Conférence internationale sur les olivines pour batteries rechargeables

OREBA 1.0

In Honor of Dr. Michel Armand

Montréal, May 25 – 28 2014

Lithium Metal Phosphates as Cathode Materials for Li-Ion Batteries Status and Future Perspectives

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Lithium Metal Phosphates as Cathode Materials for Li-Ion Batteries

Triphilite $LiFePO_4$
http://www.mindat.org/photo-202039.html

$$LiFePO_4 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} FePO_4 + Li^+ + e^-$$

non toxic
low-cost raw materials
Lower operating voltage, higher stability of electrolytes
high thermal stability in the lithiated and delithiated state

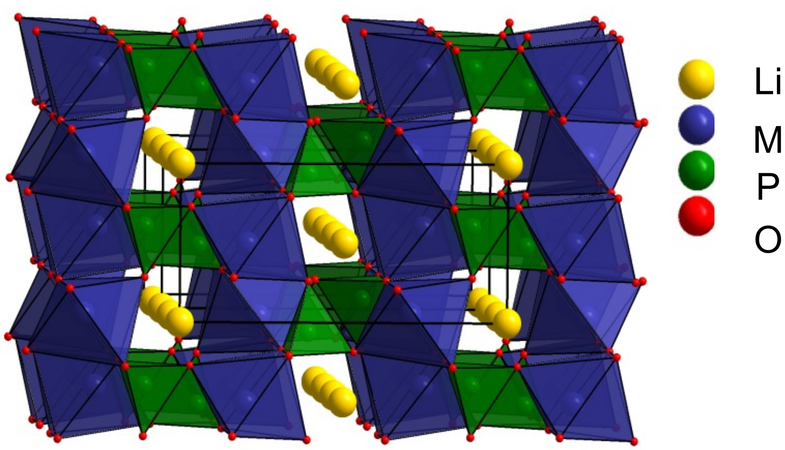
not a classical electrode material:

- Low electronic conductivity $LiFePO_4$
- Low ionic conductivity
- two-phase reaction ➔ phase boundary migration
- limited rate capability

Padhi, A.K., Nanjundaswamy, K.S., Goodenough, J.B.
Journal of the Electrochemical Society, 144 (4), 1997, 1188-1194.

Lithium Metal Phosphates as Cathode Materials for Li-Ion Batteries

$$LiMe(II)PO_4 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Me(III)PO_4 + Li^+ + e^-$$



Approaches to solve these problems

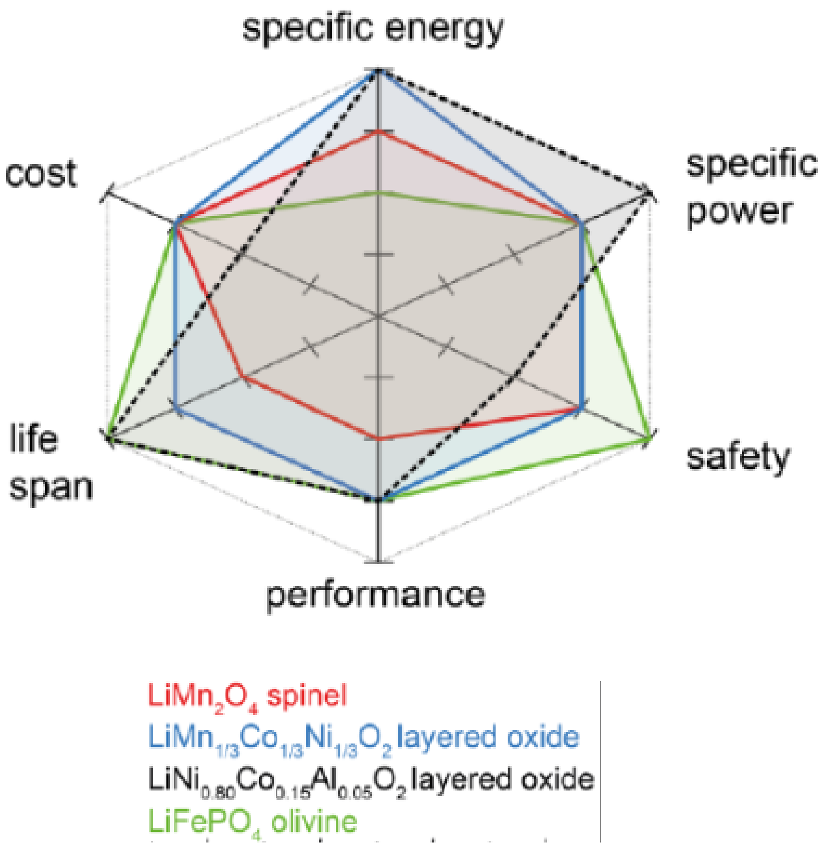
composition and structural level

nanosized material or nanostructured material

building a conductive surface network - “carbon painting”

Ravet, N., Chouinard, Y., Magnan,J.F., Besner, S., Gauthier, M., Armand, M., Journal of Power Sources, 97-98, 2001, 503-507N.

Lithium Metal Phosphates as Cathode Materials for Li-Ion Batteries - today



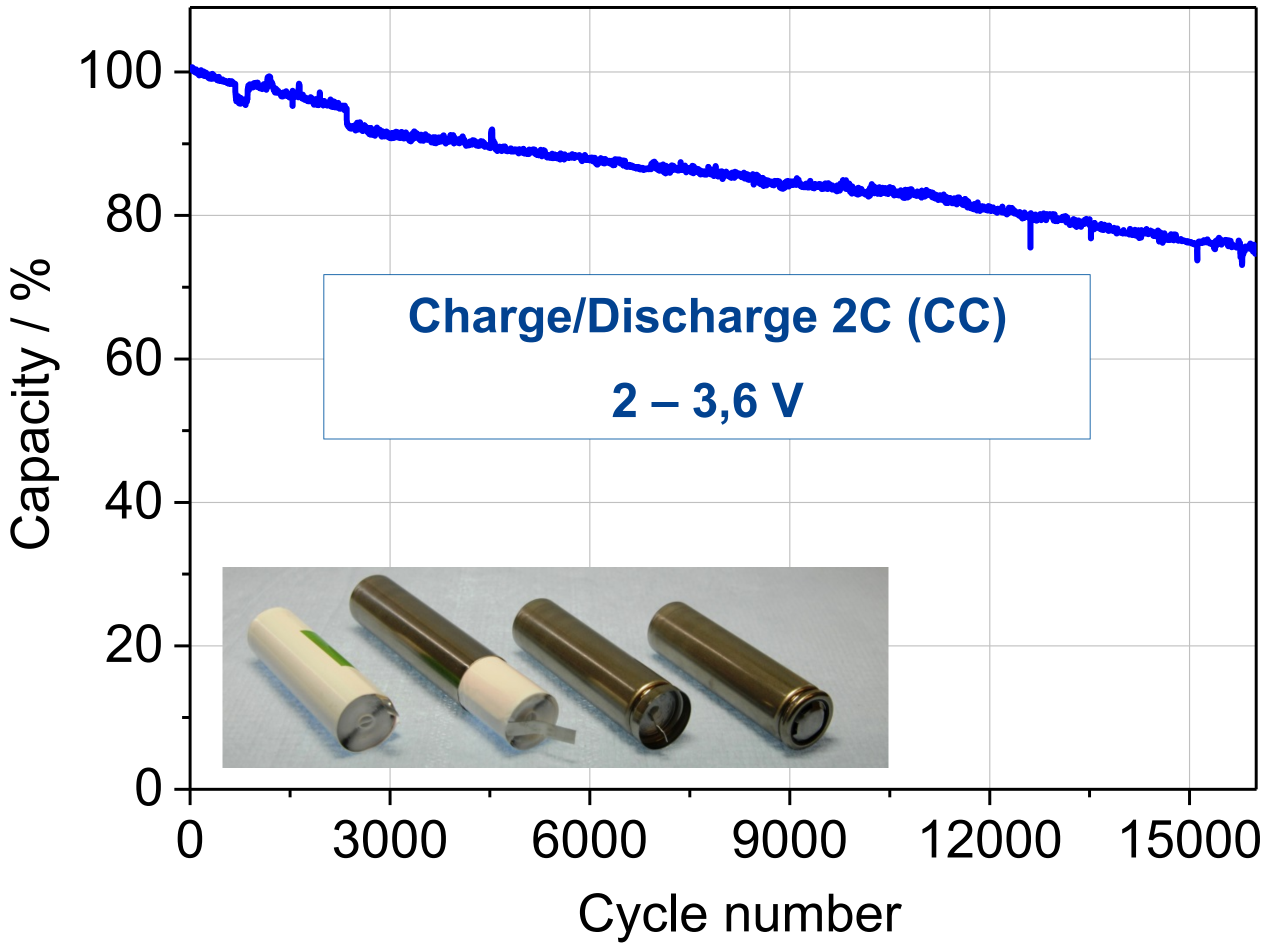
inherent safe, long life, high power material

Applications
- Low voltage applications
- E-bikes
- Hybrid electric vehicles
- Electric vehicles
- Stationary applications

