Общемосковский семинар по электрохимии

Новые катодные материалы для Li-ионных аккумуляторов

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Химический факультет, МГУ имени М.В. Ломоносова

Outline

- **Introduction**
- **Main types of cathode materials for LIB:**

  Layered ($LiMO_2$) and $LiFePO_4$
- **A_2MPO_4F fluoride-phosphates**
- **Concluding remarks**

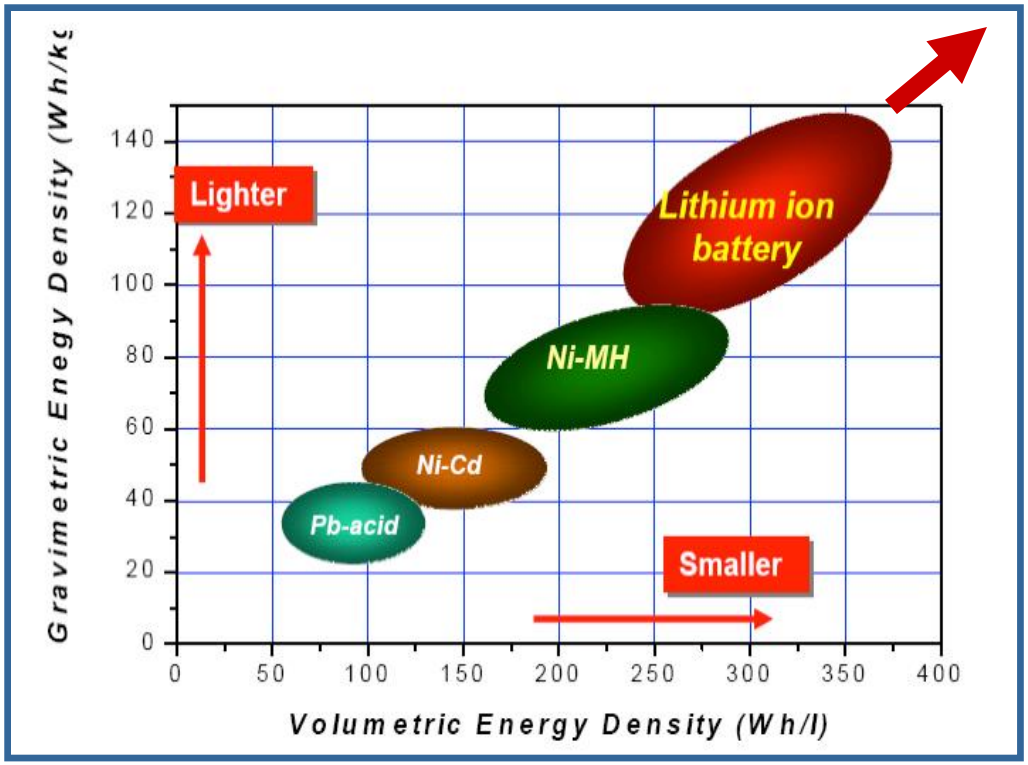
1995: «Advances in battery research are always restricted by chemistry »

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

and Crystallography!

Energy storage systems

up to 250 Wh/kg



Stationary energy storage

HEV, EV

Consumer electronics

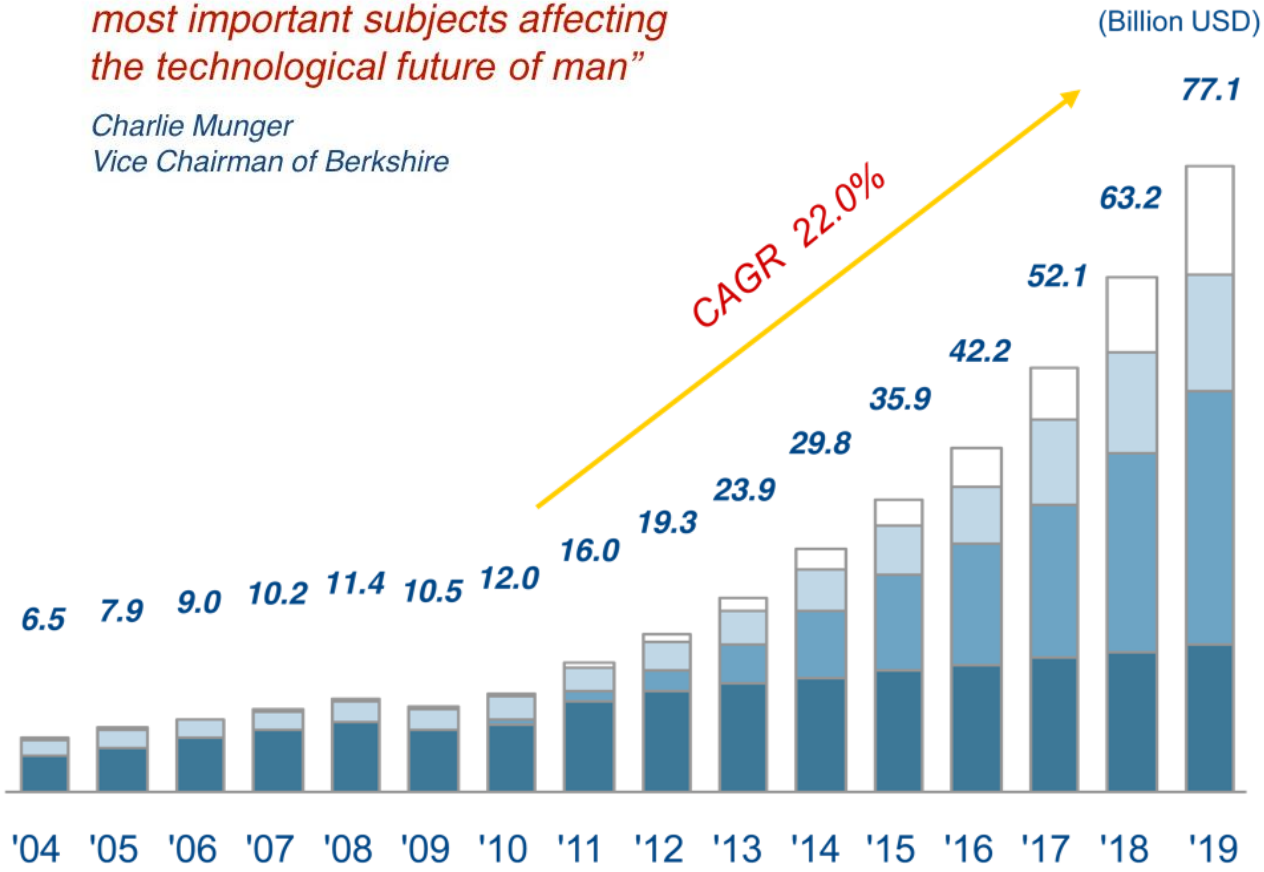
Increase of Energy and Power

INEOS: 26.09.2014

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

INEOS: 26.09.2014

Development of Electric Vehicles

La Jamais Contente - 1899

- 2 electric motors with 50 kW in total
- 200 individual Pb-PbO_2 cells
- **Total mass 1450 kg**
- Battery mass > 700 kg
- Max. speed 106 km/h

Nissan leaf - 2010

Total weight	1500 kg
Batteries weight	**300 kg**
Stored Energy	**24 kWh**
Power	120 h.p.
Distance	**70 – 220 (150) km**
Maximum speed	150 km/h

Cathode material – $LiMn_2O_4$
(E_g = 80 Wh/kg)

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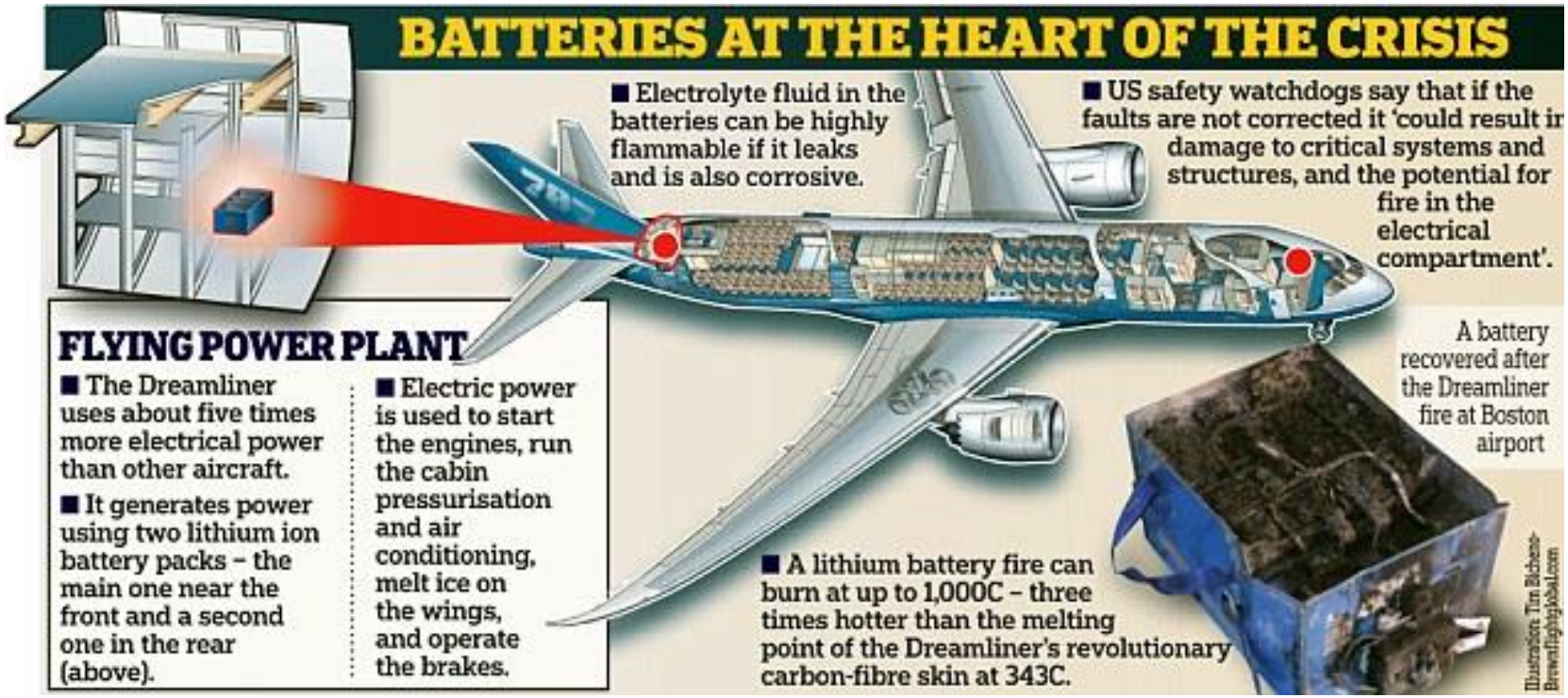
Safety problem



Daily Mail, 20.01.2013

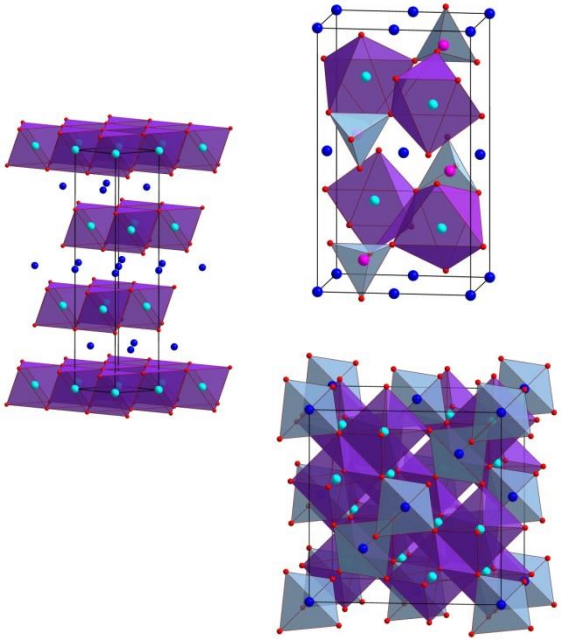
INEOS: 26.09.2014

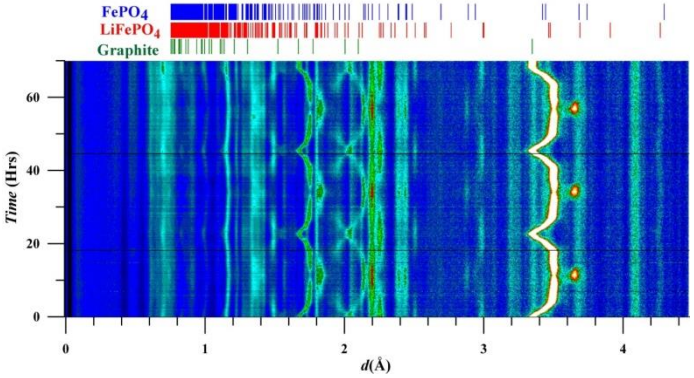
Impact of crystallography

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

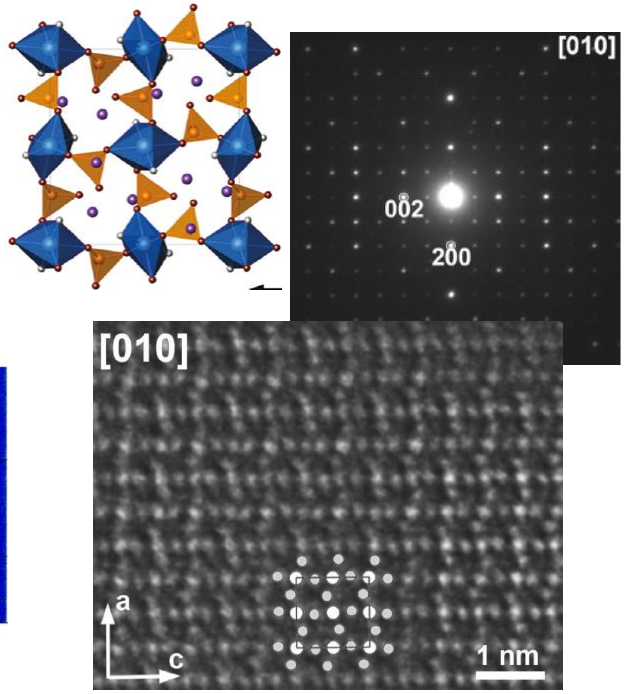
Crystallographic aspects of electrochemical reactions:
- *in situ* and *ex situ* X-ray and neutron diffraction studies
- spectroscopic methods (EXAFS, XPS, XANES etc)
- microstructure evolution

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





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



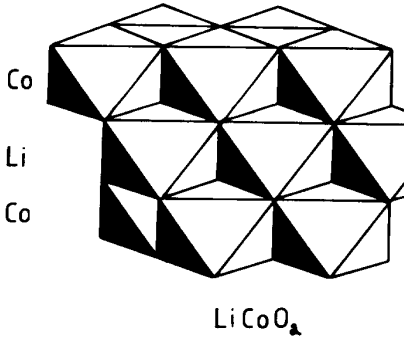
J. Hadermann et al. ,
Chem. Mat. 23 (2011) 3540

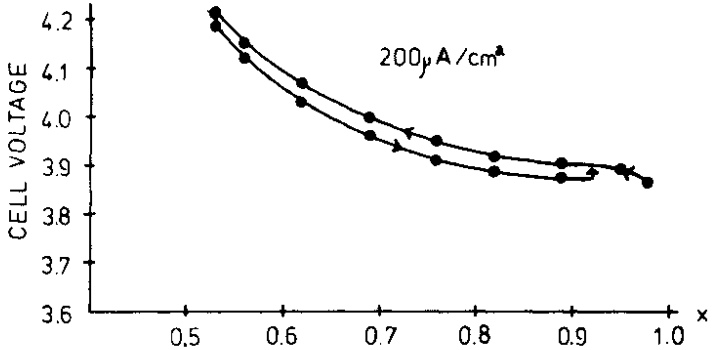
Main discovery

Mat. Res. Bull., Vol. 15, pp. 783-789, 1980. Printed in the USA.
0025-5408/80/060783-07$02.00/0 Copyright (c) 1980 Pergamon Press Ltd.

