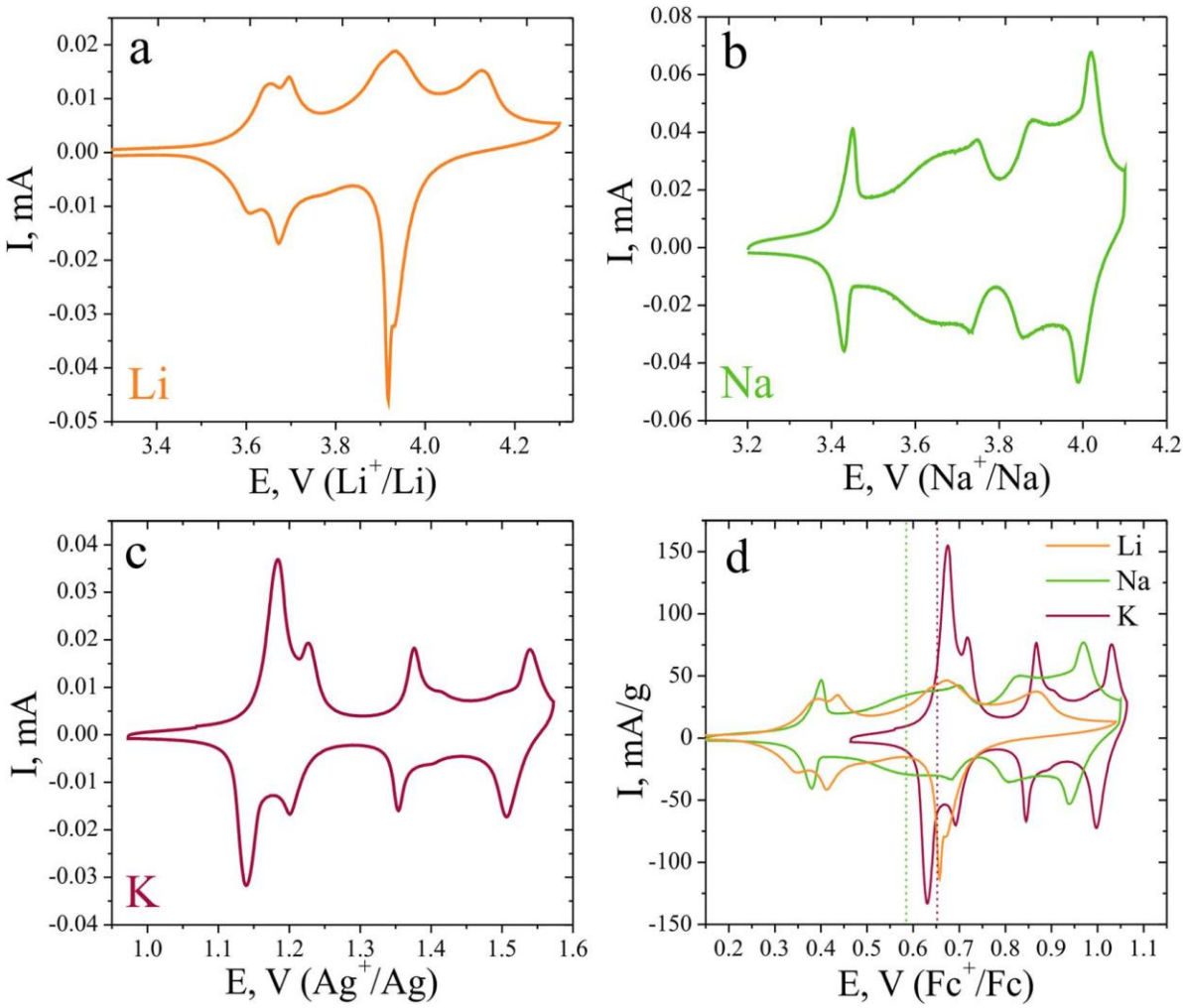
"Depotassiation"





Versatility of the KTP framework!