- 2010 – 2014 more than 1.000 scientific publications

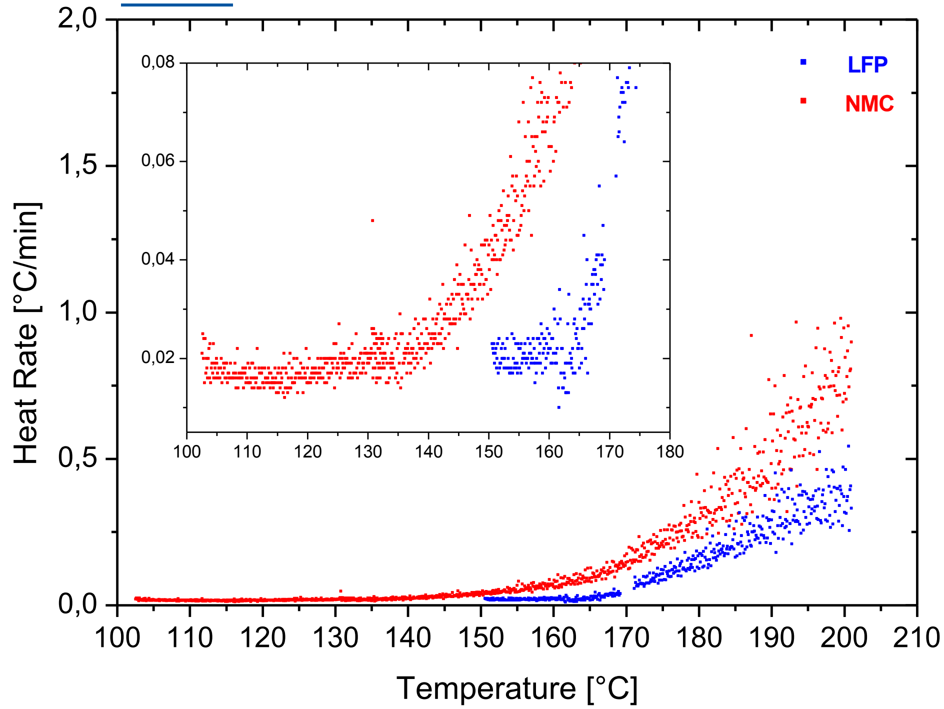
- initiated research on other polyanion material classes

Excellent Cycling Life
18650 cell Amorphous carbon//LFP
70 Wh/kg



Higher Safety of LFP Compared to Layered Oxides

ARC



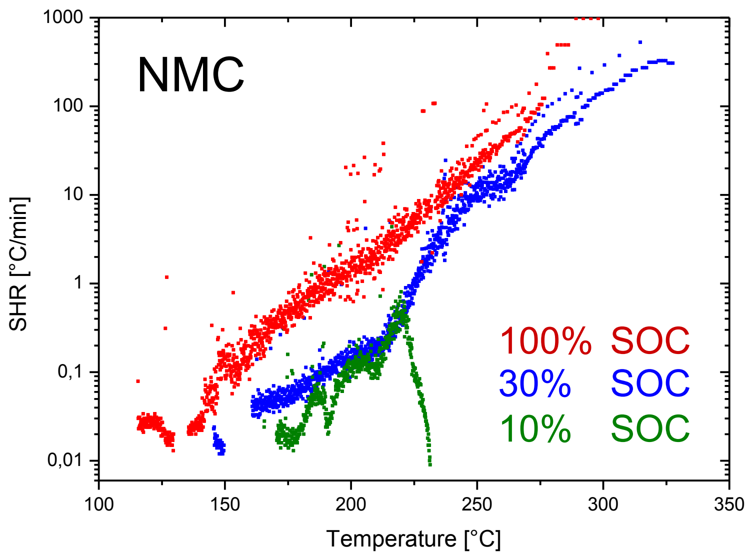
- LFP cell: self heating is lower and shifted to higher temperature

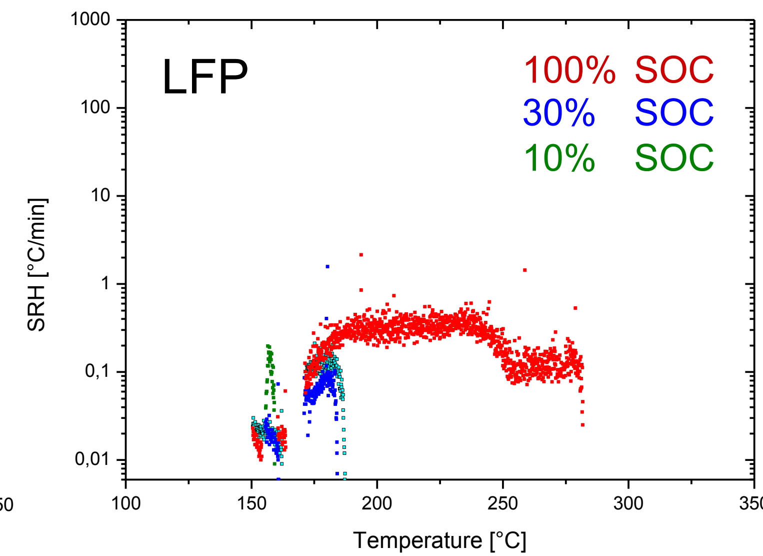
Thermal Abuse Test

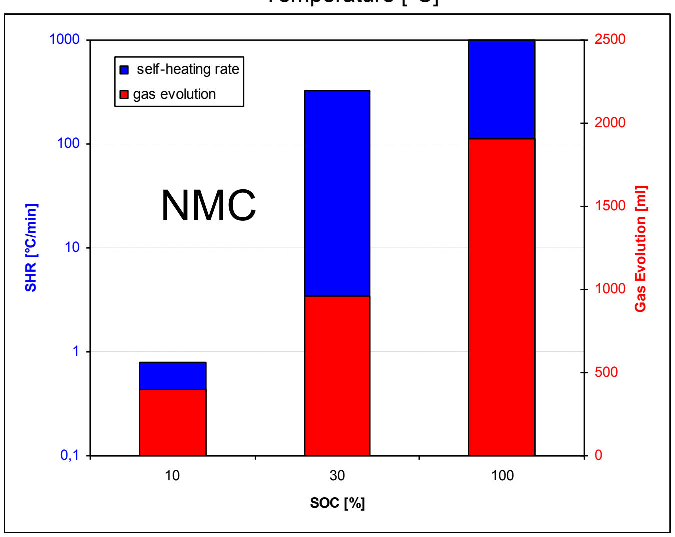
- LFP 18650 cell:
  Hazard level 3 (no thermal runaway)
- NMC 18650 cell:
  Hazard level 4 (thermal runaway)