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



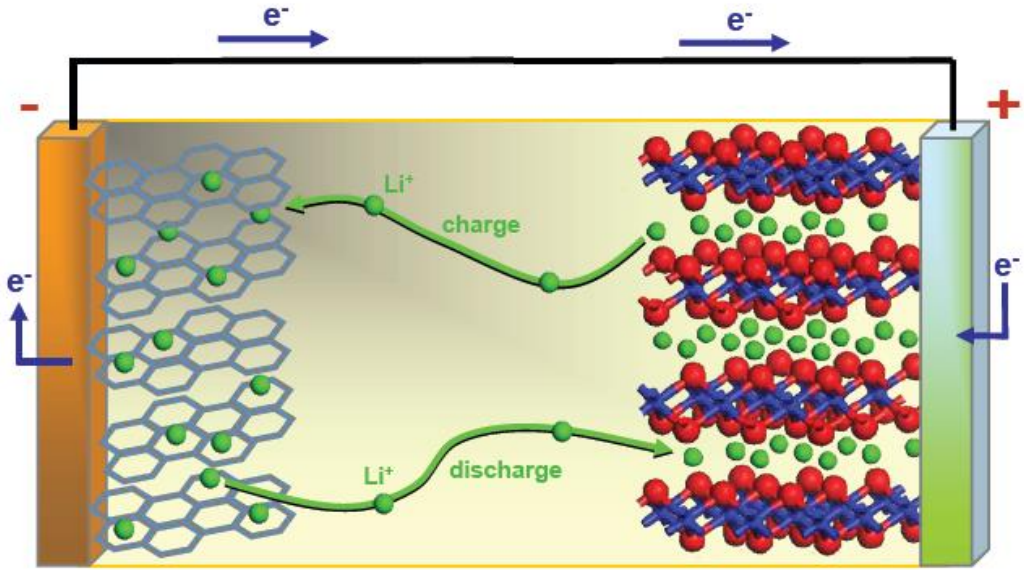


thetic route requires use of a starting high-temperature material that allows low-temperature extraction of lithium. The resultant phase need not necessarily be thermodynamically stable.

Examination of the known Li^+-ion solid

Li-ion battery

Concept (1980) Commersialization: Sony (1990)



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

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

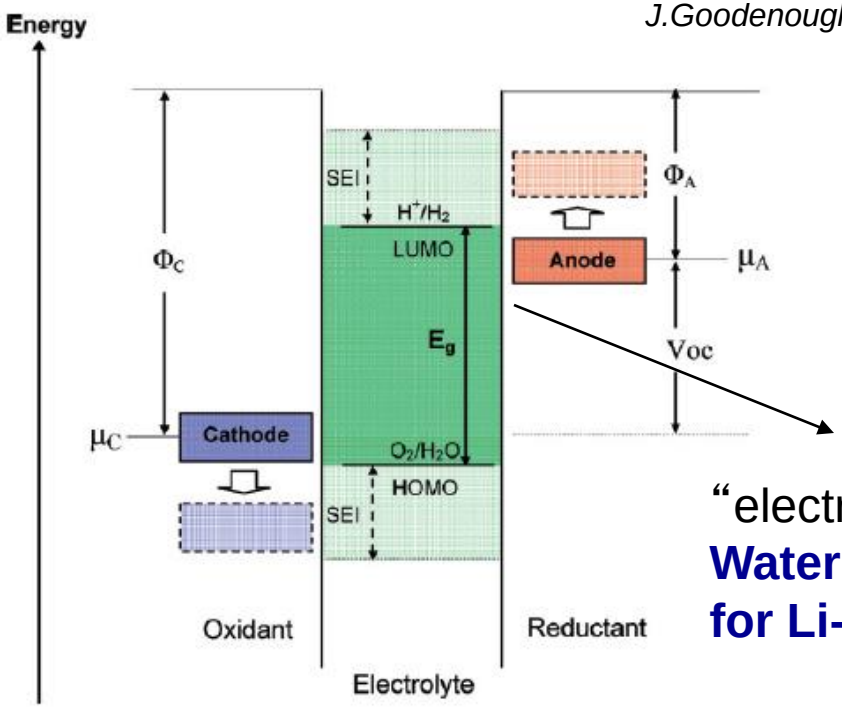
Voltage: 3.6 V **E^o (cathodic) – E^o (anodic) = E^o (cell)**

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

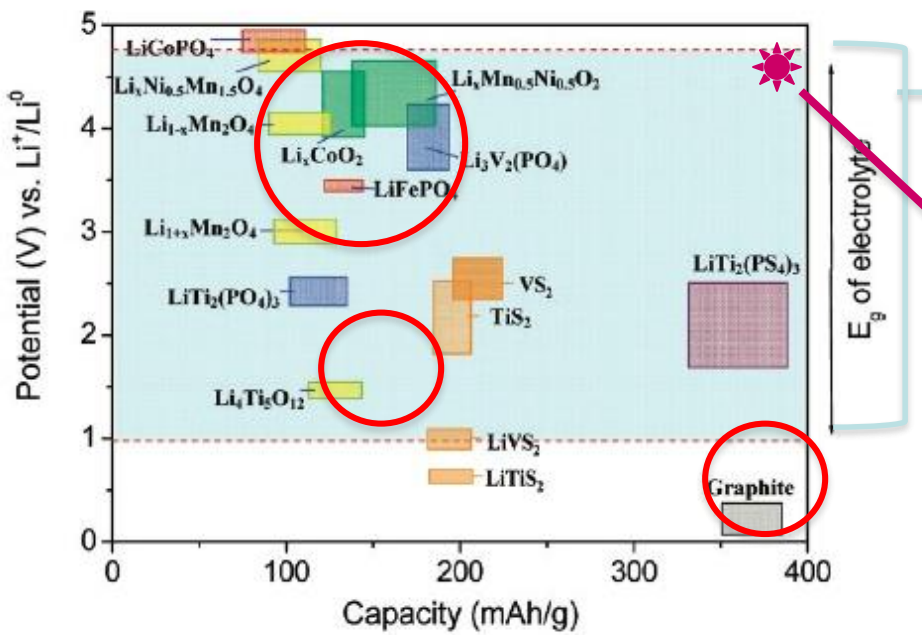


"electrolyte window"
Water – 1.23 V,
for Li-electrolytes – up to 4 V

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

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

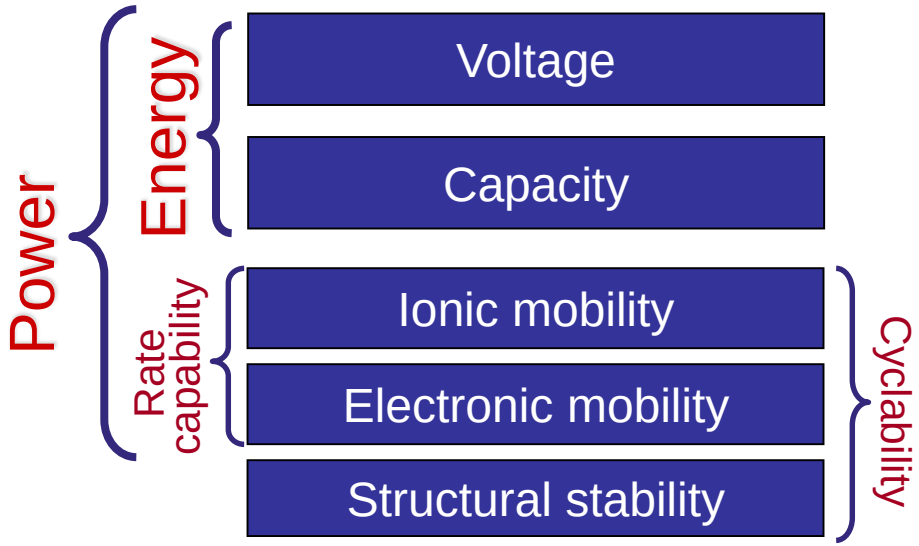
(Oxidation and reduction of electrolyte outside the window)

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



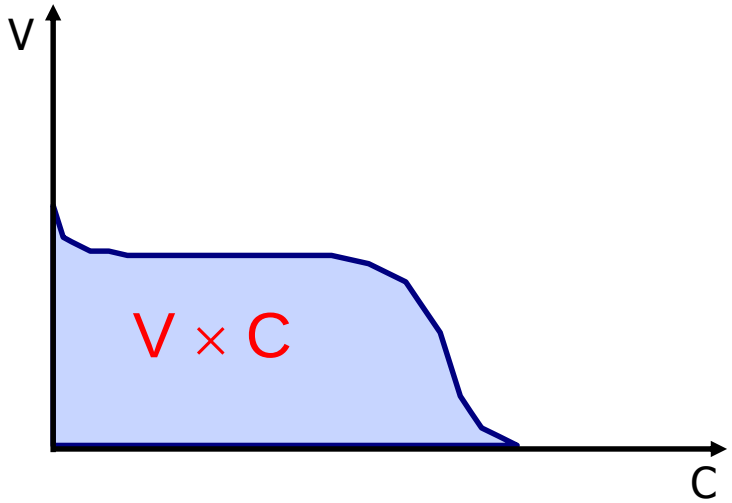
$M^{n+}/M^{(n+1)+}$ redox potential

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

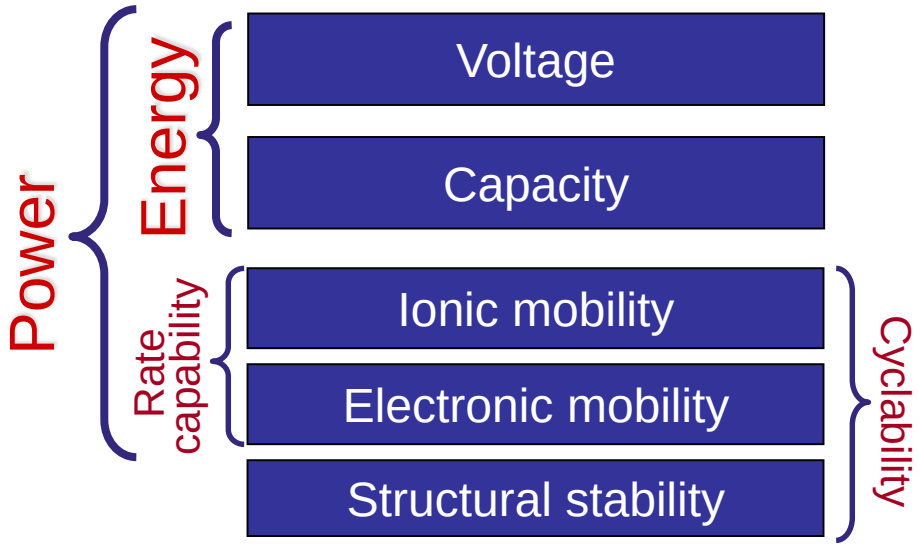
Δn → *number of e^- or Li^+*

M → *Molecular weight (g)*

Energy = Voltage x Capacity



Cathode materials: characteristics and requirements



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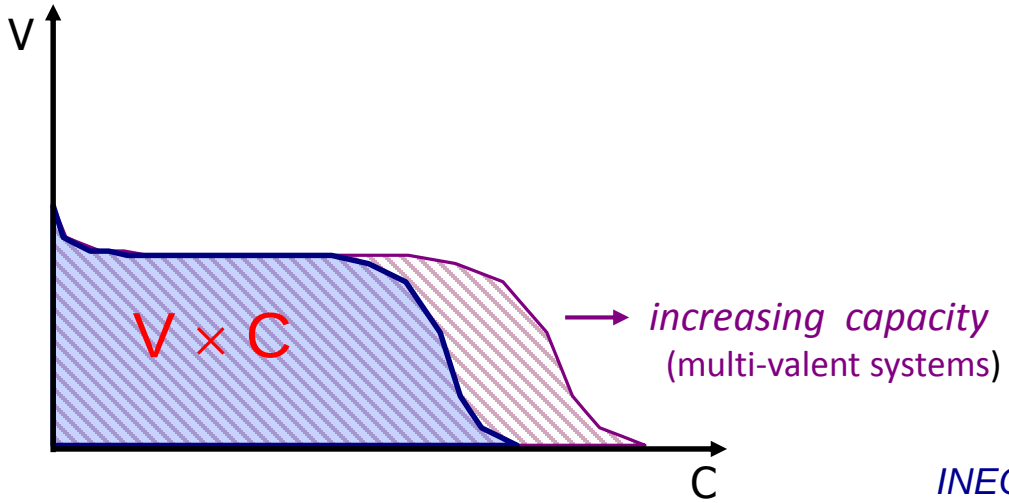

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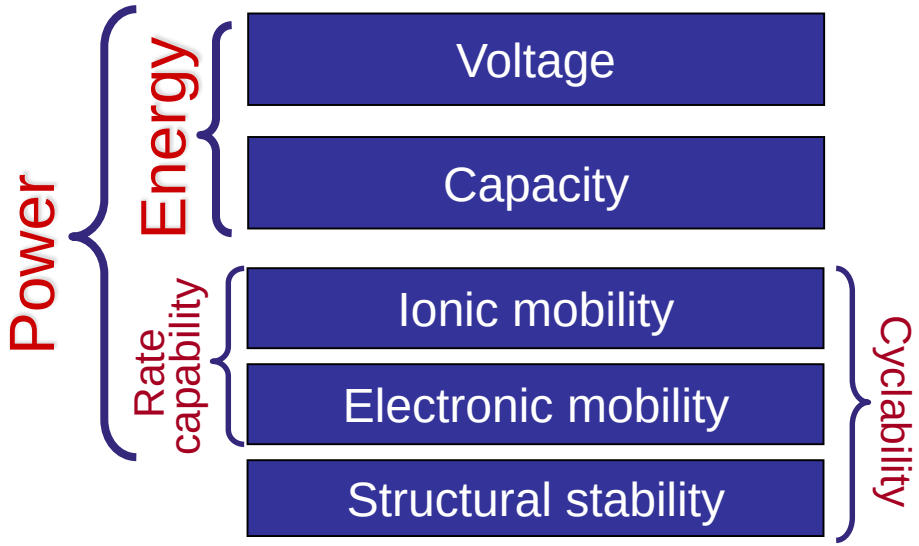