$KVPO_4F$ against Li, Na and K



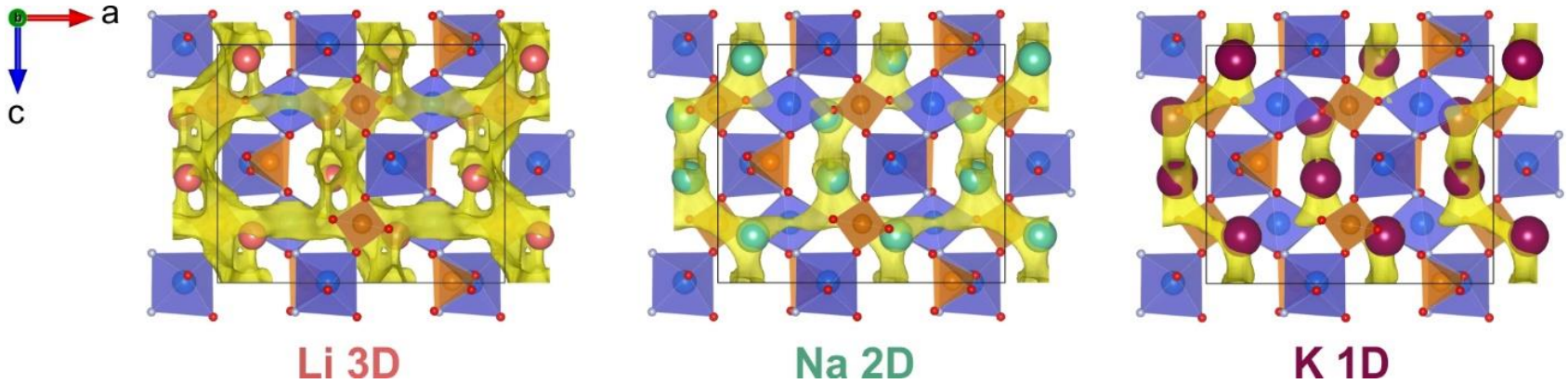
3-electrode cell configuration

Electrolyte:
1M APF6 or AClO4 in EC/DEC

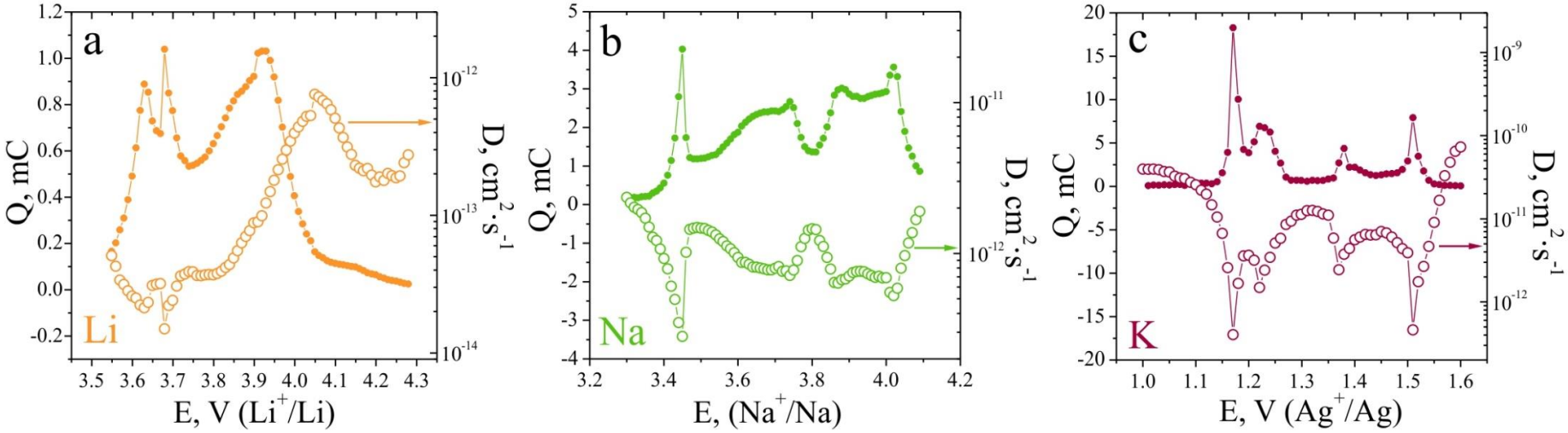
Counter electrodes:
Li, Na or AgCl/Ag

Alkali ion diffusion

Bond Valence Energy Landscapes



From PITT: D(Li) < D(Na) < D(K) ≈ 10^{-13}–$4\cdot10^{-11}$ $cm^2\cdot s^{-1}$:



V.Nikitina et al. JES 164 (2017)

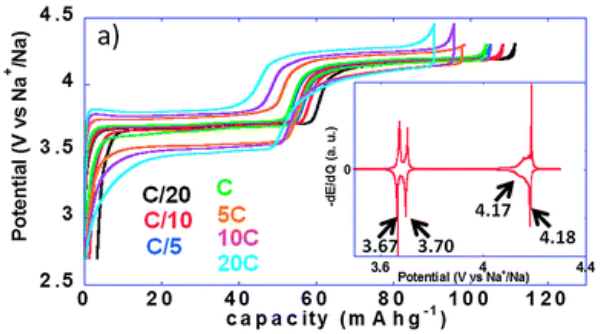
Fluoride-phosphates based Me-ion battery prototypes

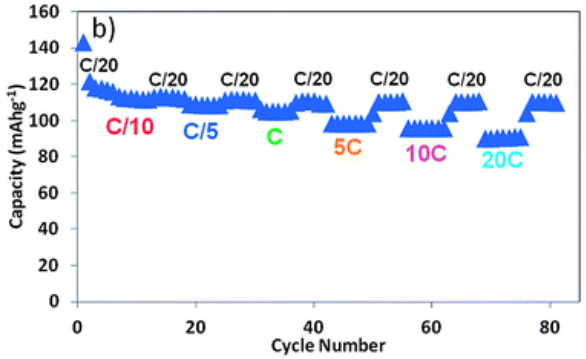
ENERGY RS2E
The french network on electrochemical energy storage

http://www.energie-rs2e.com/en/news/na-ion-batteries-promising-prototype

$Na_3V_2(PO_4)_2F_3$ / Hard carbon

110 Wh/kg 18650 Na-ion battery





A. Ponrouch et al, Energy Environ. Sci., 2013,6, 2361-2369

IBA-2016 meeting in Nantes, France:
RS2E announced a **new 3.8 V LiVPO4F Li-ion battery prototype (outperforming LiFePO4 based Li-ion battery)**

Fluoride phosphates are commercially viable cathode materials!

Na-ion batteries are coming on the market!!! KIB?

Acknowledgements

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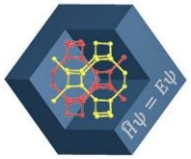
Artem Abakumov, Keith Stevenson

EMAT, RUCA, Antwerp

Dmitry Batuk, Joke Hadermann, Olesya Karakulina



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Artem Kabanov, Vladislav Blatov