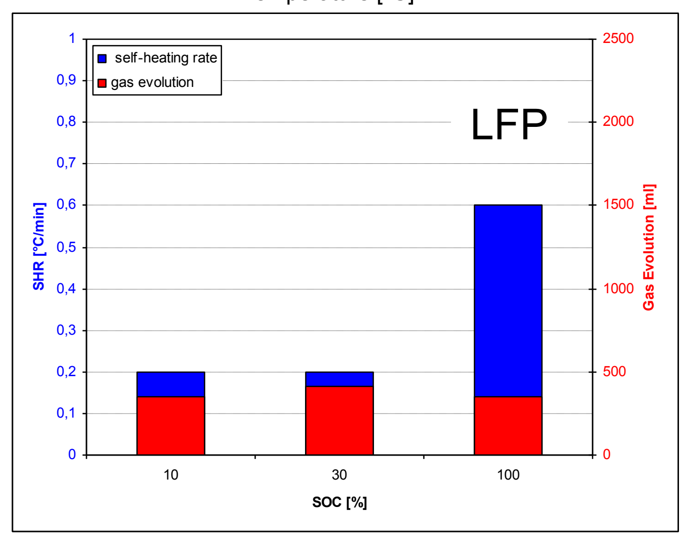
→ LFP cell is more safe

Excellent Safety Compared to Layered Oxides

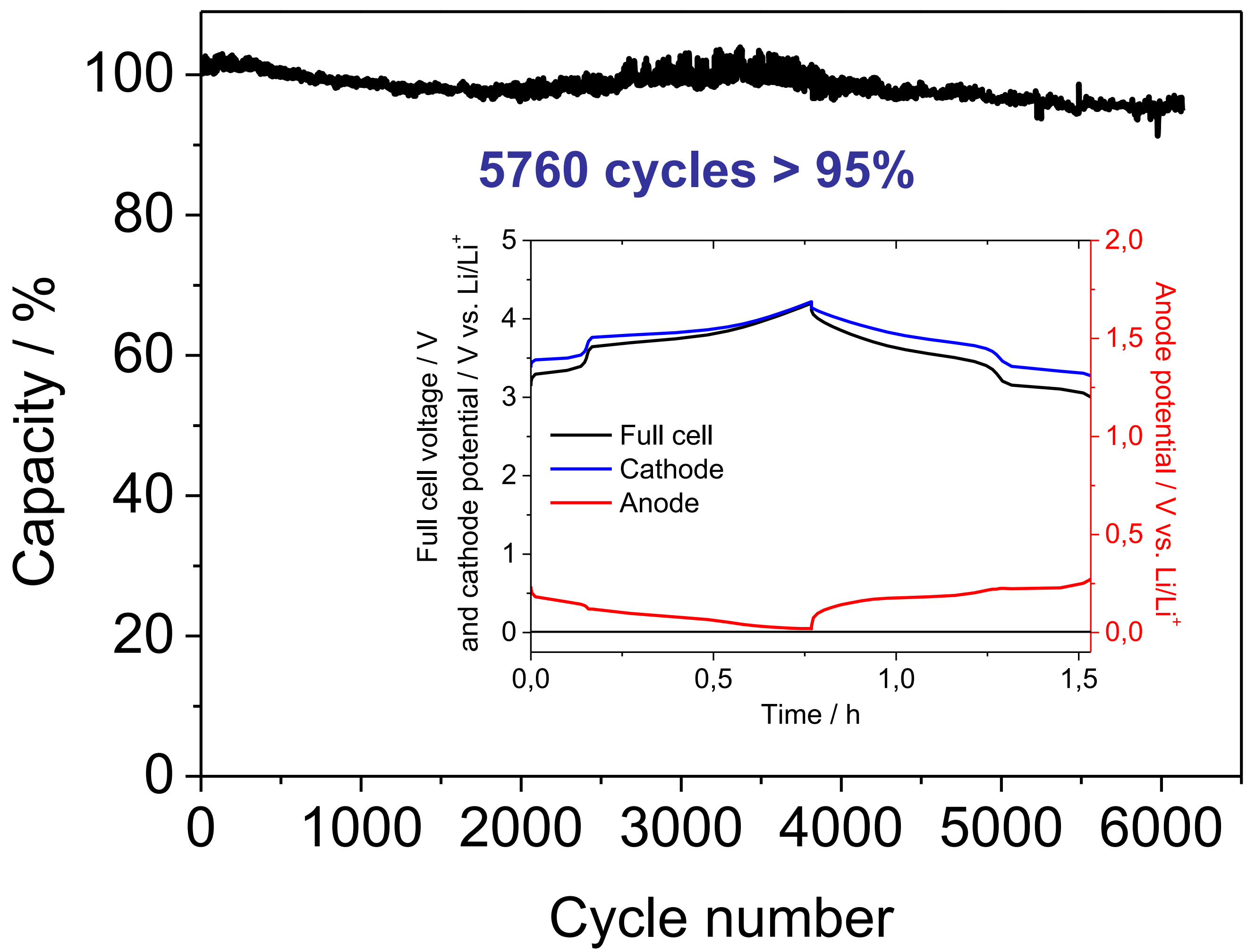








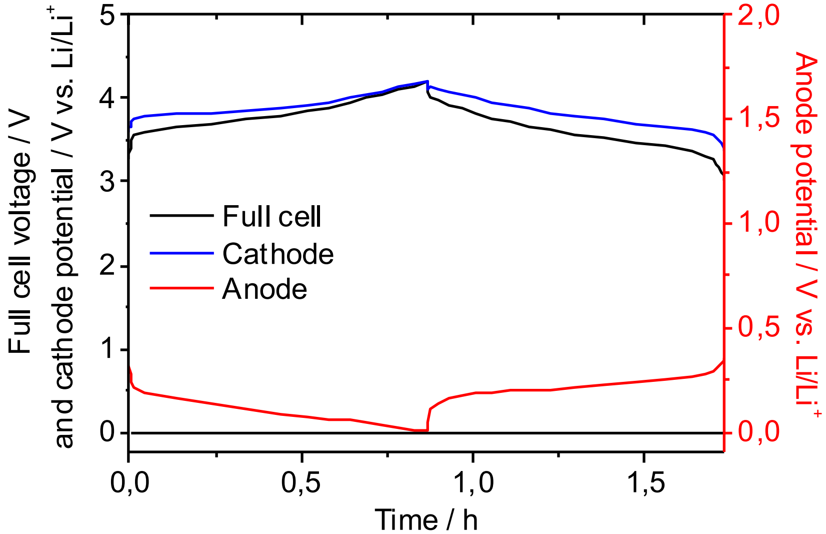
Routes to improve energy density: LFP//NMC Blends

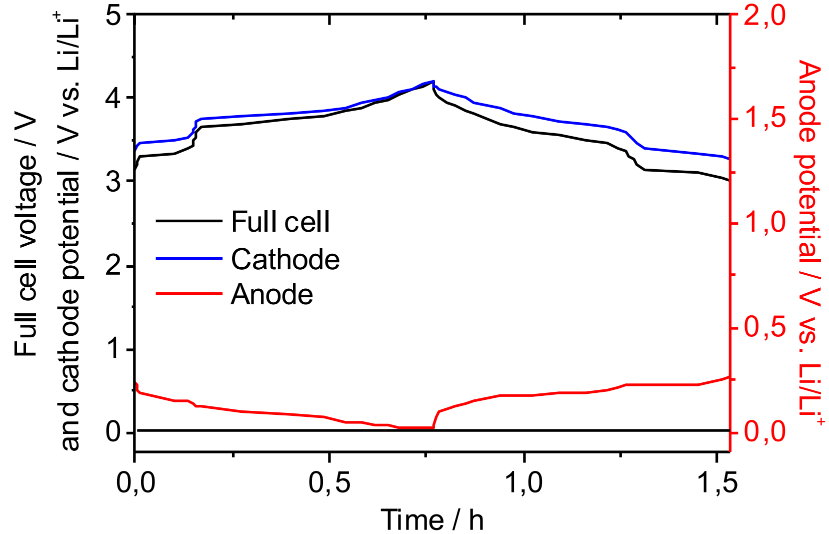


NCM/LFP blend 3:1; 93% AM/ 3% CB/ 1% Gr/ 3% binder

Loading: 14 mg cm^{-2}; electrolyte EC:EMC (3:7) + 2 wt. % VC

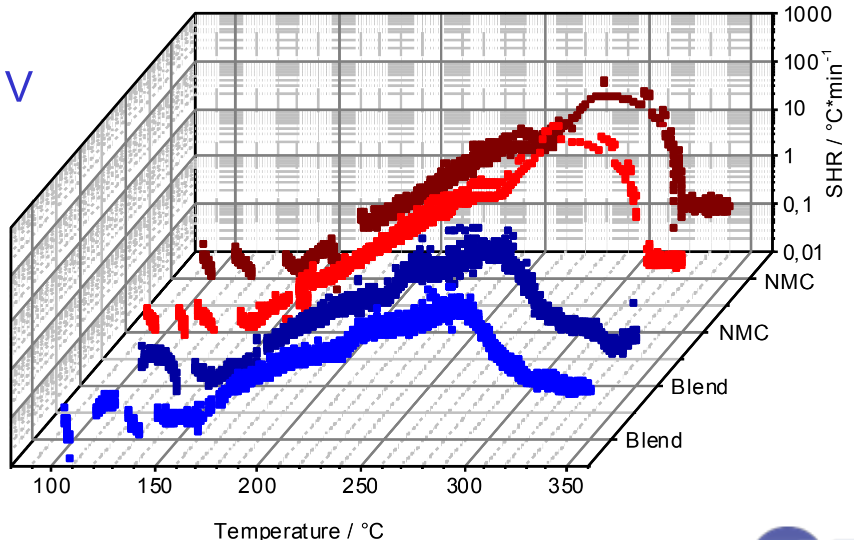
Routes to improve energy density: LFP//NMC Blends



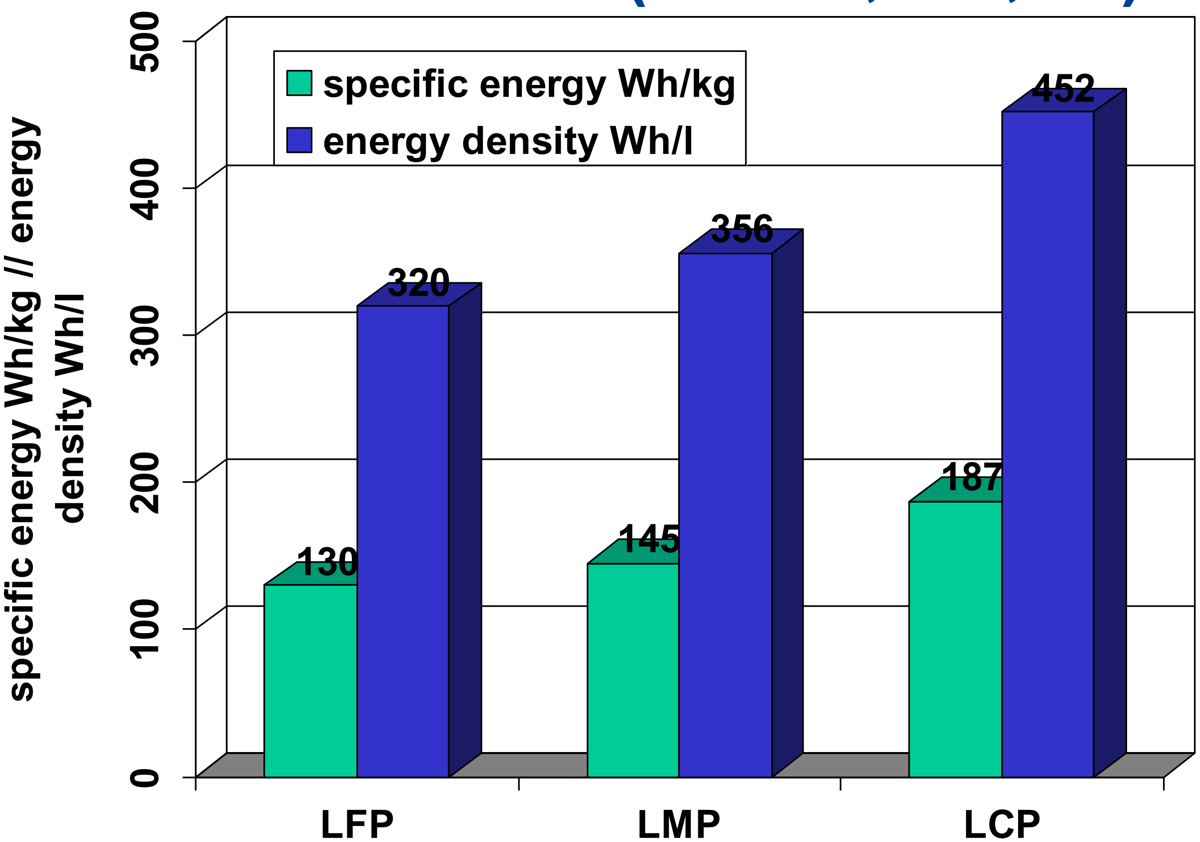


Charged/discharged C/5 between 3,0and 4,2 V
50 cycles 1 C CC/CD room temperature
Charged C/10 to 4,2 V

Maximum self heating rate
NMC: 280°Cmin^{-1}
Blend: 18°Cmin^{-1}



From $LiFePO_4$ to higher voltage $LiMePO_4$ (M: Mn, Co, Ni)



Baseline LFP 18650 cell

Projected specific energy for 18650 cells assuming comparable specific capacity for manganese and cobalt based materials