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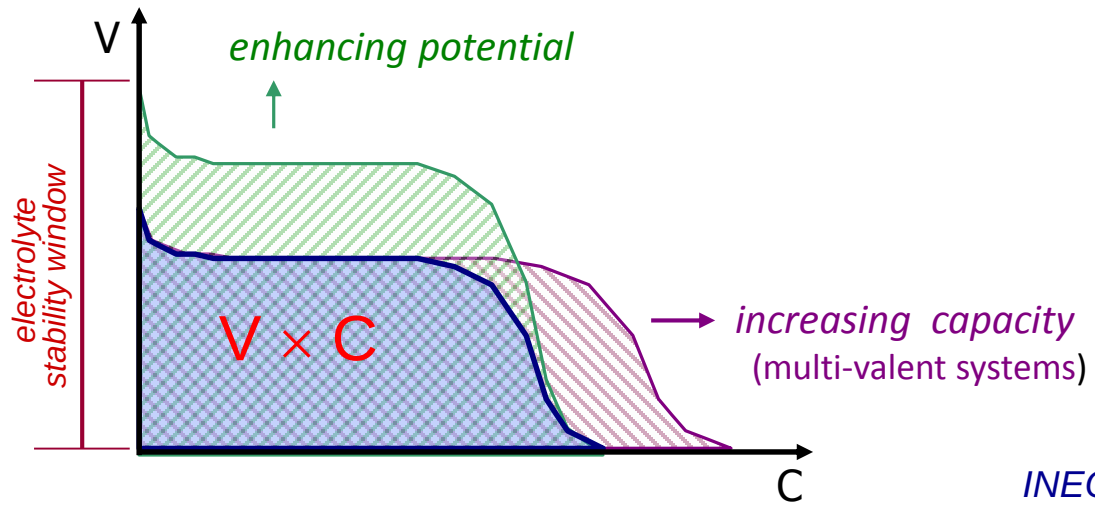
Energy = Voltage x Capacity

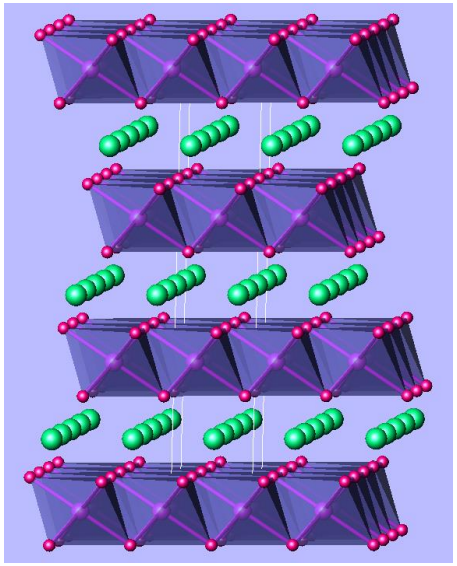
≤ 4.8 V (vs. Li/Li^+)



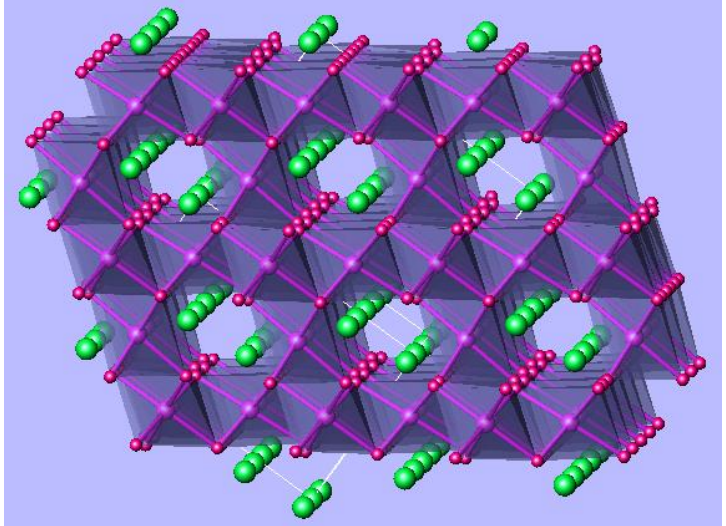
Selection of composition

Main Structure Types

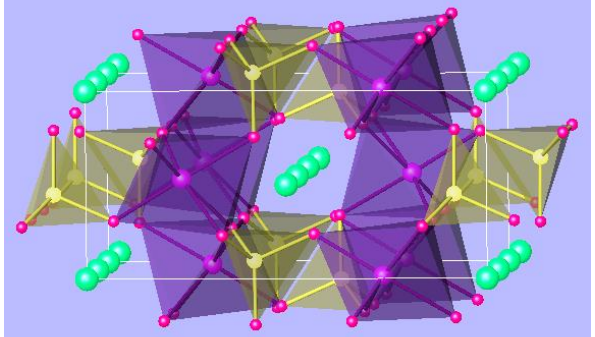
$LiCoO_2$



$LiMn_2O_4$



$LiFePO_4$

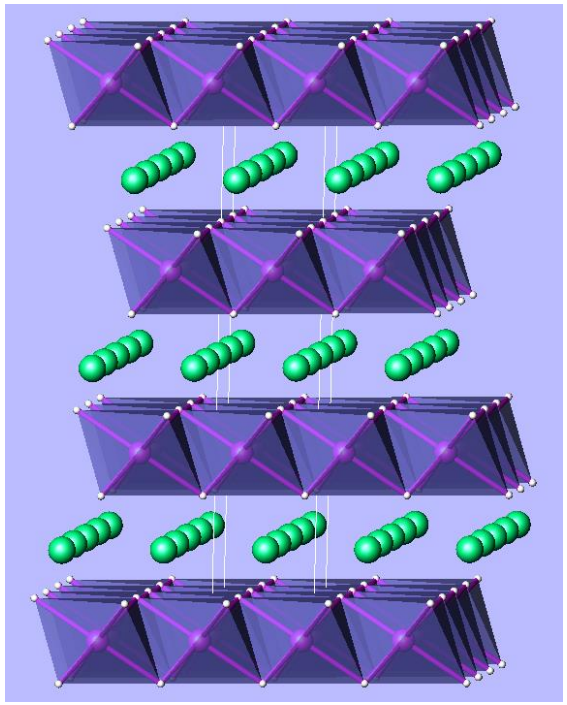


Hexagonal close packing

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

Layered $LiMO_2$ oxides



α-$NaFeO_2$

$LiMO_2$ (M = Fe, Mn, Co, Ni)

Li^+ - 0.74 Å

	Mn^{3+}	Fe^{3+}	Co^{3+}	Ni^{3+}
RVI, Å	0.58 (LS) 0.65 (HS)	0.55(LS) 0.65(HS)	0.525(LS) 0.61(HS)	0.56(LS) 0.60(HS)

Co^{3+} LS ($t_{2g}^6 e_g^0$) ←→ HS ($t_{2g}^4 e_g^2$)

	Fe	Mn	Ni	Co
Market price of metal [$/kg]	0.23	0.5	13	25
Atomic contents in crust [ppm]	50000	950	75	25
Permissible amount in air [mg/m^3]	10	5	1	0.1
Permissible amount in water [mg/L]	300	200	13.4	0.7

Problems:

Cation disorder

Stability (oxygen evolution, structure transformation)

Cost

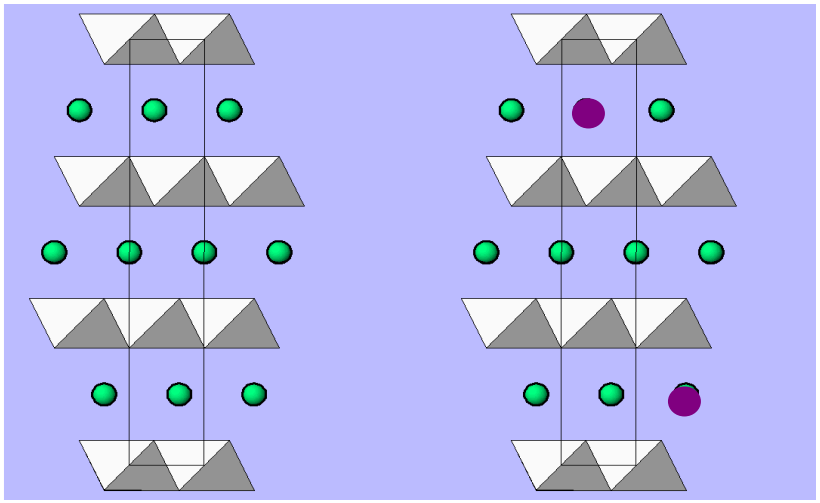
Ecology

Influence of cation disorder

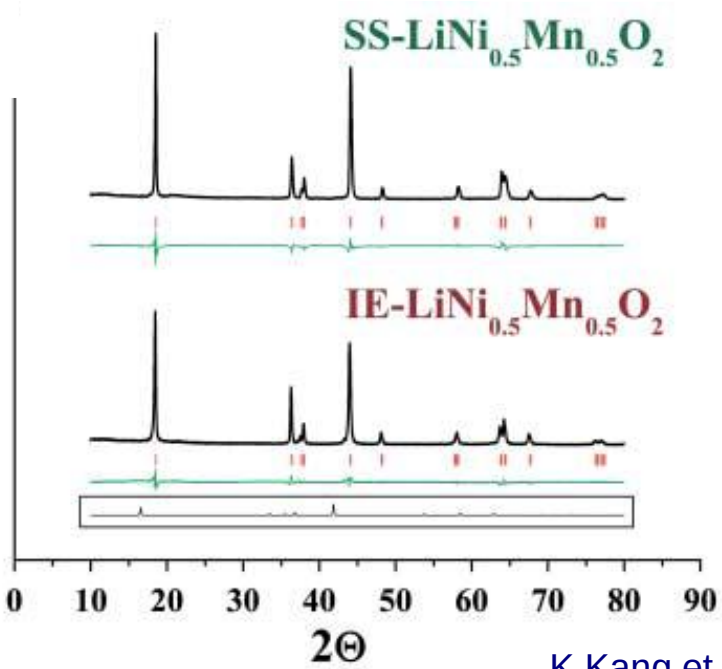
Suppression of cation disorder: synthesis by cation exchange from $NaNi_{0.5}Mn_{0.5}O_2$

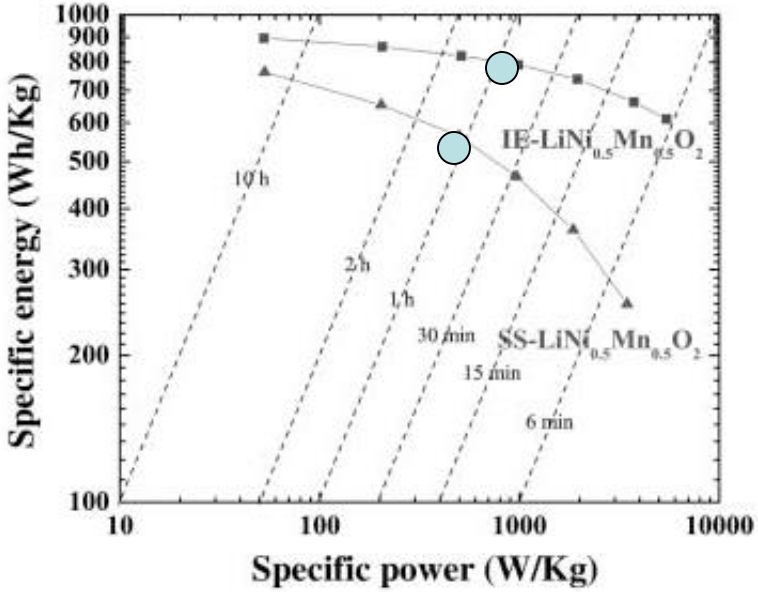
Δc = 0.06 Å

Li-slab 2.59 Å (SS) and 2.65 Å (IE)



α-$NaFeO_2$ **$Li_{1-y}N_{i1+y}O_2$**

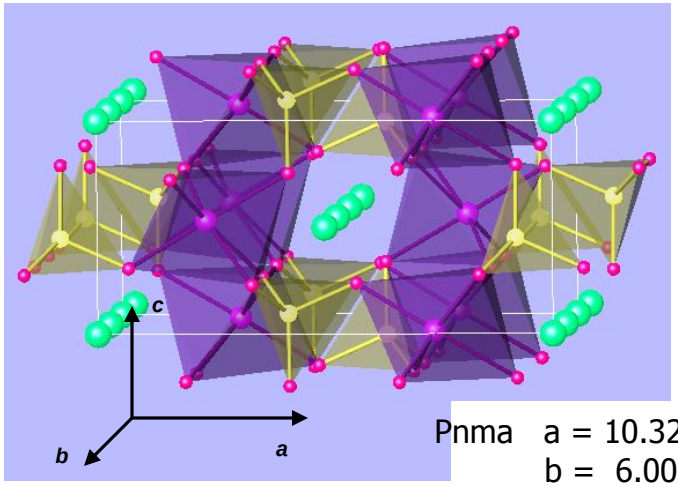




K.Kang et al. Science 311 (2006) 977

$LiFePO_4$ - 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

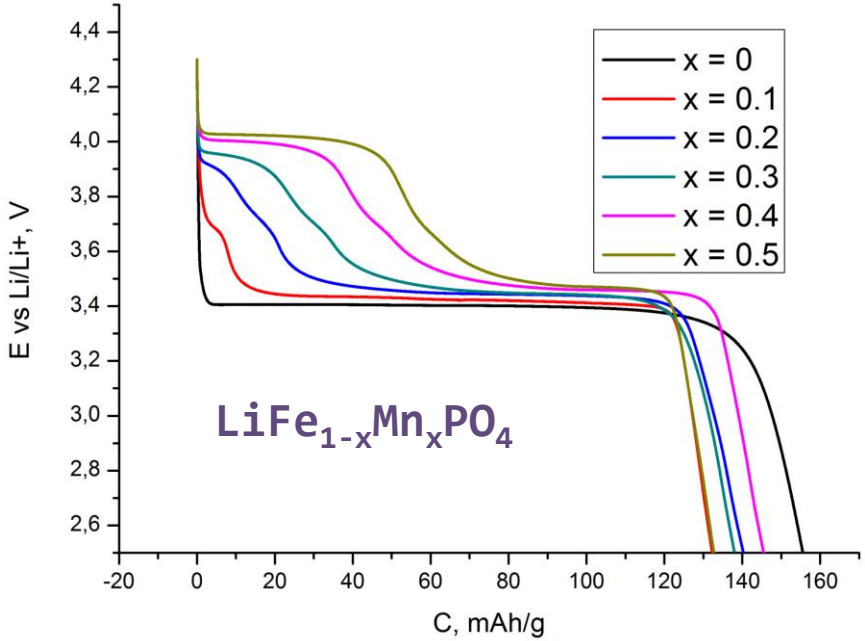
Advantages:

- stable material (3D structure + PO_4)

  $LiFePO_4 \leftrightarrow FePO_4 + Li^+ + e^-$
- ecologically friendly
- cheap

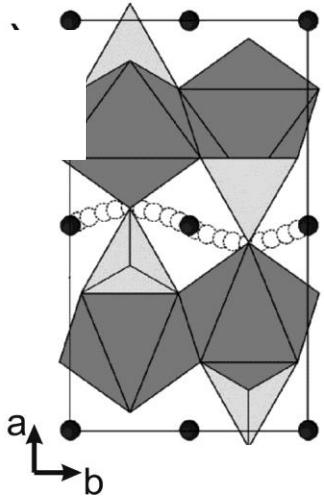
Disadvantages:

- 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)

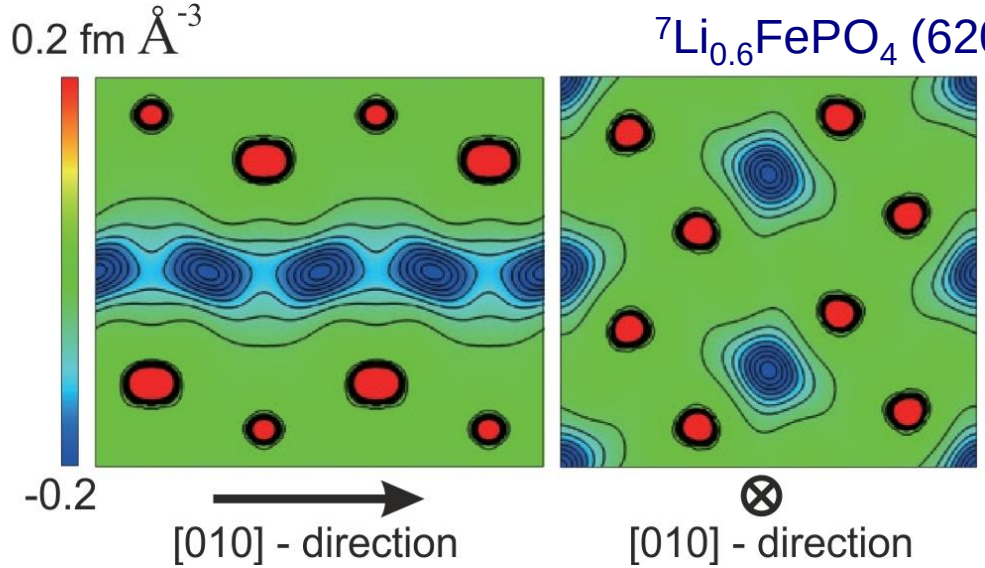


A. K. Padhi, et al., *J. Electrochem. Soc.* 144 (1997) 1609

Li-ion diffusion pathway



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



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

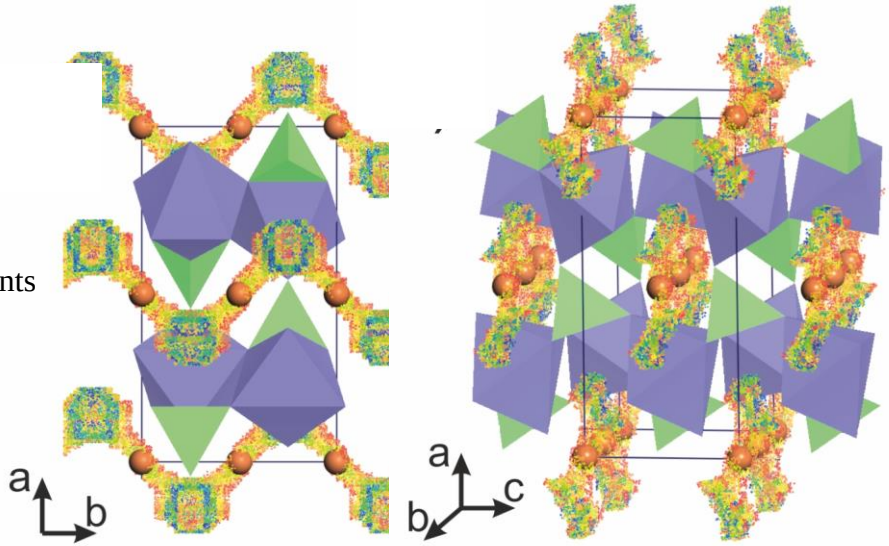
NPD/MEM*: S.I. Nishimura et al. Nature Materials 7 (2008) 707*

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

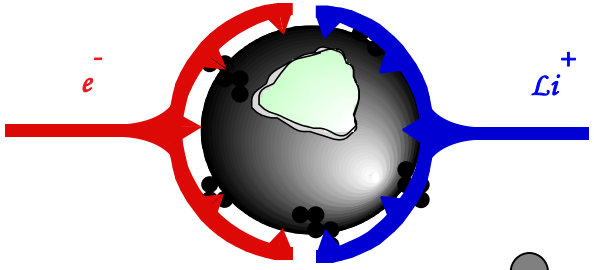
M. Sale, M. Avdeev, *J. Appl. Cryst*. 45(2012),1054



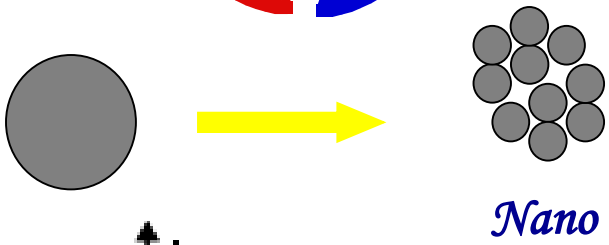
INEOS: 26.09.2014

$LiFePO_4$: transport properties improvement

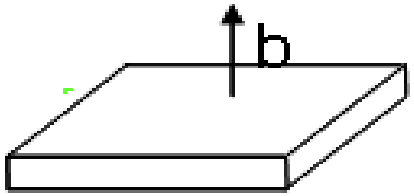
Carbon coating



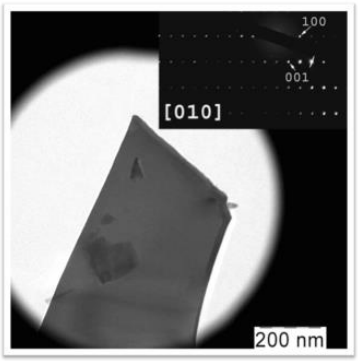
Nano-structuring

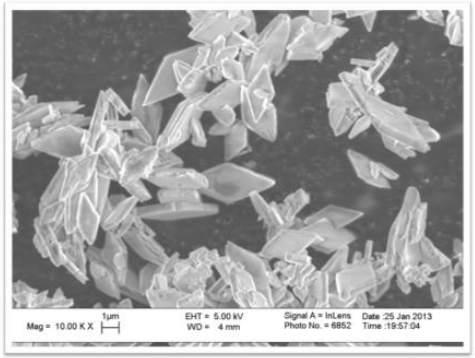


Morphology optimization

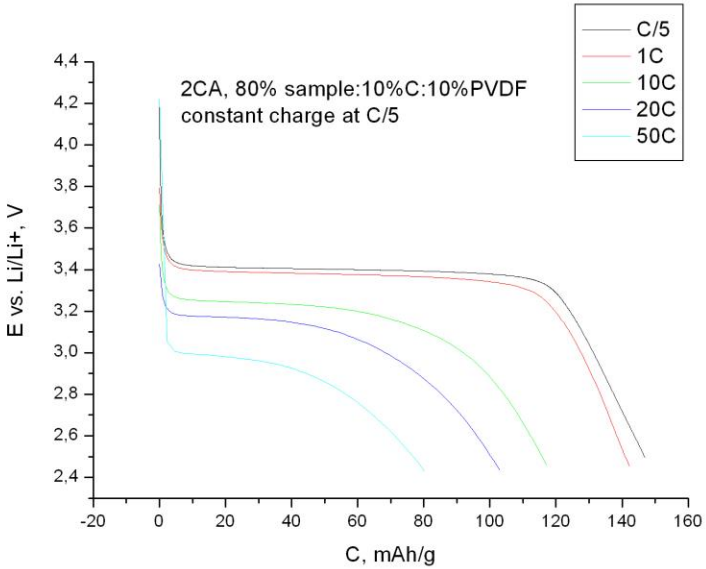


Platelet-type particles





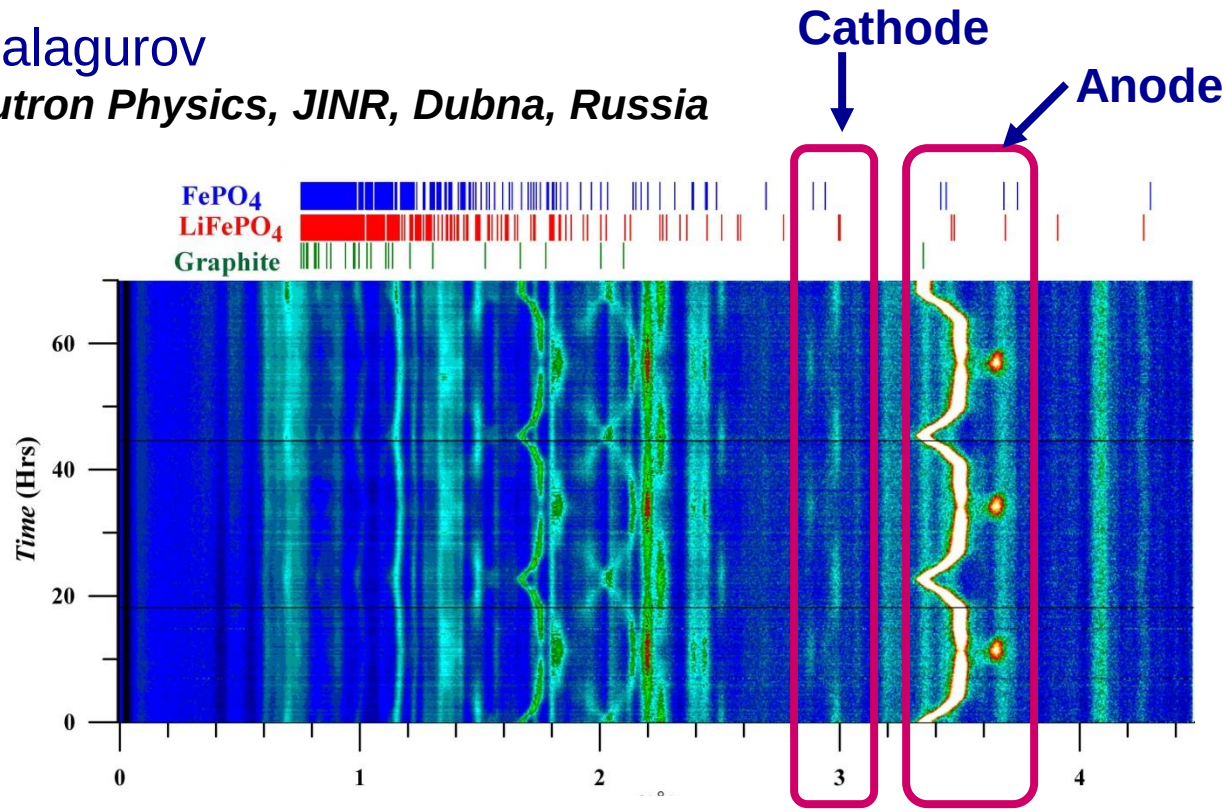
HT-synthesis



IN-SITU NEUTRON DIFFRACTION ANALYSIS OF Li-ION BATTERIES

I.A. Bobrikov, A.M. Balagurov

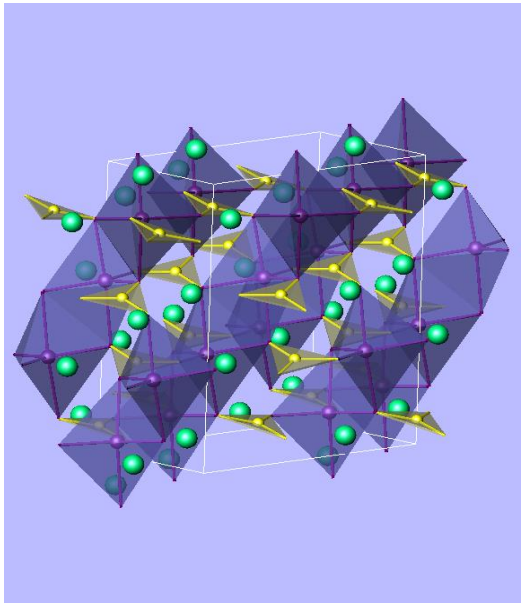
Frank Laboratory of Neutron Physics, JINR, Dubna, Russia



SOC, %	Battery №1 (LFP only, C=2Ah)		Battery №2 (LFP + V, C=10Ah)	
	$FePO_4$	$LiFePO_4$	$FePO_4$	$LiFePO_4$
0	43(9)	57(5)	37(9)	63(9)
45(5)	66(9)	34(4)	68(8)	31(3)
100	93(13)	7(3)	100(11)	0

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

Lithium Transition Metal Borates



$LiFeBO_3$

Yamada et al., Adv. Mater. 22 (2010) 3583

Advantage:
1)Capacity (~ 220 mA·h/g)
2)Small volume change (~ 2%)
3)Solid Solution Behavior