- higher energy density compared to LFP based cells
- reduce the energy density gap to layered lithium metal oxides
- increased abuse tolerance compared to layered oxides
- LCP higher capacity compared to LMNO

From $LiFePO_4$ to $LiMePO_4$ Me = Mn, Co
Challenges and strategies

- low electronic conductivity $LiMnPO_4 << LiFePO_4$

→ **nanosize particles and carbon coating**

- strain between charged and discharged state (lattice mismatch)

  $LiFePO_4/FePO_4$ 6,6%

  $LiCoPO_4/CoPO_4$ 7,1% (intermediate phase Li_xCoPO_4 reported)*

  $LiMnPO_4/MnPO_4$ 9,0%

  generation of Jahn-Teller ion Mn^{3+}
- instability of the delithiated states $Mn(III)PO_4$** and $Co(III)PO_4$ **

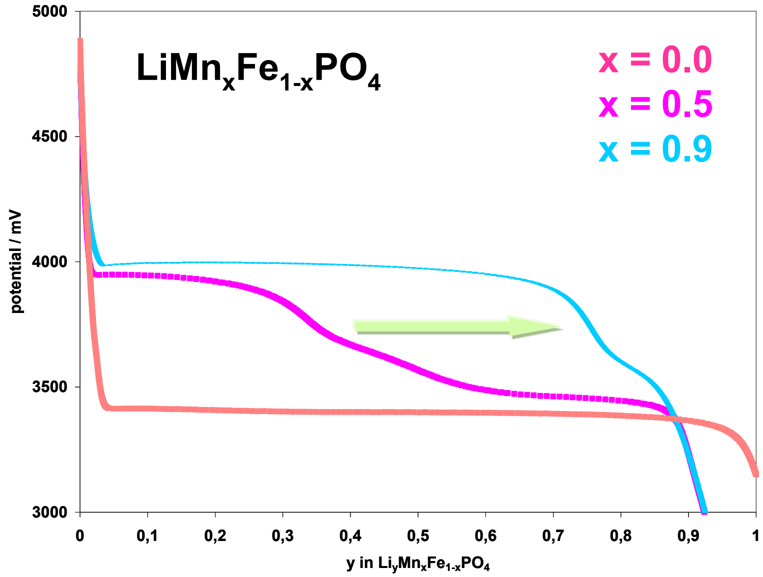
→ **$LiM(1)_xM(2)_{1-x}PO_4$** or **$LiM(1)_xM(2)_yM(3)_{1-x-y}PO_4$** for longer cycling life

- low electrolyte stability

N.N. Bramnik, K. Nikolowski, D. M.Trots, H. Ehrenberg,. Electrochemical and Solid-State Letters, 2008, 11, A89.*
S.–W. Kim., J. Kim., H. Gwon., K. Kang., J. Electrochem. Soc. 2009, 156(8), A635–A38.**
L. Wang, F. Zhou, G. Ceder, Electrochem. Solid–State Lett. 2008, 11(6), A94–A96.**
G. Hautier, A. Jain, S. Ong, B. Kang, C., R. Doe, G. Ceder, Chem. Mater. 2011, 23, 3495–3508**

From $LiFePO_4$ to $LiMePO_4$ Me = Mn, Co
Challenges and strategies

$LiM(1)_xM(2)_{1-x}PO_4$ or **$LiM(1)_xM(2)_yM(3)_{1-x-y}PO_4$** for longer cycling life

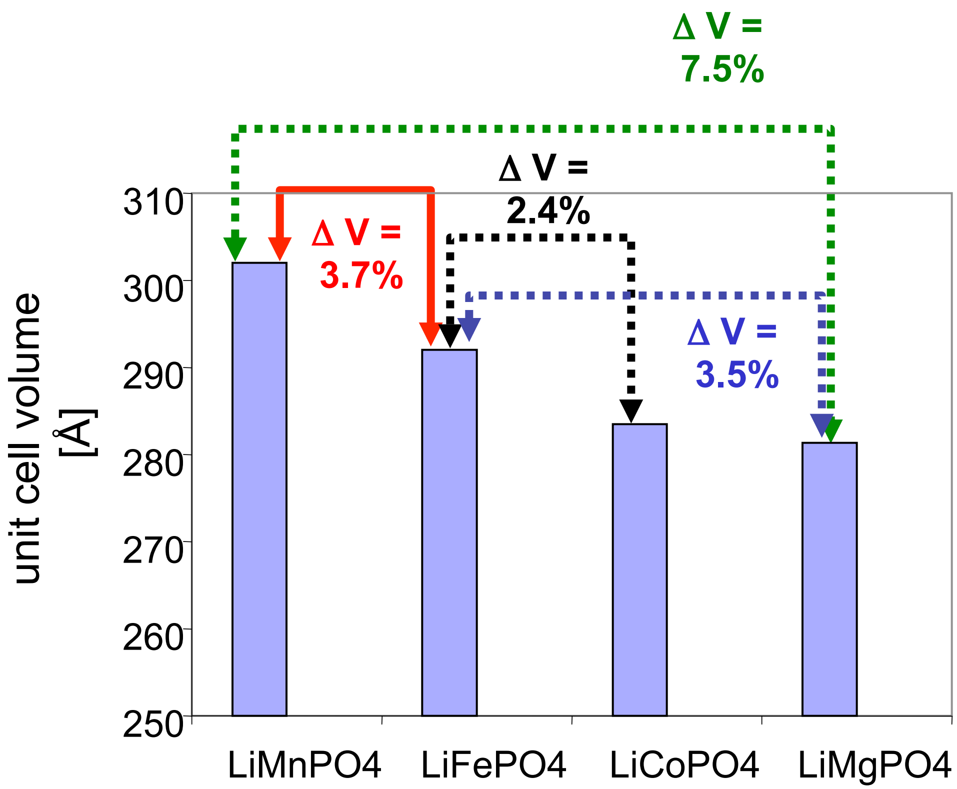


solid–solution series $LiMn_yFe_{1-y}PO_4$*, high power $LiMn_{0.8}Fe_{0.2}PO_4$*

A.Yamada, S.C. Chung, J. Electrochem. Soc. 2001, 148(8), A960–A967, A. Yamada,Y. Kudo, K.–Y. Liu, J. Electrochem. Soc. 2001, 148(7), A747–A754

D. Aurbach et al. Angewandte Chemie, 2009, 121(45), 711-715

Mixed phospho olivines to compensate structural changes



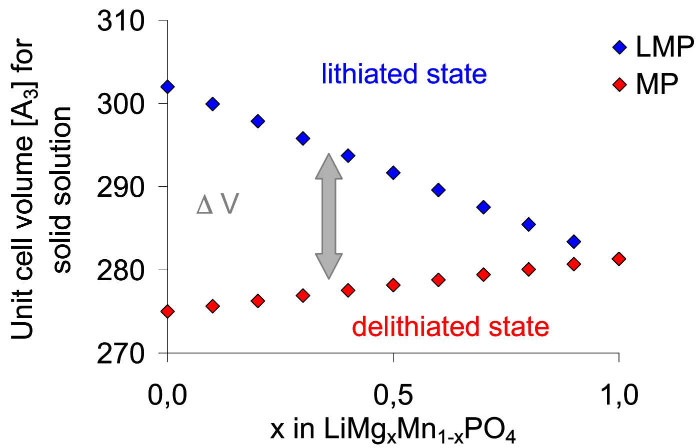
Unit cell volumes of the Phospho-Olivine Phases change in the series:
Mn > Fe > Co > Mg > Ni

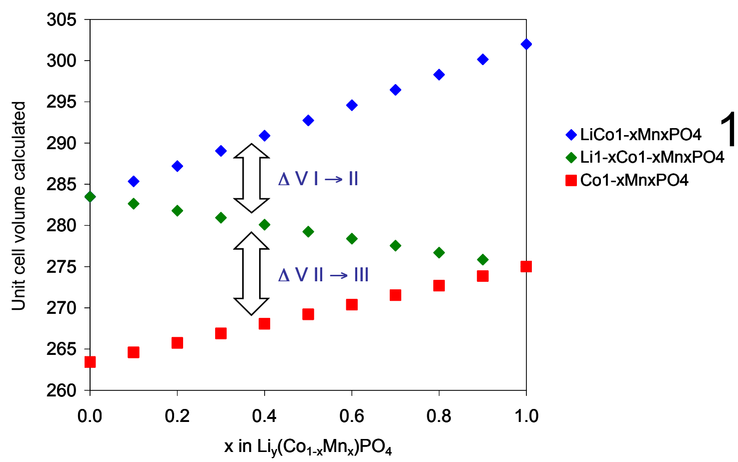
Large difference between $LiMgPO_4$ and $LiMnPO_4$
→ strong influence of substitution expected

Lithiated state:
solid solution of $LiMn^{II}PO_4$ und $LiMg^{II}PO_4$

Delithiated state –
solid solution of $Mn^{III}PO_4$ and $LiMg^{II}PO_4$

Expected influence of partial substitution





Consequences:

smaller ΔV between charged and discharged phase
→ lower lattice mismatch
→ reduced strain at phase boundary

decreasing amount of Mn(III) d^4
→ stabilisation of delithiated phase

1 Lithium per formula unit
→ lower lattice mismatch
→ reduced strain at phase boundary
→ mixed valent regions, solid solution regions

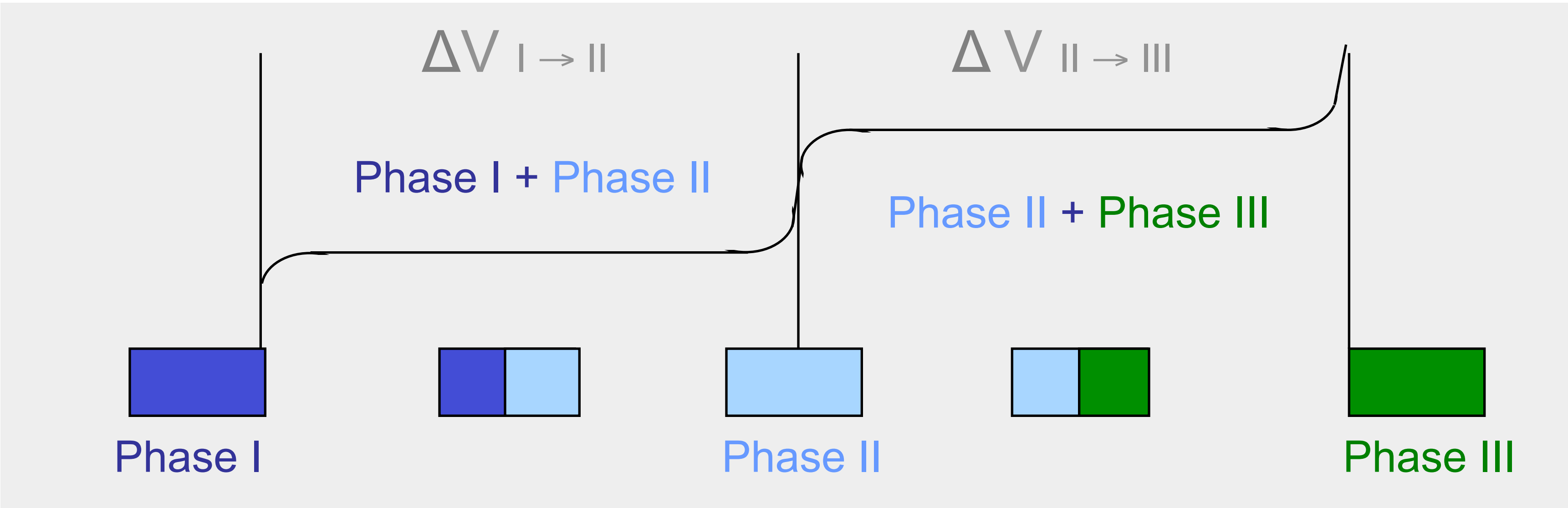
Dynamic stability – electrochemical active M
ΔV LMP/MP example Co-Mn

Step I: $LiMn(II)_{0.5}Co(II)_{0.5}PO_4 \rightarrow Li_{0.5}Mn(III)_{0.5}Co(II)_{0.5}PO_4 + 0.5Li^+ + 0.5e^-$

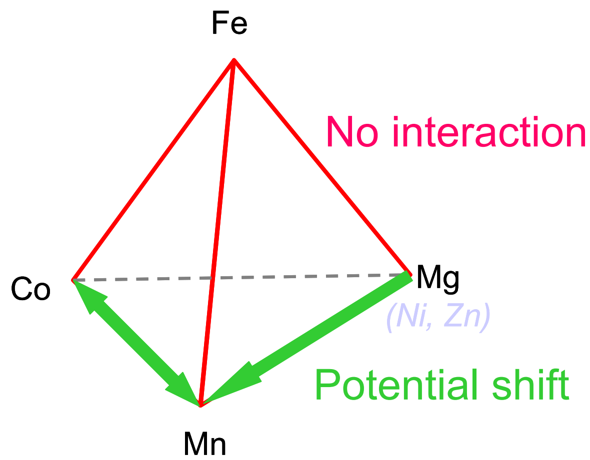
Phase I → Phase II

Step II: $Li_{0.5}Mn(III)_{0.5}Co(II)_{0.5}PO_4 \rightarrow Mn(III)_{0.5}Co(III)_{0.5}PO_4 + 0.5Li^+ + 0.5e^-$

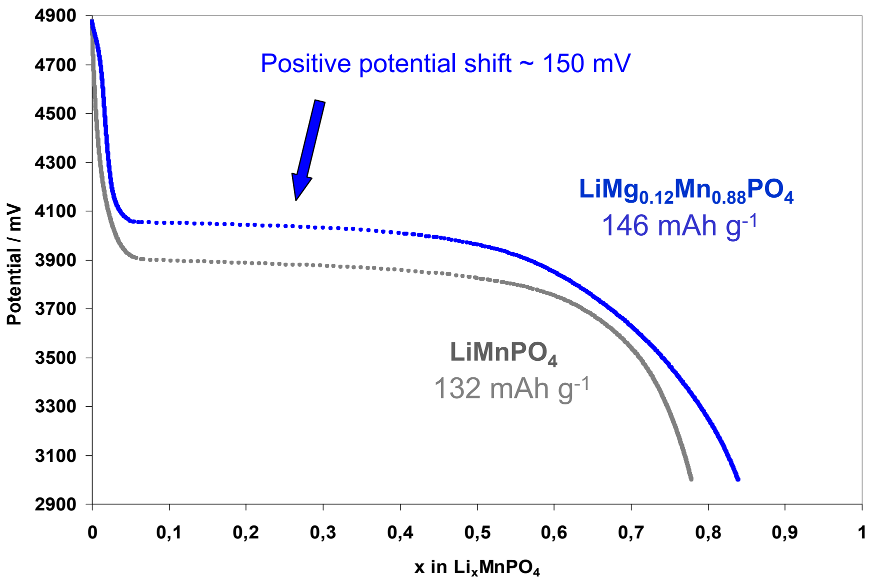
Phase II → Phase III

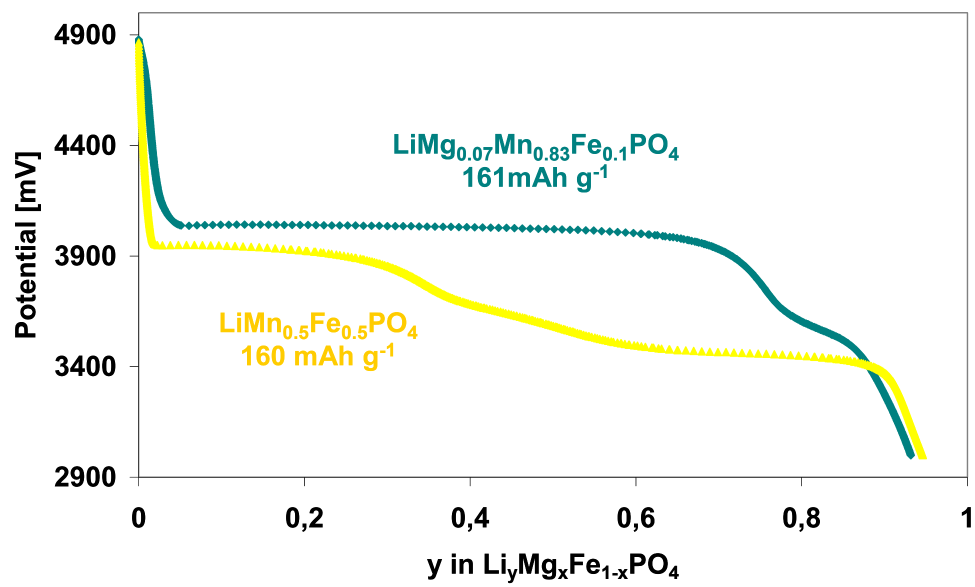


Effect of partial substitution on potential



- Mg shifts Mn plateau to more positive values
- no influence on Fe plateau





Higher Oxidation States of Manganese in the Olivine Structure?

- Li:M ratio restricts the redox-chemistry in olivines to M(II)-(III) step
- partial substitution of Manganese fixes Li^+ in the charged olivine structure

$$M(II) \rightarrow M(III)$$

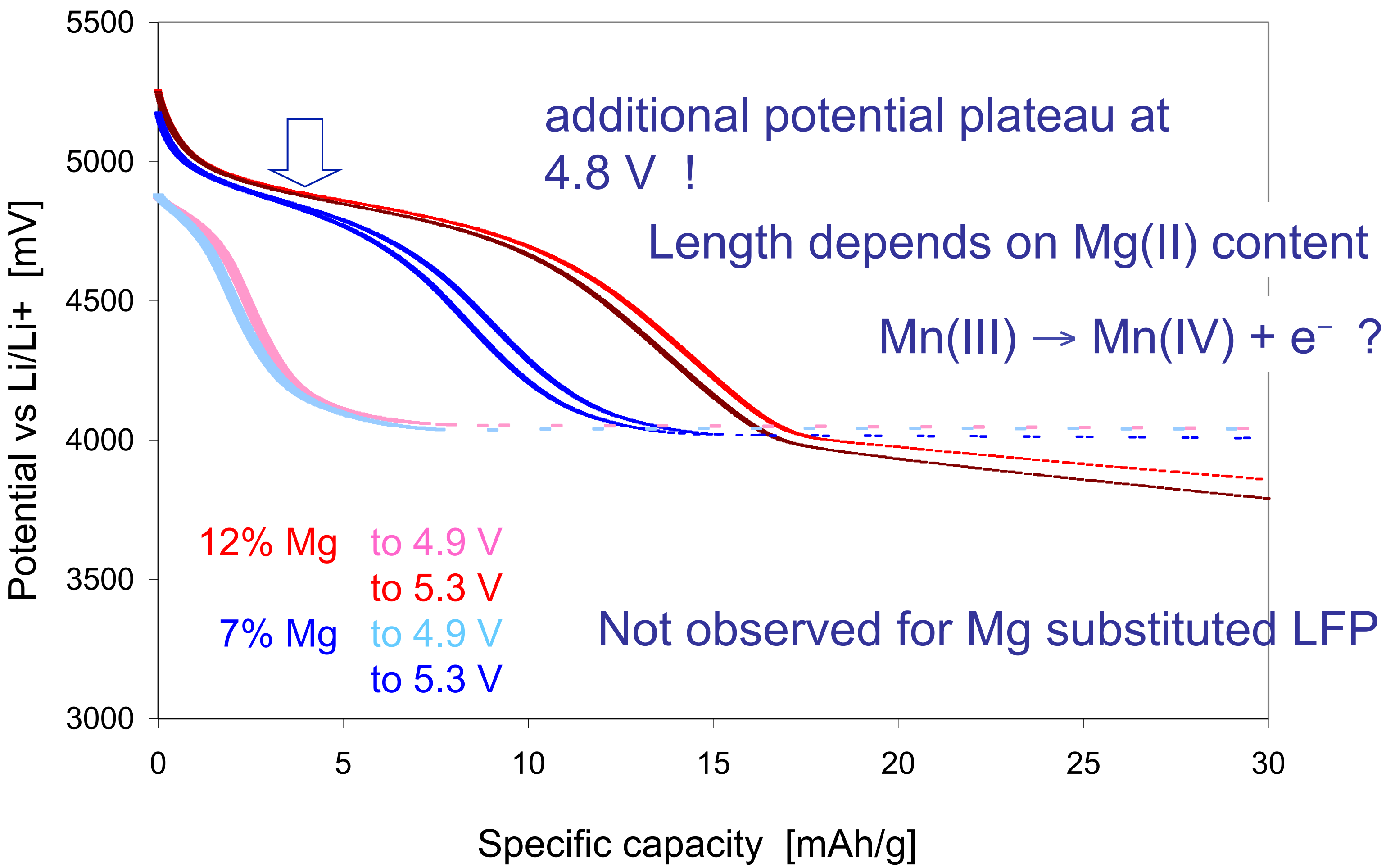
$$Li[Mg^{II}_x Mn^{II}_{1-x}]PO_4 \rightarrow Li_x[Mg^{II}_x Mn^{III}_{1-x}]PO_4 + (1-x)\ Li^+ + (1-x)\ e^-$$