Disadvantage:
Low potential E ~ 3V ➔ **Moderate Eg**
Surface degradation

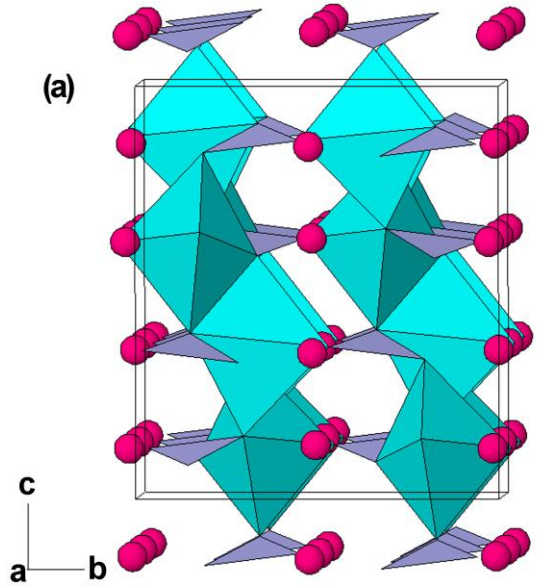
↓

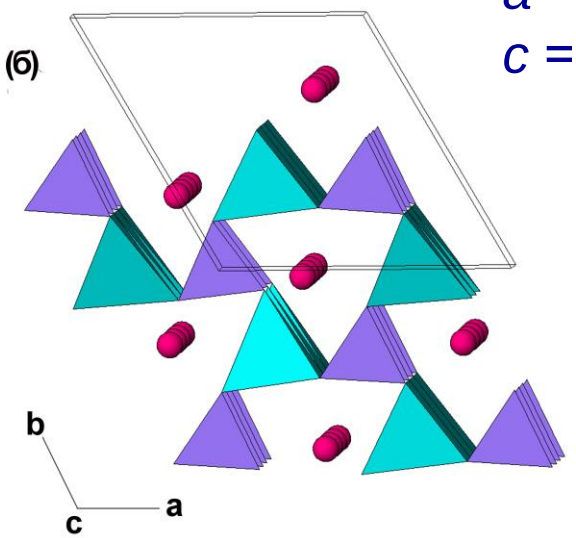
Replace Fe by Mn: m-$LiMnBO_3$ (3.7V) or h-$LiMnBO_3$ (4.1V)

Kim et al., J. Electroch. Soc. 158 (2011) A309

Lithium Manganese Borates

a = 5.193 Å
b = 8.960 Å
c = 10.362 Å
β = 91.80°

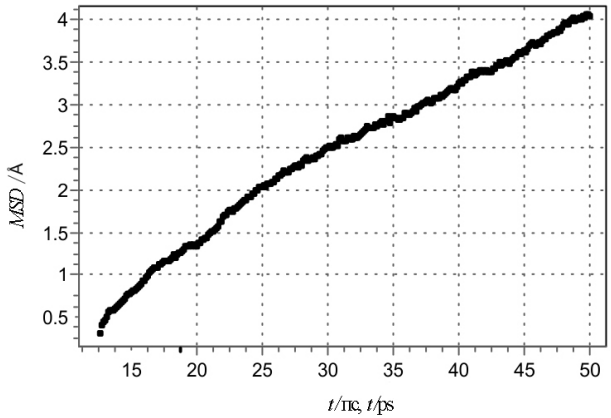




a = 8.175 Å
c = 3.151 Å

MD simulation – DL-POLY, > 20.000 atoms

D_{RT} (cm²/s) ~ 10^{-12} 10^{-15}



Stabilization of m-LiMnBO3 by partial replacement of Mn by Zn (~ 15%)

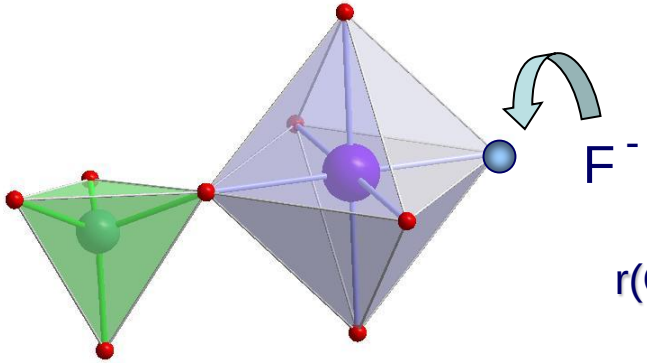
Stafeeva, Lobanov et al.

Search for new cathode materials

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

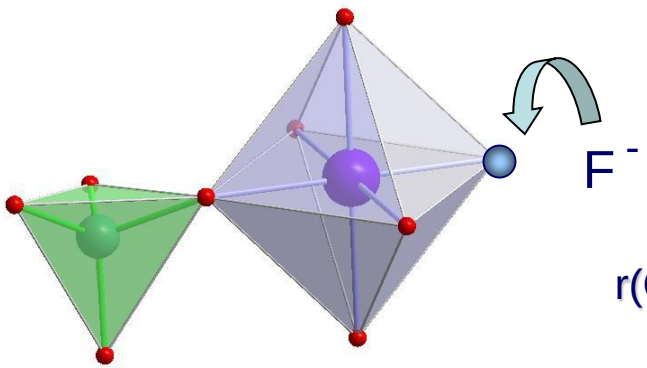
* A.K. Padhi et al. , *J. Electrochem. Soc.* 144 (1997) 1188

Search for new cathode materials

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

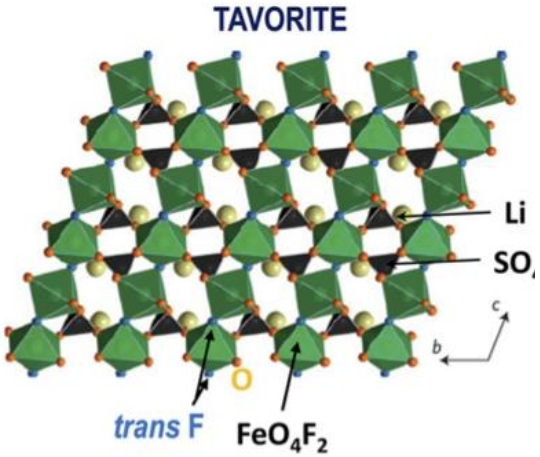
Compounds with two anions: $(XO_m)^{n-}$ and F^-

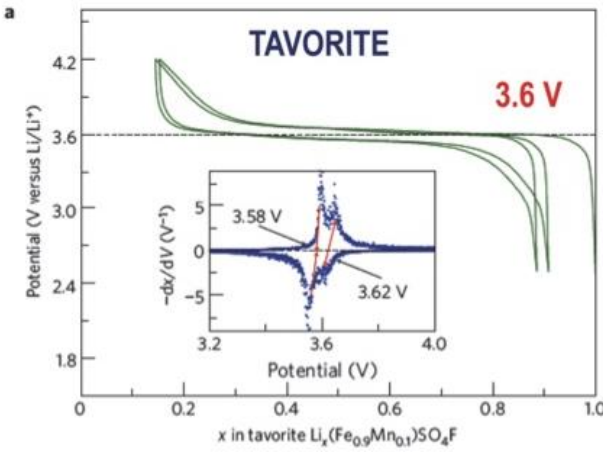
$(SO_4)^{2-}$ and F^-
$LiMSO_4F$**

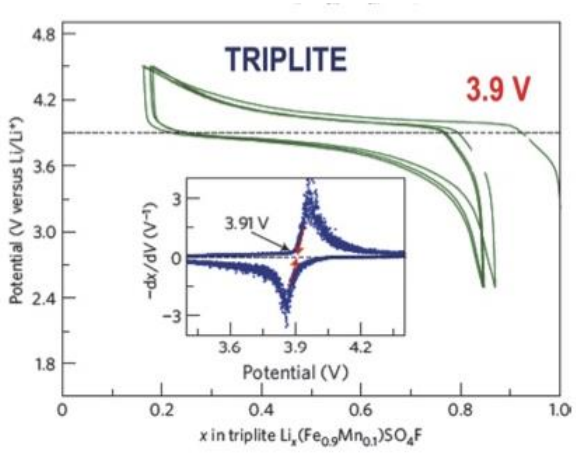
$(PO_4)^{3-}$ and F^-
$LiMPO_4F$, **Li_2MPO_4F**

* A.K. Padhi et al. , *J. Electrochem. Soc.* 144 (1997) 1188
** G. Rousse and J.M. Tarascon, *Chem. Mat*. 26 (2014) 394

Fluoride-sulphates: $LiFeSO_4F$

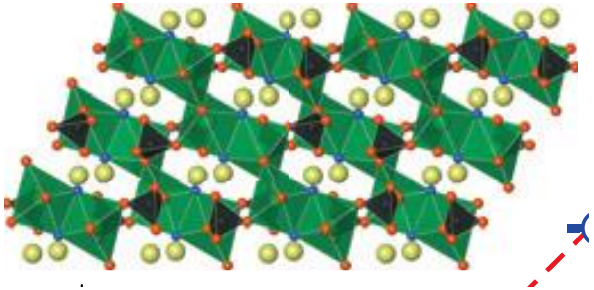




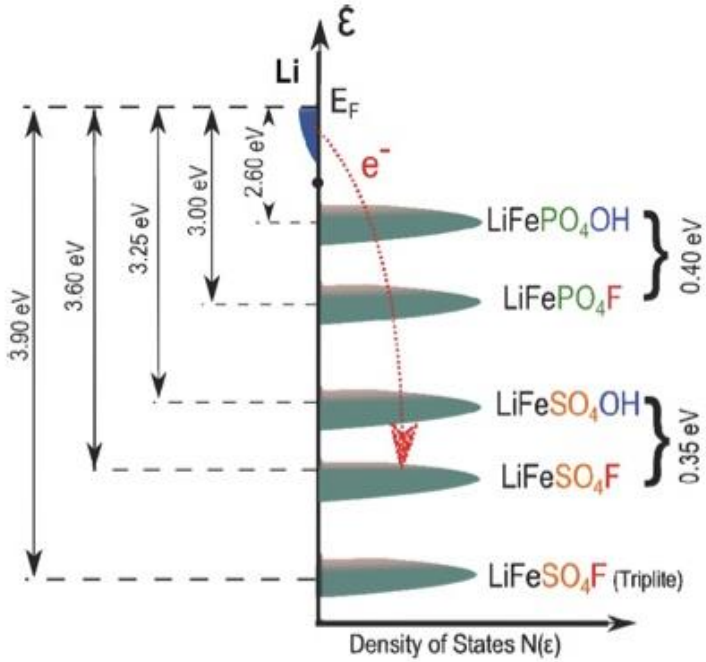


$FeSO_4 * H_2O + LiF \xrightarrow{300°\ C,\ IL} LiFeSO_4F + H_2O$

tavorite



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



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

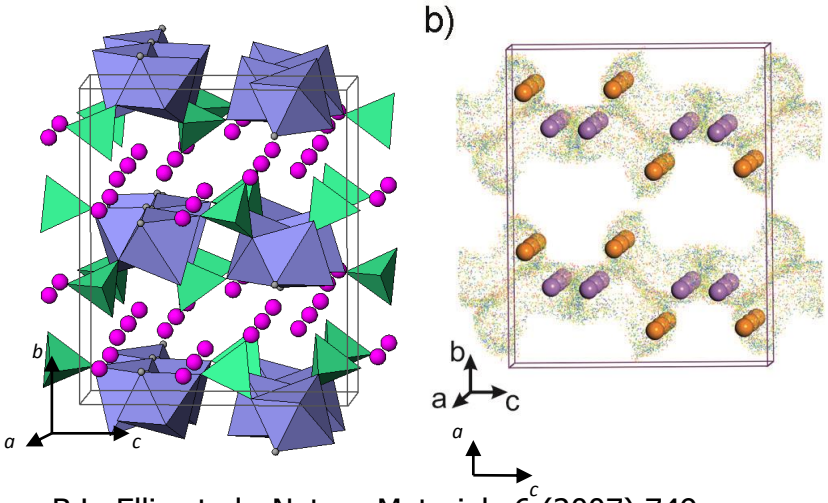
P. Barpanda et al, Nature Mater. 10 (2011) 772

Fluoride-phosphates: Li_2MPO_4F

different conjugation of MO_4F_2 octahedra,

Li_2FePO_4F – 2D (E_{av} = 3.4V)

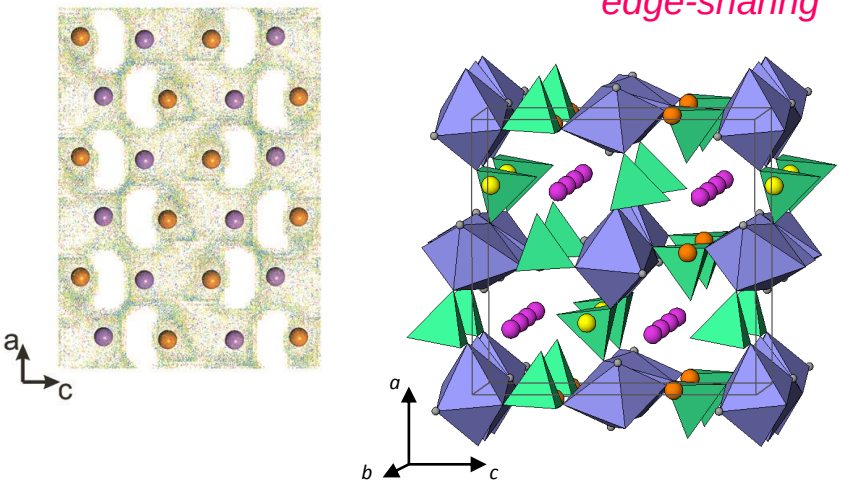
face-sharing and corner-sharing



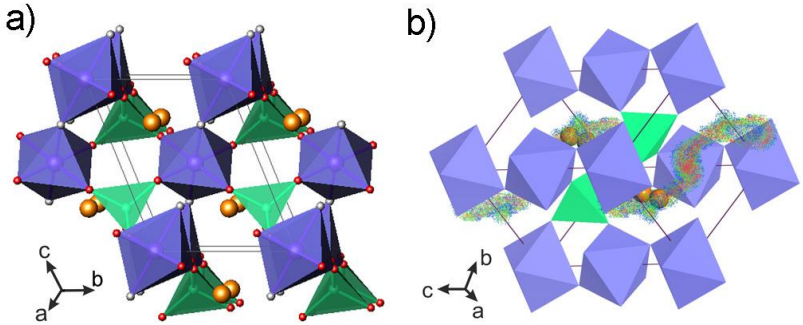
B.L. Ellis et al. Nature Materials 6 (2007) 749