$$M(III) \rightarrow M(IV)$$

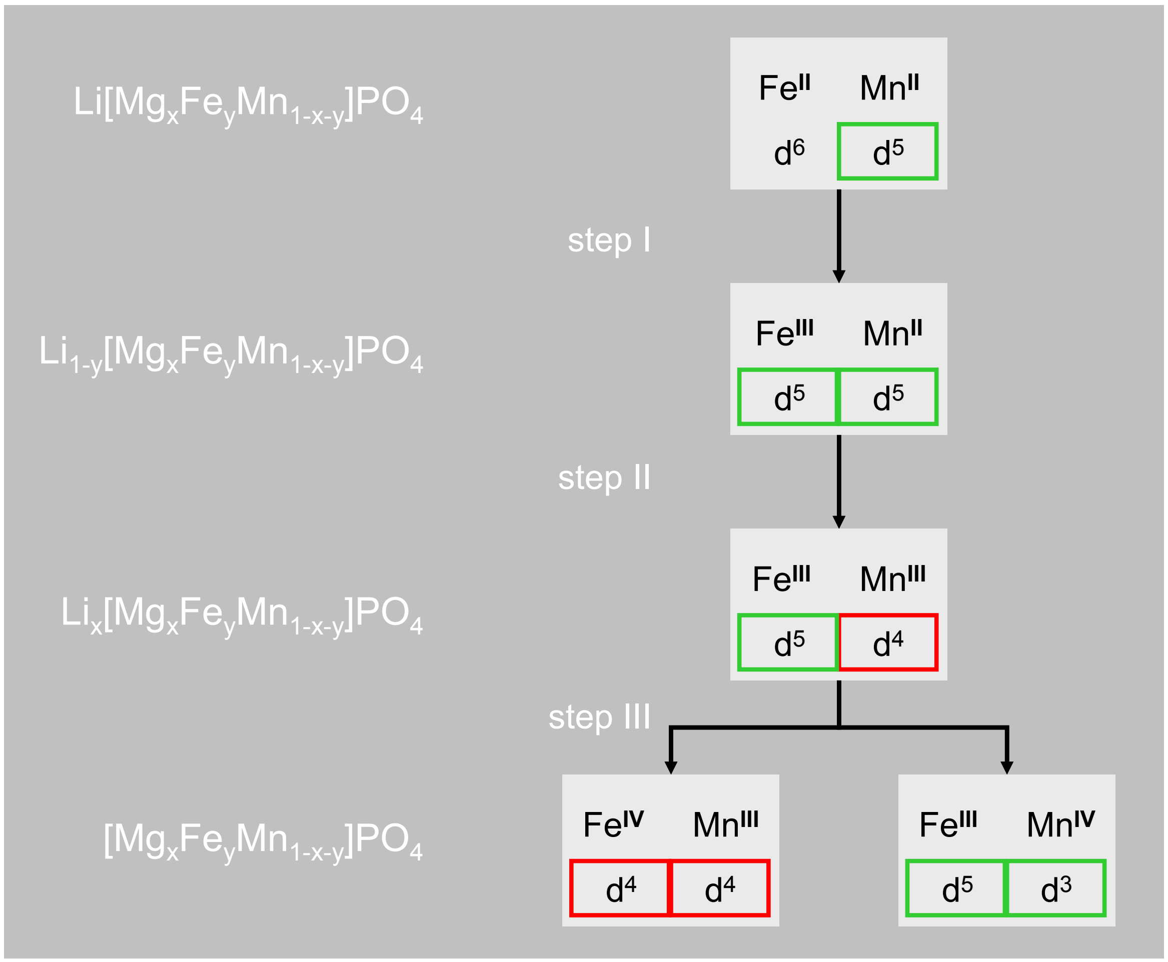
$$Li_x[Mg^{II}_x Mn^{III}_{1-x}]PO_4 \rightarrow [Mg^{II}_x Mn^{IV}_x Mn^{III}_{1-2x}]PO_4 + x\ Li^+ + x\ e^-$$

- in $LiMnPO_4$, $LiFePO_4$ and $LiMn_xFe_{1-x}PO_4$ with and without Mg

First discharge profile after charging to 5.3 V
LMP - 7% Mg and 12%Mg



Formal oxidation states and electronic configurations



Symmetric configurations

stabilisation of the structure

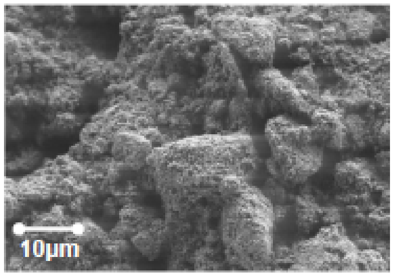
Jahn-Teller-Ions

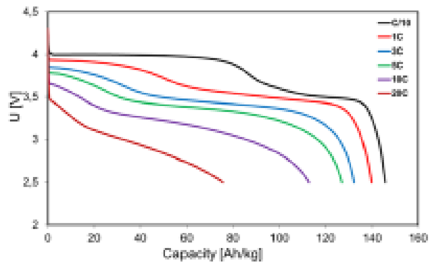
distortion destabilisation‘ of structure

Influence of powder morphology

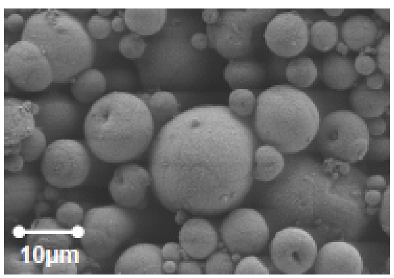
CLARIANT

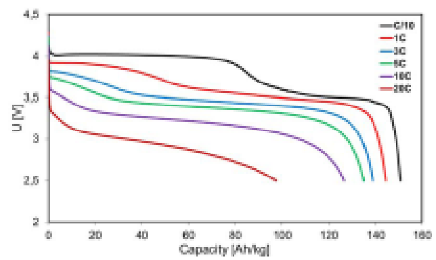
Li(Mn,Fe)PO_4- EXM 2336 ($LiFe_{0,33}Mn_{0,67}PO_4$)





LFMP – **powder type**
Electrode density = 1,50 g/cc
Press density = 1,69 g/cc
C content = 2,4 wt %





LFMP **spherical type**
Electrode density = 1,98 g/cc
Press density = 2,28 g/cc
C content 2,8 wt %

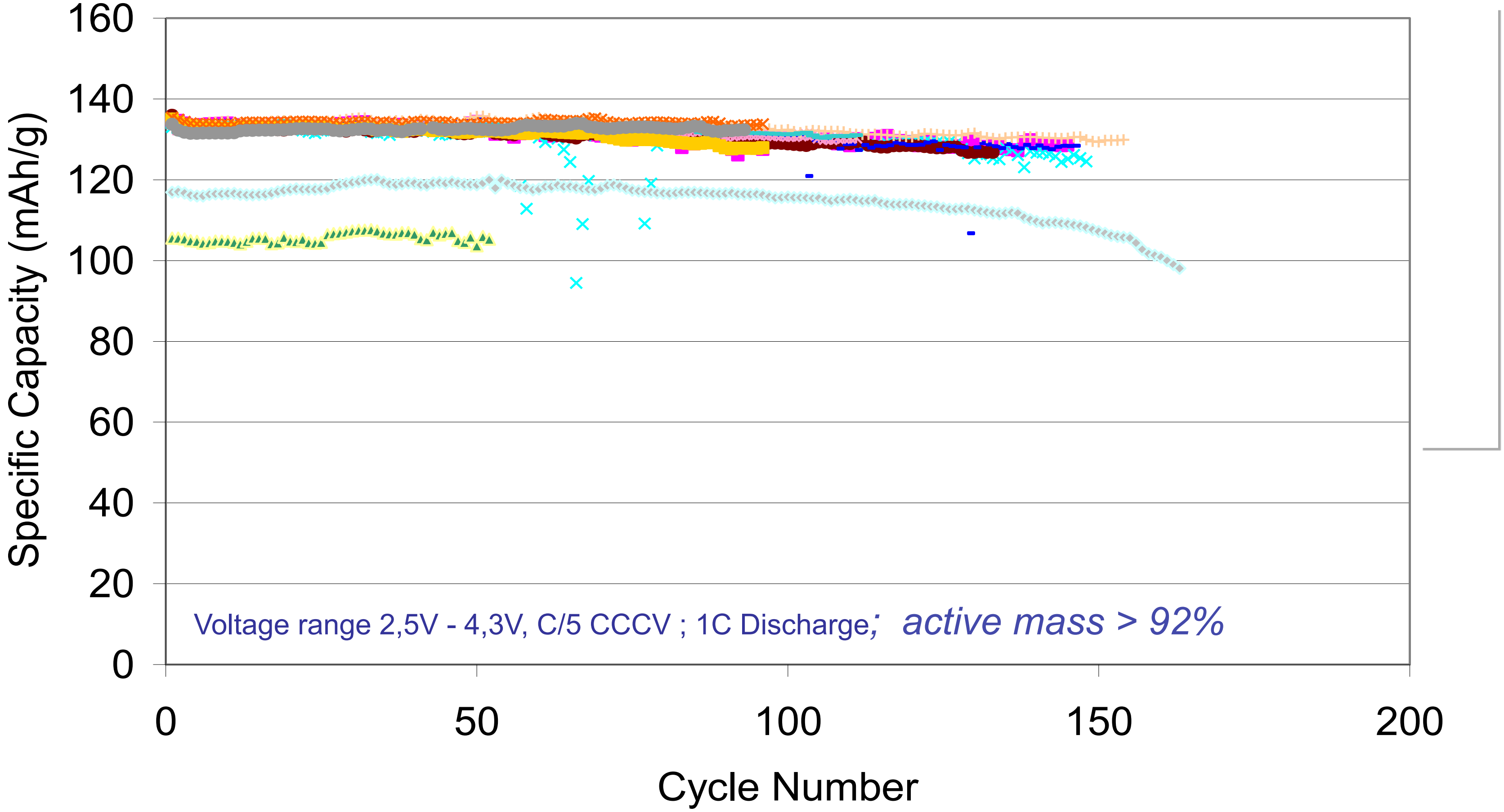
Control of particle size and morphology -

spherical agglomerates for better processability

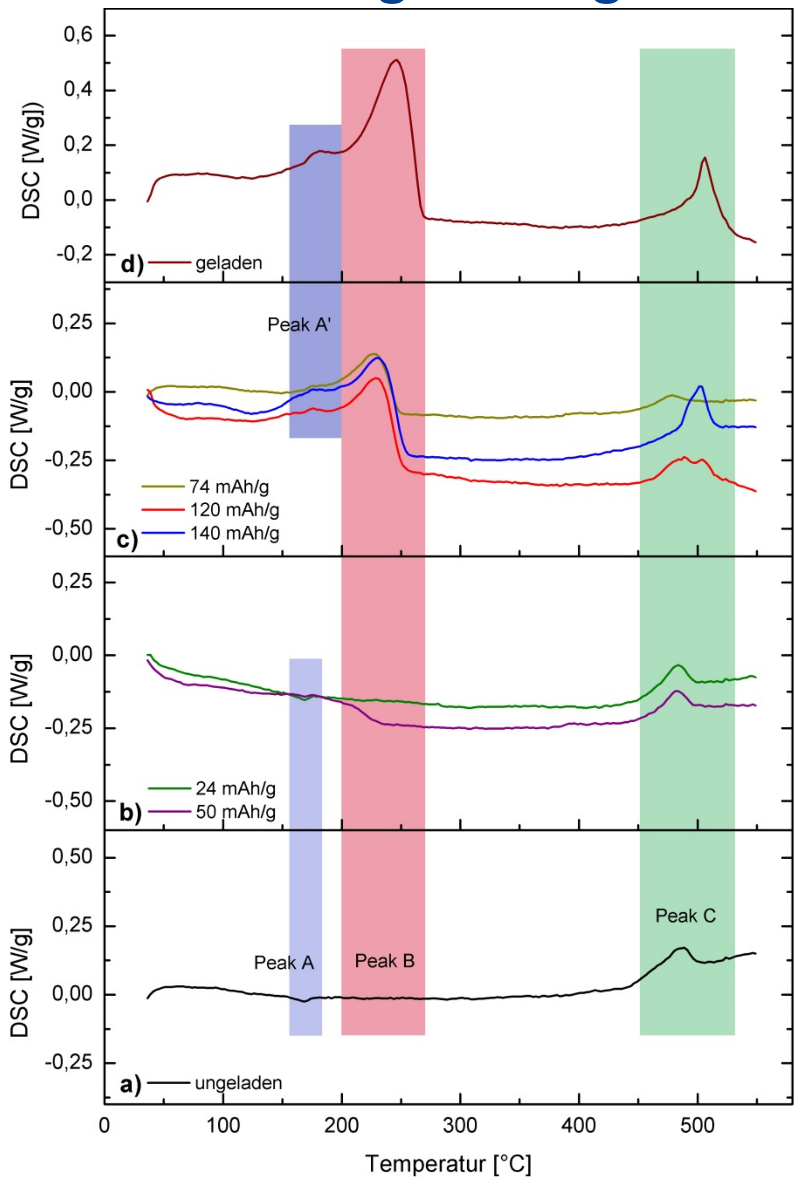
with comparable electrochemical performance

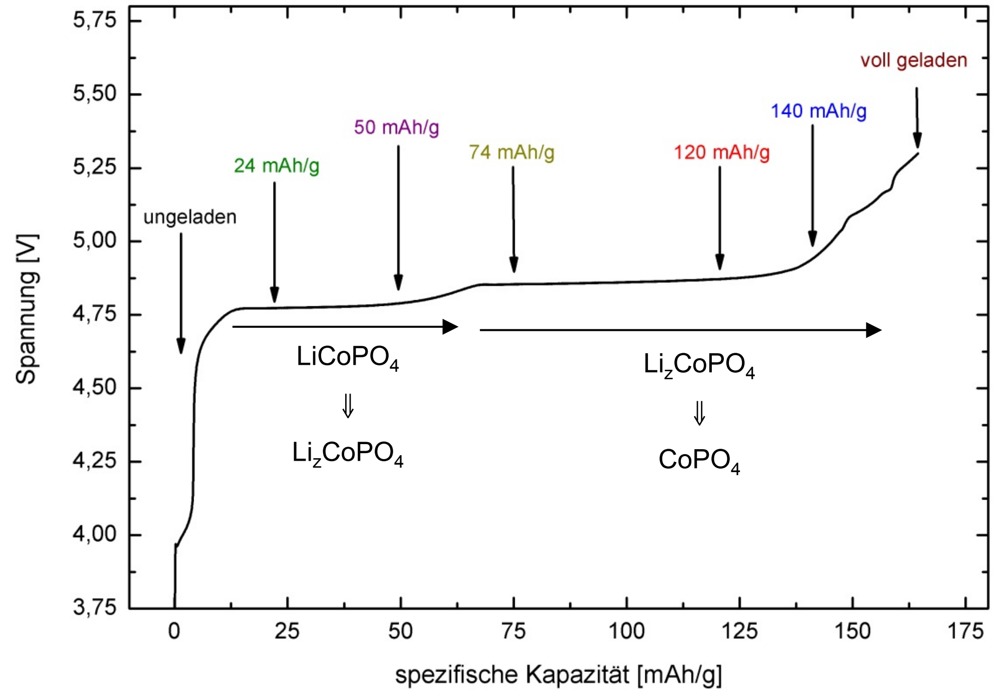
ZSW

Li(MnFe)PO_4 cycling stability



High voltage $LiCoPO_4$ different states of charge





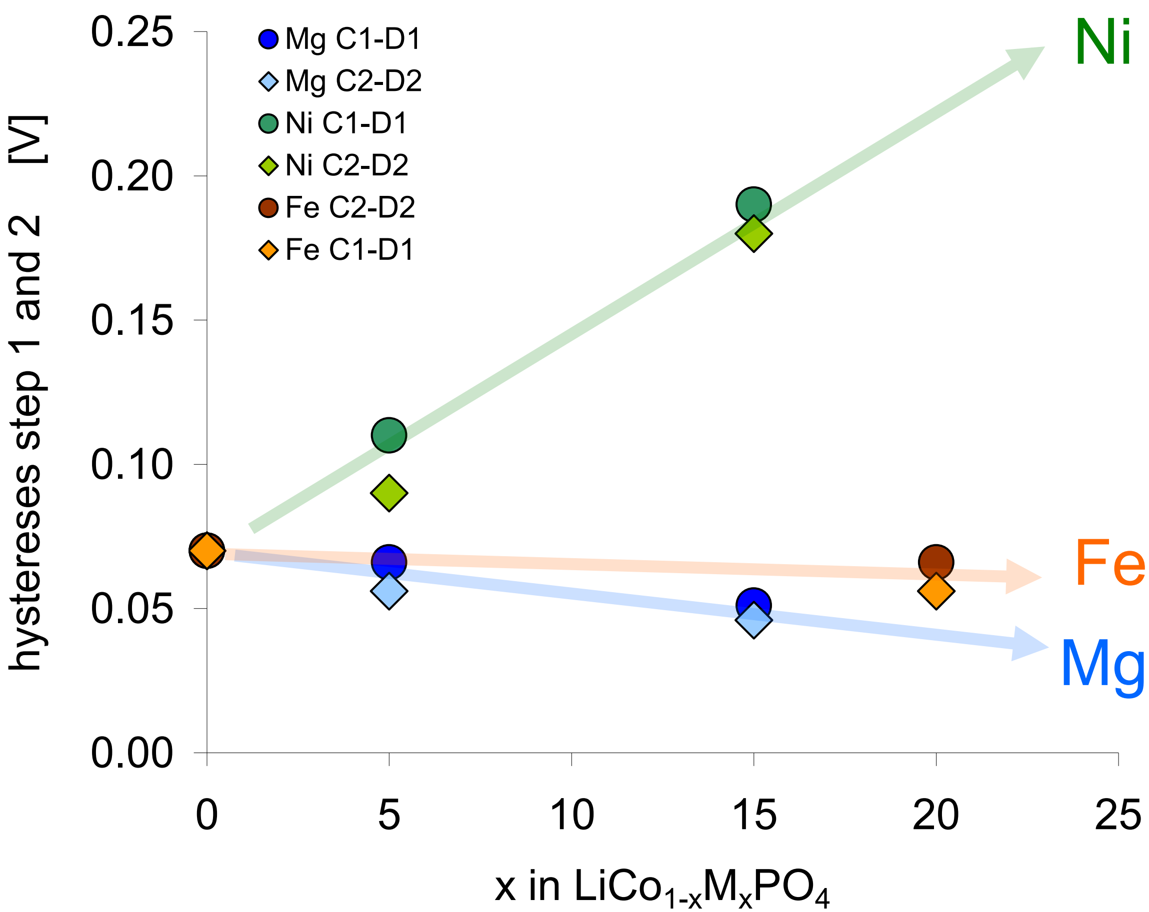
	Enthalpy Peak B [J/g]	Mass loss – 270°C [%]
uncharged	-	0,2
24 mAh/g	-	0,2
50 mAh/g	-	0,3
74 mAh/g	50	0,8
120 mAh/g	79	1,0
140 mAh/g	117	1,4
Charged	163	2,4