Li_2MO_4F (M=Ni, Co) – 3D

edge-sharing



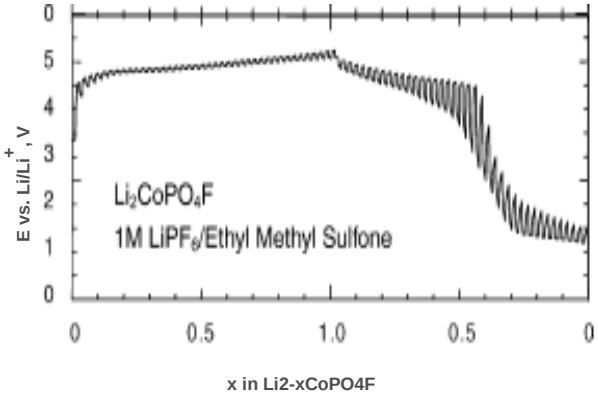
From Tavorite: $Li_{1+x}FePO_4F$ (E_{av} = 3.0V)



corner-sharing

N. Recham et al., Chem. Mat. 22 (2010) 1142

T.N. Ramesh et al., Electrochem. And Solid State Lett. 13 (2010) A43



Ni-phase: M. Dutreilh et al. JSSC 142 (1999) 1

Co-phase: S. Okada et al., J. Power Sources 146 (2005) 565

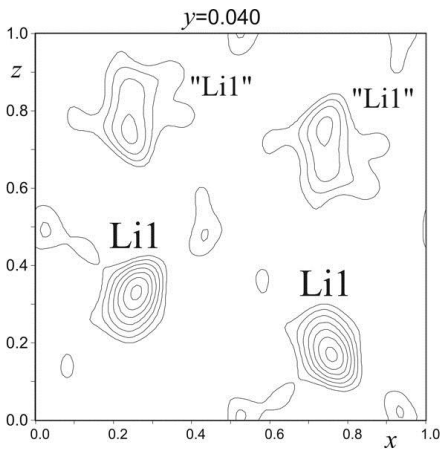
Crystal structure of Li_2CoPO_4F by Precession Electron Diffraction

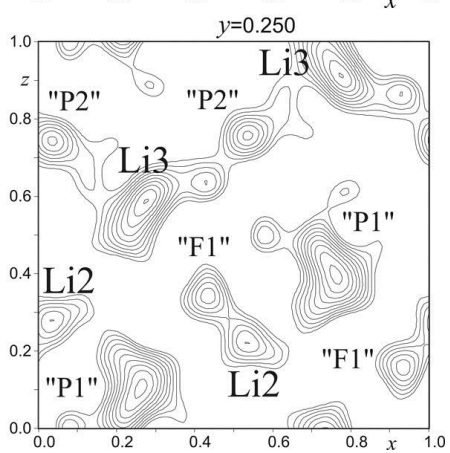
Vainshtein, B.K. (1964) Structure analysis by electron diffraction. New York: Pergamon Press

326 intensities (≈ $|F|^2$) for structure determination were taken from 13 different zones

Co and P were found by direct methods (SIR2008), O(F) and Li from Fourier maps

Structure was refined by JANA 2006 (PO4 was used as rigid body)





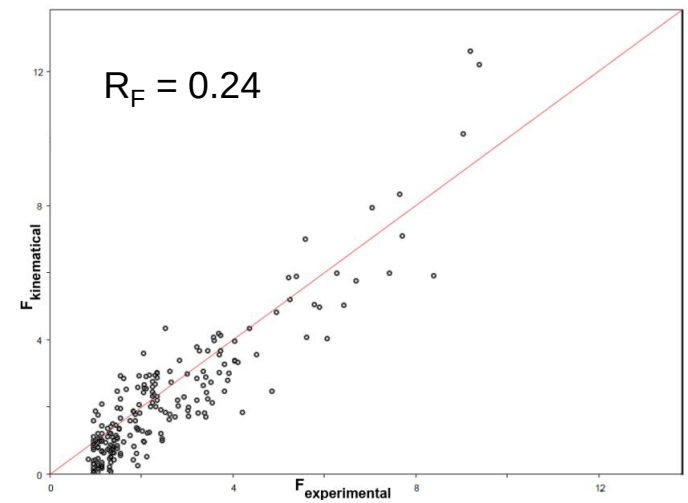
Difference Fourier maps

Detectability of light atoms (Vainstetn):

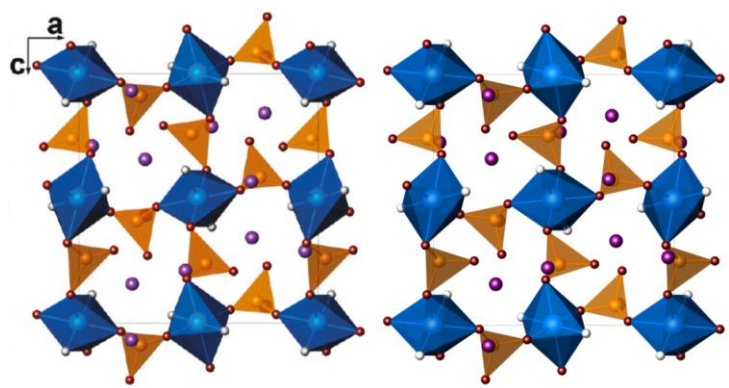
$$w = \left(\frac{Z_{light}}{Z_{heavy}} \right)^{\alpha}$$

XRD: $\alpha = 1.25$ ED: $\alpha = 0.7$

The Li positions are 3 times more "visible" in Li_2CoPO_4F with PED than with XRD!



PED



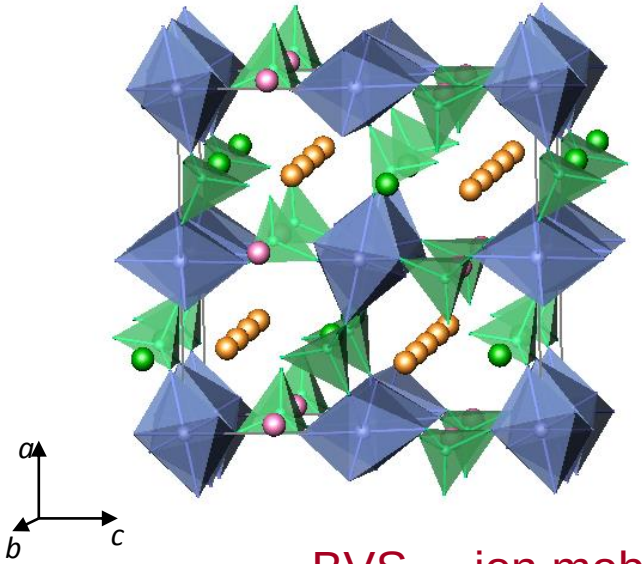
SXPD

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

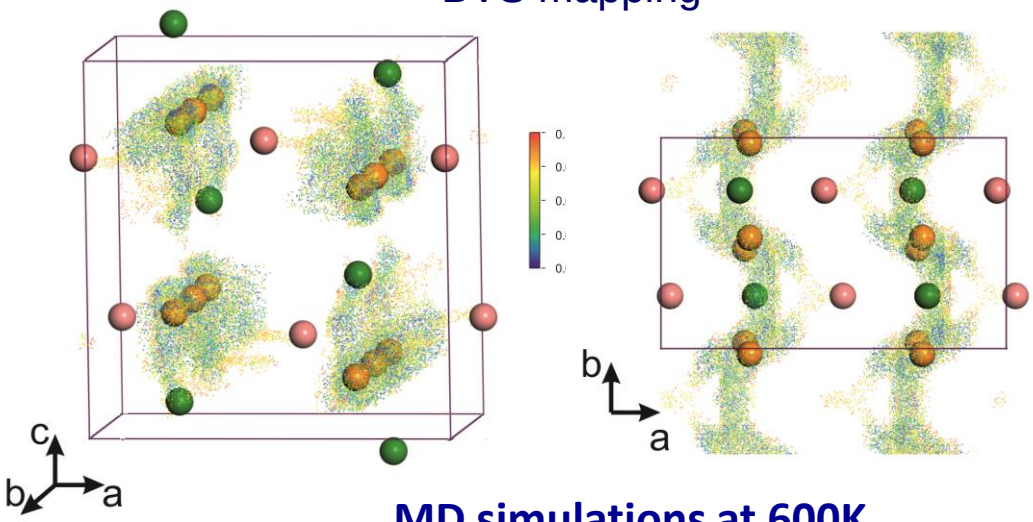
INEOS: 26.09.2014

3D-Li_2CoPO_4F: crystal structure

S.G.: Pnma



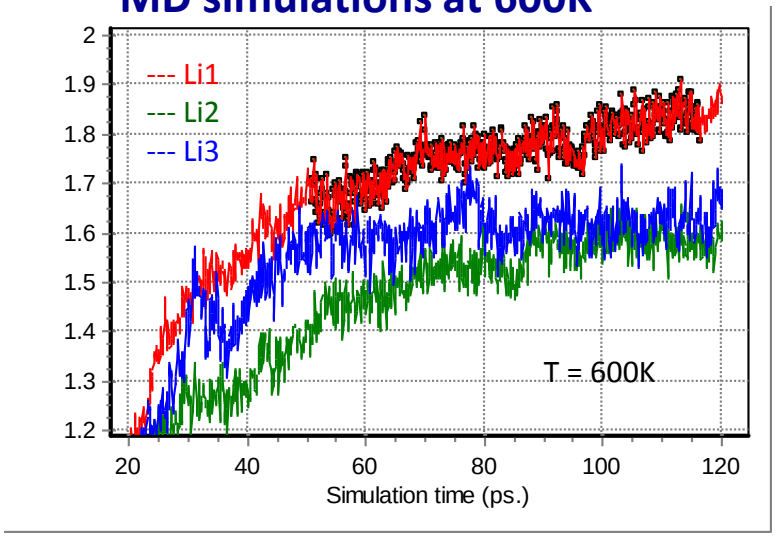
BVS mapping



	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

MD simulations at 600K

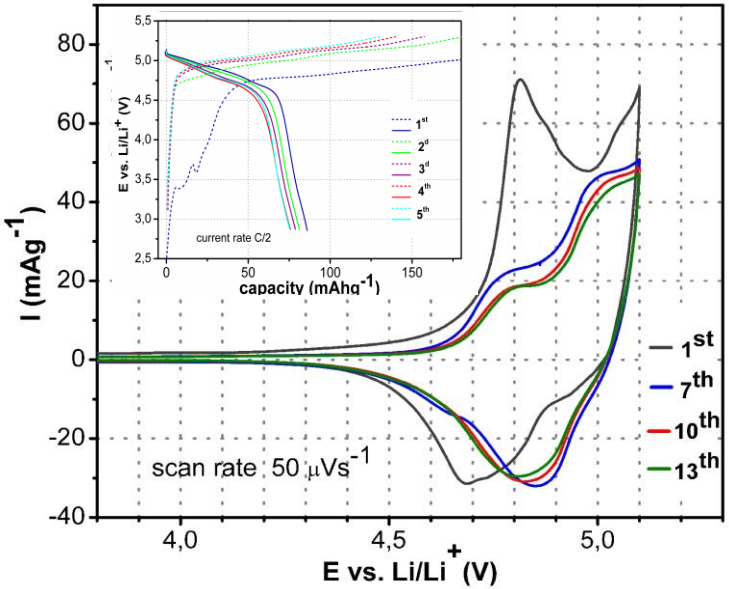


D(Li3)~0 (plateau is reached)

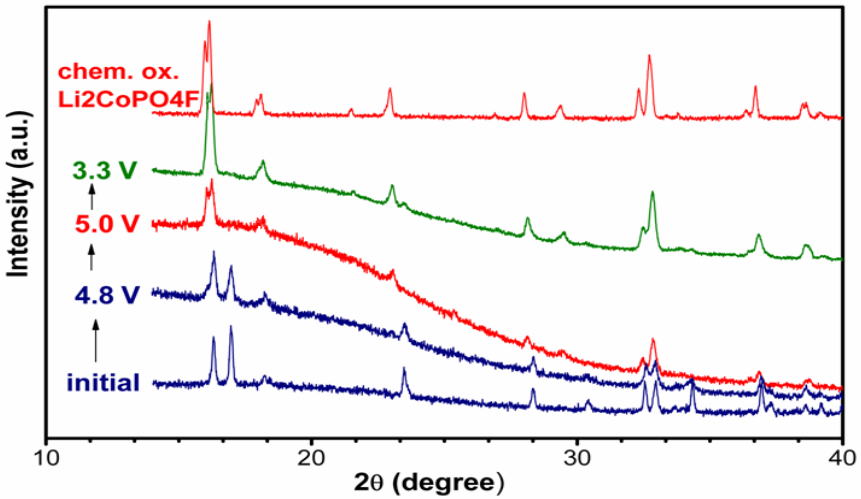
D(Li2) = $9.5*10^{-8}$ cm^2/s

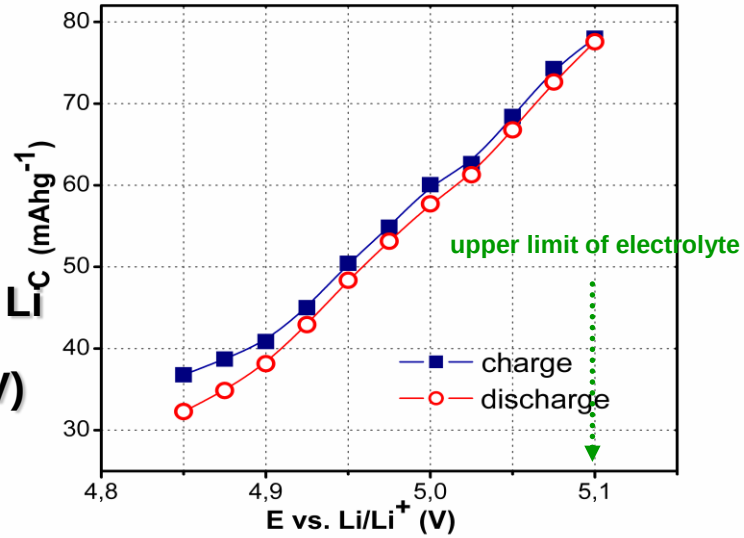
D(Li1) = $3.3*10^{-7}$ cm^2/s

Li_2CoPO_4F: electrochemical measurements



CV in the potential range 3.0-5.1 V at the scan rate 50 µVs-1. The insert- charge-discharge performance at C/2 cycling rate.



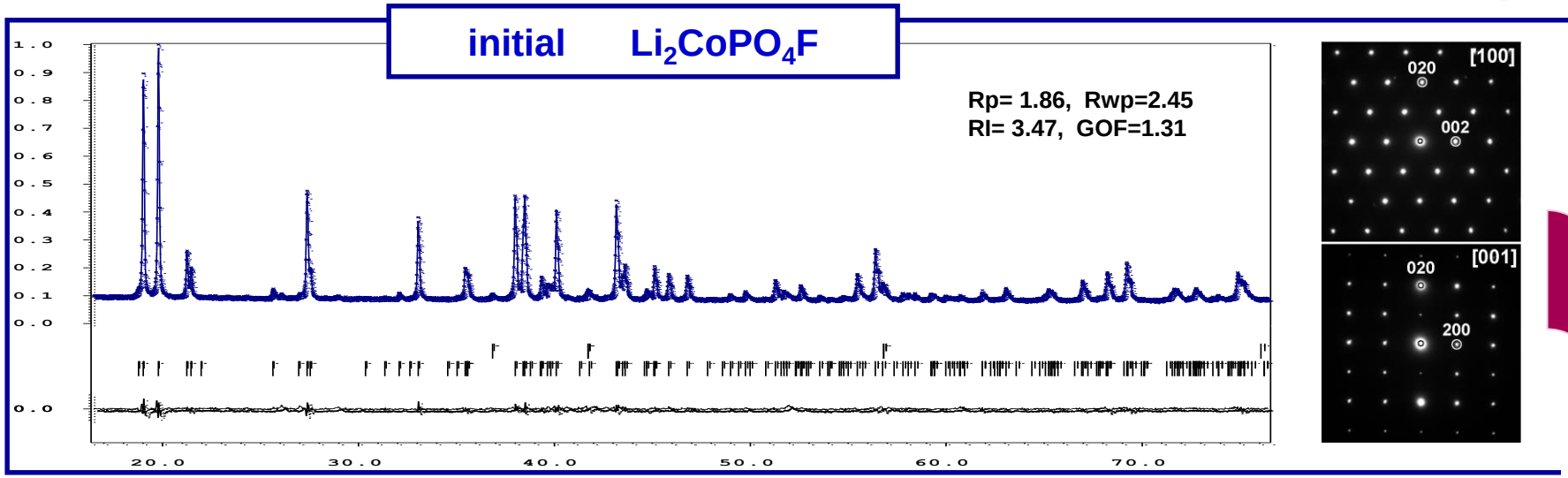


Capacity vs. voltage: from potentiostatic step measurements (4.2 V and variable anodic potentials)

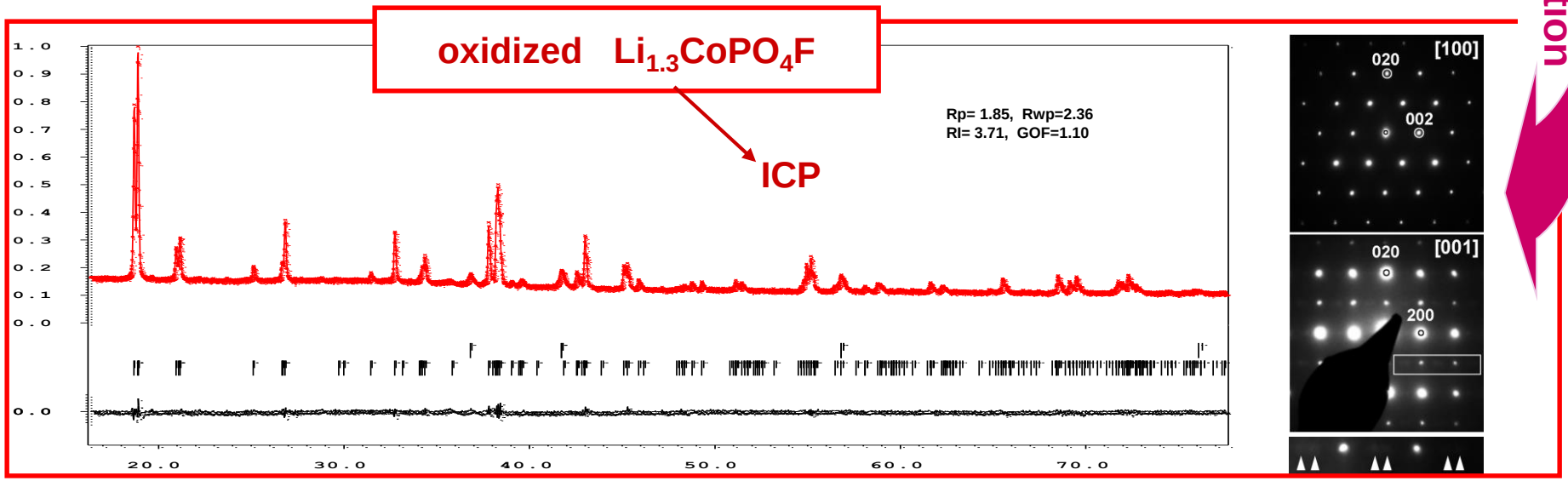
- **discharged capacity of 80 mAh/g ~ 0.55 mole Li**
- **slope : ~ 0.7 V per 1Li mole (x=1 at about 5.5 V)**
- **"solid solution" behavior**
- **structure transformation at >4.8 V**

Li_2CoPO_4F: structure refinement

XRD Rietveld refinement | **ED study**



oxidation



- **confirmation of SG *Pnma* for oxidized sample**
- **diffuse satellites (q ~ 0.85a*) appeared for oxidized sample**

Li_2CoPO_4F: structure transformation upon Li-extraction

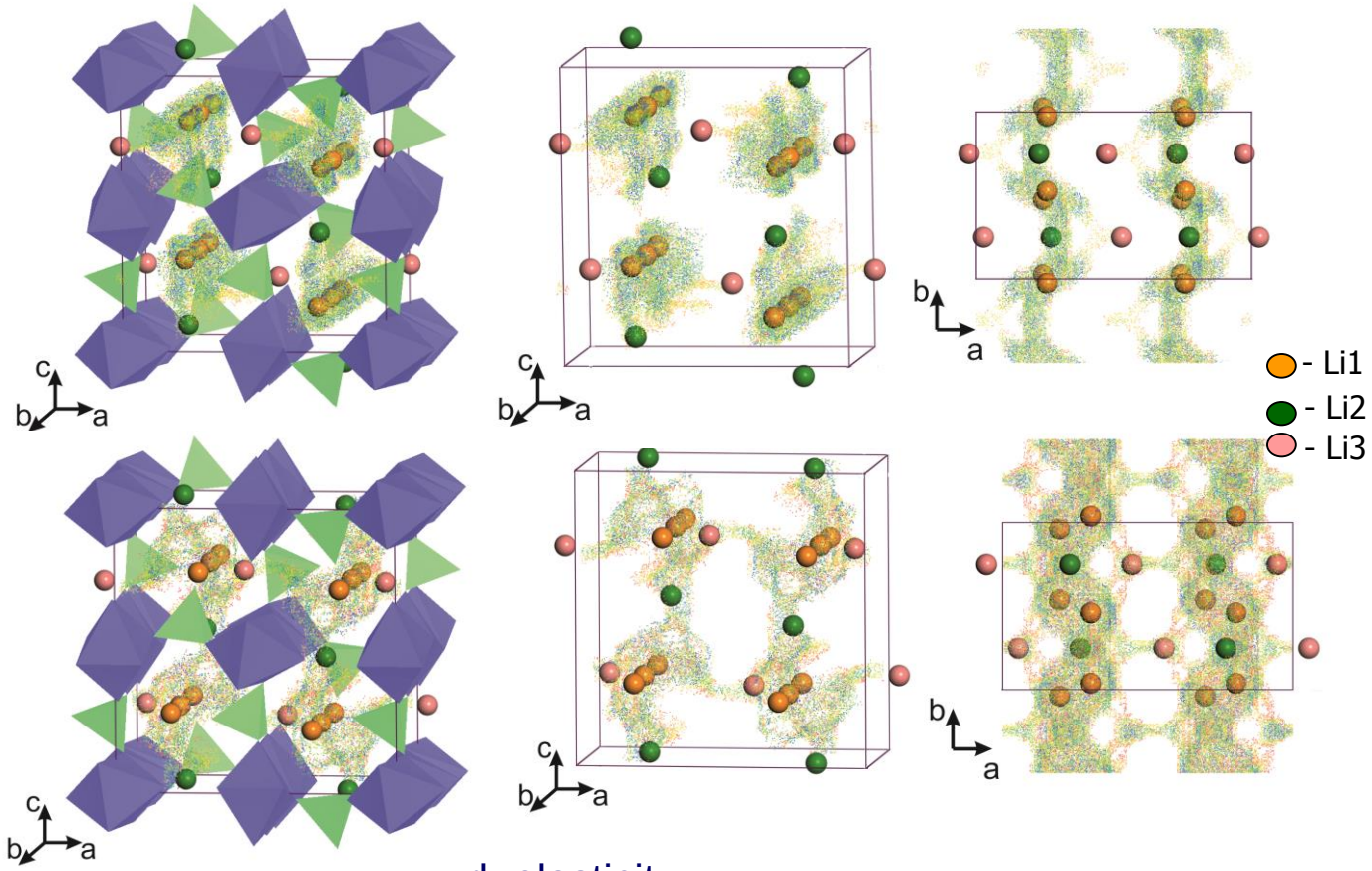
Li_2CoPO_4F

a =10.45452(8) Å
b = 6.38525(5) Å
c = 10.87550(9) Å
V=725.99(1) Å^3

oxidation (- Li^+)

$Li_{1.3}CoPO_4F$

a = 10.94923(9) Å
b = 6.28318(8) Å
c = 11.0680(11) Å
V=760.43(1) Å^3



- volume expansion of Δ V ~ 5% → framework elasticity
- enlarging of diffusion channels
- involving of Li2 in diffusion : extraction of 1.5 Li^+ per f.u. ??? **at 5.9 V (?)**
- unit cell expansion favors Li^+-ion diffusion in the modified framework
- **"fine structure tuning "**

to decrease the working potential !

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

$Li_2(Co_{1-x}M_x)PO_4F$ with M=Fe, Mn

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

- **narrow range of solid solutions:**

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

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

"framework elasticity": **Li^+ → Na^+**

0.76 Å **1.02 Å**

N.R. Khasanova et al., Beilshtein J. Nanotech. 4 (2013) 860

$NaLiFePO_4F$: preparation and characterization

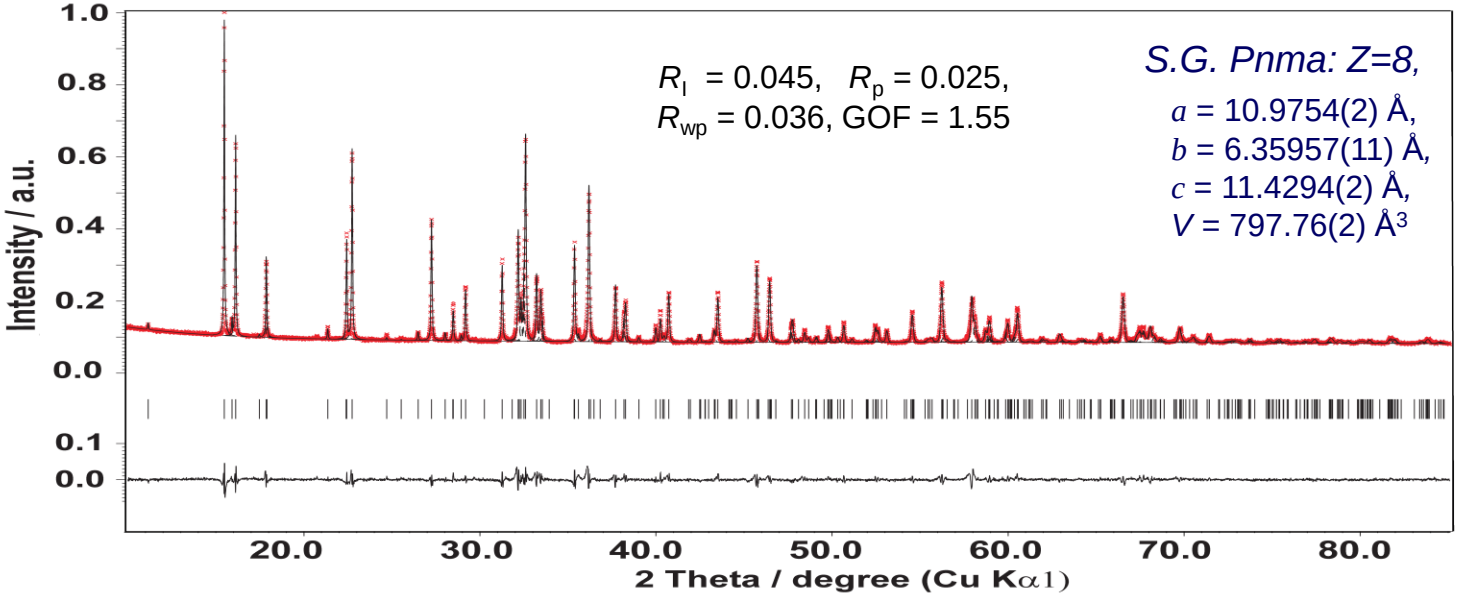
Synthesis: $LiFePO_4(C) + NaF \xrightarrow[\text{Ar-flow}]{\sim 650\text{-}670^\circ C} NaLiFePO_4F(C)$

ICP analysis: $Na_{1.01}/Li_{1.05}/Fe_{0.97}/P_{1.00}$

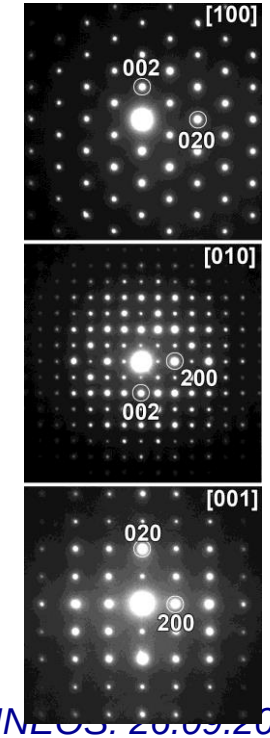
X-ray diffraction

	a, Å	*b*, Å	*c*, Å	*V*, Å^3
$NaLiFePO_4F$	10.977 (2)	6.3627(11)	11.429 (2)	798.6(3)
Li_2CoPO_4F	10.4578(13)	6.3887(5)	10.877(2)	726.1(2)

Rietveld refinement

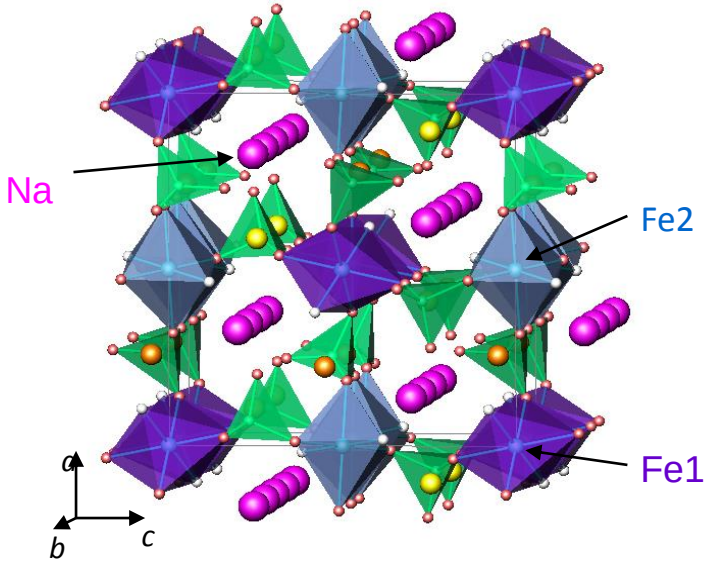


Electron diffraction

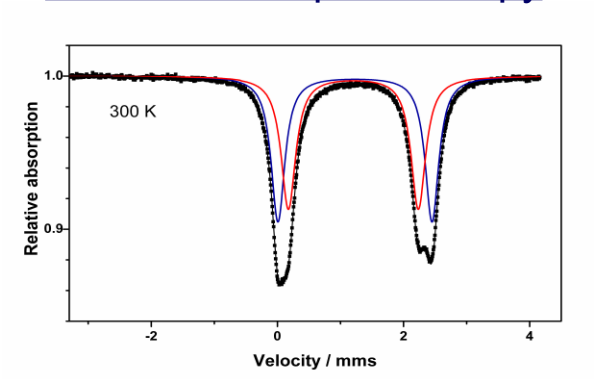


H.Mizuta, ECS Fall Meeting, 2011, Abstract No. 404.
N.R. Khasanova et al., J. Chem. Mat. 24 (2012), 4271.
H. B. Yahia et al. Dalton Trans. 41 (2012), 11692.

$NaLiFePO_4F$: structure and properties



- Mössbauer spectroscopy

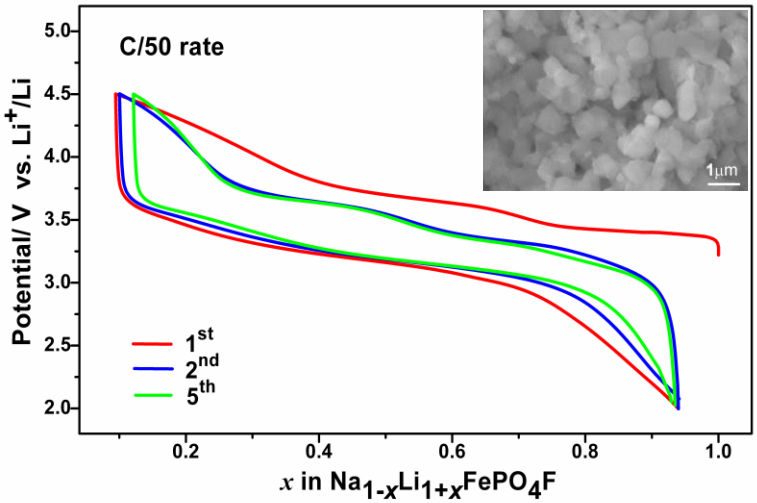


- **complete ordering of Na^+ and Li^+ ions**
- **Fe^{2+} on the two octahedral sites**

- **Electrochemical performance**

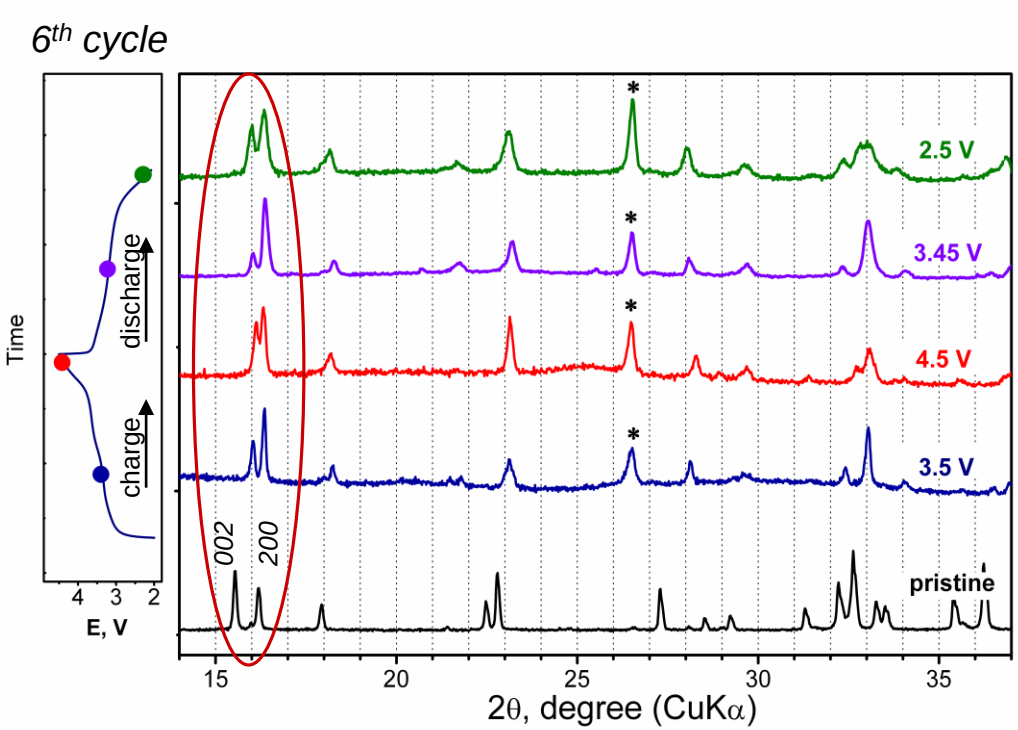
Li-cell, 1M $LiPF_6$ in EC/DMC

- **reversible deintercalation with discharge capacity of ~110 $mAhg^{-1}$**

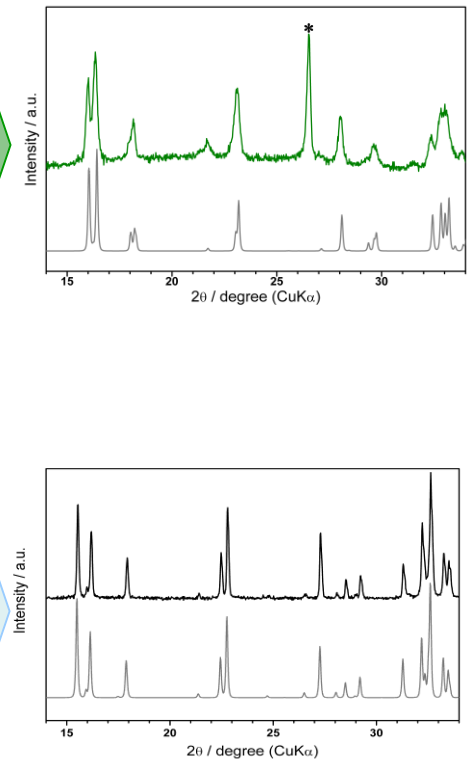


$NaLiFePO_4F$: *ex-situ* investigation

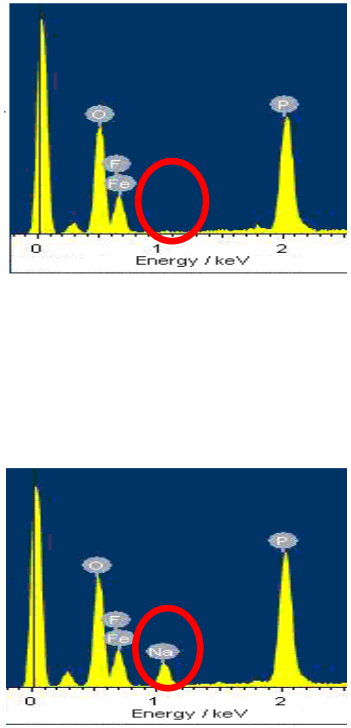
XRD pattern



Simulation



EDX



- shift of peaks
- redistribution of intensities for *002* and *200* peaks
- EDX data

3D- Li_2FePO_4F

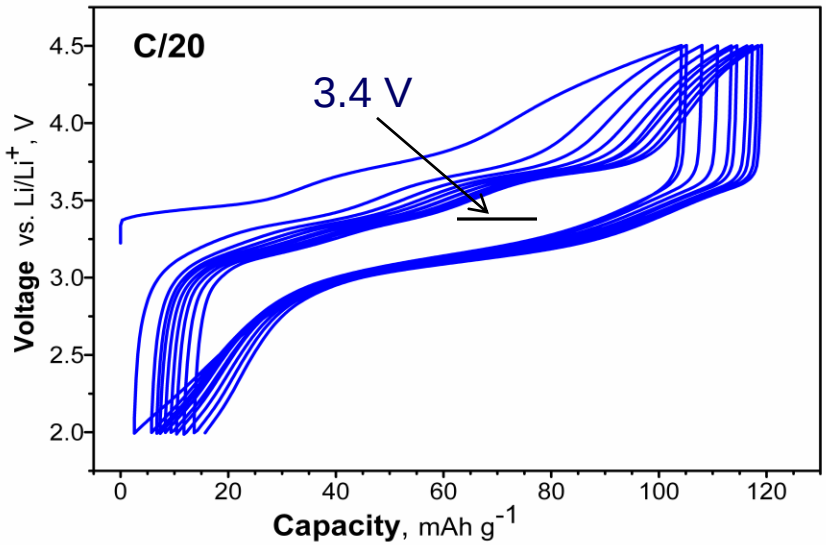
a = 10.775(5)Å
b = 6.266(4) Å
c = 11.027(6) Å
V = 744.5(6) Å^3

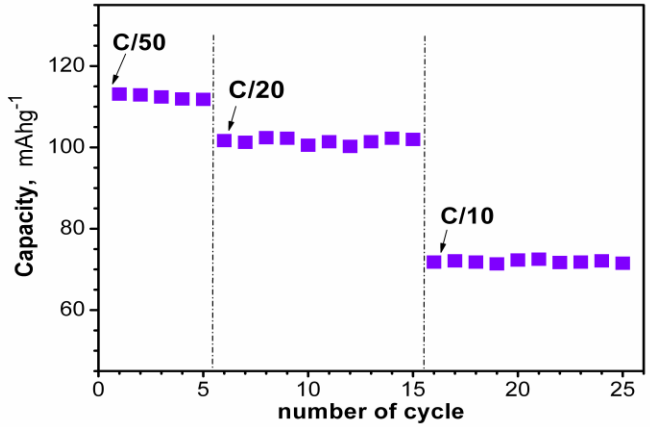
- continuous shift of peaks → solid solution behavior
- volume change between charged and discharged states of 1.7%

INEOS: 26.09.2014

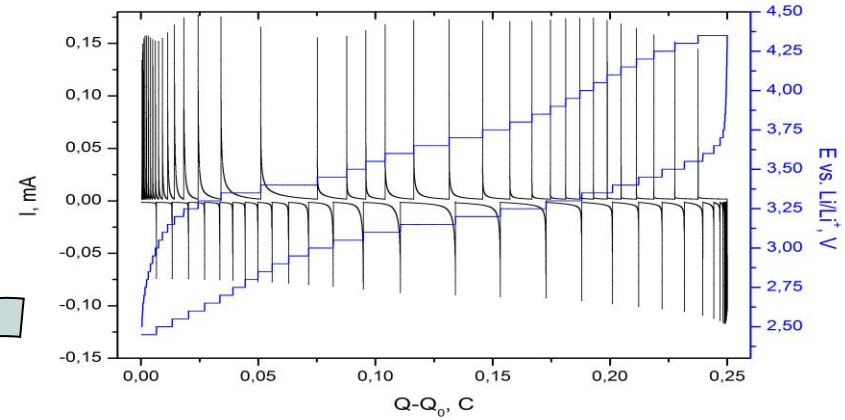
Li_2FePO_4F: electrochemical performance

Li-cell, 1M $LiPF_6$ in EC/DMC





- PITT: 2.7-3.7-2.7 V (vs. Li/Li^+), 0.05 V step



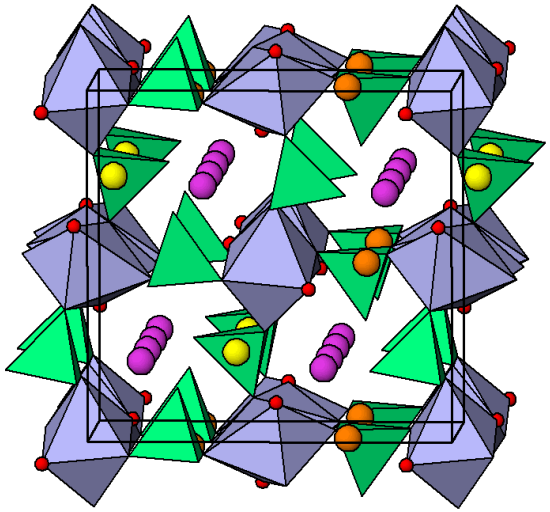
- discharge capacity ~114 mAh/g (0.84 Li)
- working potential ~ 3.4 V
- stable cycling
- "solid solution" de/intercalation mechanism (no interfacial problems)

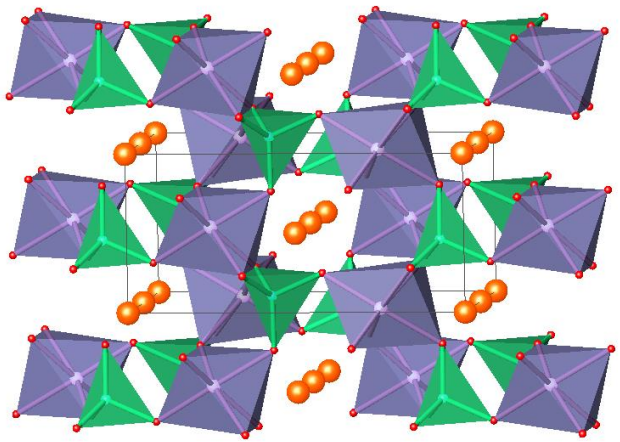
$D \sim 10^{-11}$ cm^2/s

$LiCoO_2$: $D \sim 10^{-9}$ cm^2/s $LiFePO_4$: $D \sim 10^{-15}$ cm^2/s

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

Concluding remarks: Li_2MPO_4F vs. $LiFePO_4$





	solid solution		2-phase mechanism
D_{chem}	$\approx 10^{-10}$ cm^2/s		$\approx 10^{-15}$ 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**	-

Perspectives of Fluoride-phosphates as cathodes for LIB

Chemical composition	Dimensionality of polyhedra network / Li-ion diffusion pathway	Average potential vs. Li^+/Li^0 (V)	Theoretical specific capacity (mAh/g)/ energy (Wh/kg)*
$LiFePO_4$	3D / 1D	3.43	170 / 583
$LiVPO_4F$	3D/ 1D	4.2	156 / 655
Li_2VPO_4F	3D/ 1D	1.8	150 / 270
Li_2FePO_4F (tavorite type)	3D/ 1D	2.9	146 / 423
Li_2FePO_4F (layered type)	2D / 2D	3.3	146 / 482
Li_2FePO_4F (3D type)	3D / 1-2D	3.4	146 / 496
Li_2MnPO_4F	3D / 2D	3.9	147 / 573
Li_2CoPO_4F	3D / 1-2D	5.1	143 / 730

J. Barker et al., Electrochem. Solid-State Lett. 6 (2003); B.L. Ellis et al., Nature Mat. 6 (2007); N. Recham et al., Chem. Mater. 22 (2010) 1142.

E.V. Antipov et al., submitted to IUCr Journal

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