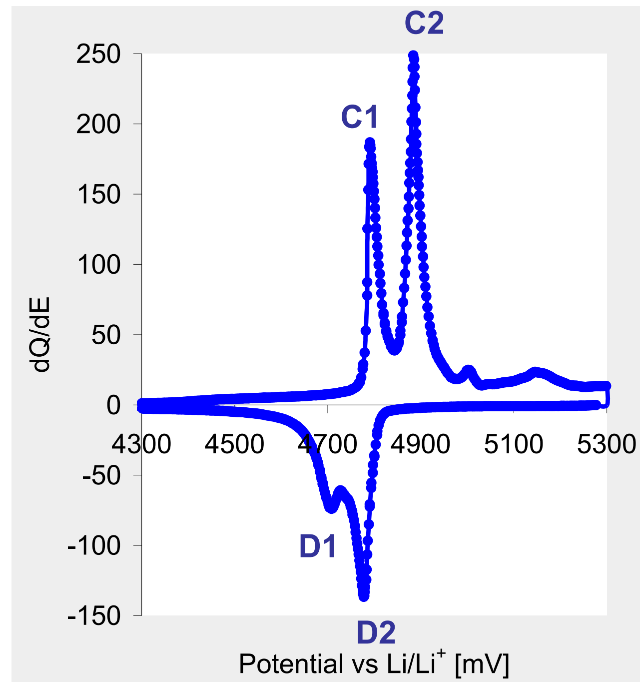
no exothermic reaction until the second plateau

⇒ Li_zCoPO_4 thermal stable

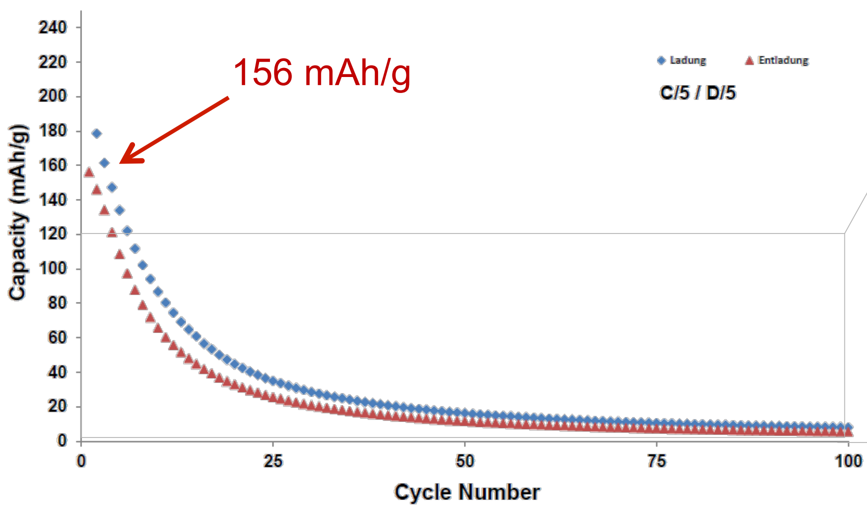
⇒ exothermic decomposition of $CoPO_4$

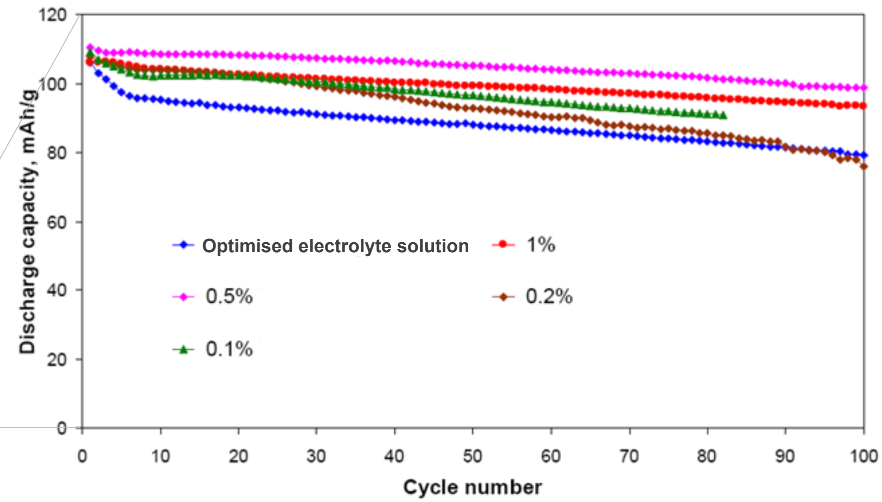
Influence of partial substitution of Co by Ni, Mg or Fe on the hysteresis of $LiCoPO_4$





Influence of electrolyte



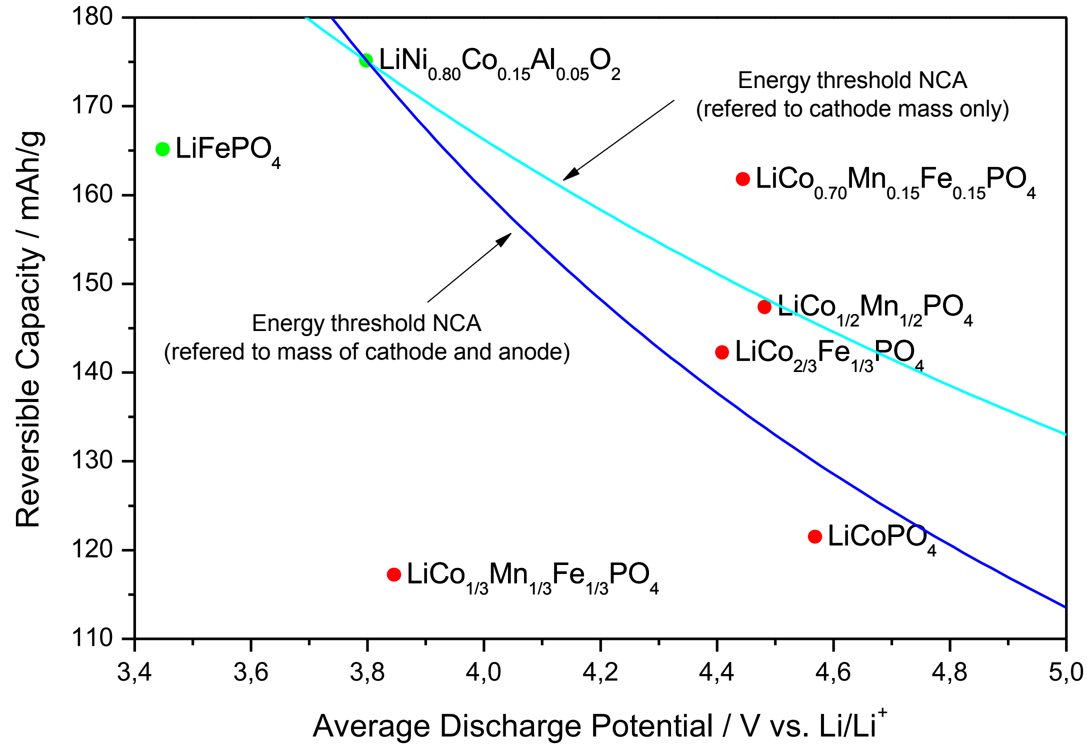


- Standard electrolyte without additives
- High initial capacity, high capacity fading

- Optimized high voltage electrolyte plus additives
- Lower initial capacity, higher cycling stability

E. Markevich, R. Sharabi, H. Gottlieb, V. Borgel, K. Fridman, G. Salitra, D. Aurbach, G. Semrau, M.A. Schmidt, N. Schall, C. Bruenig, Electrochemistry Communications 15 (2012), pp 22-25

Calculated Energy Density of Mixed Phosphates From Measured Data



Summary

- LFP well established **safe and long life** electrode material
- Lithium mixed metal phosphates are promising as high voltage cathode materials
- Partial substitution of Mn by other metals leads to higher stability and performance
- Mixed Lithium Manganese Cobalt phosphates can give similar or even higher specific energy compared with layered oxides and higher safety
- Progressing studies of the underlying charge/discharge mechanism will lead to a deeper understanding
- Adjustment of composition and structure, selection of proper cell components as binder, separator, electrolyte will lead to further breakthroughs for the high voltage materials

- **Thanks to John Goodenough and Michel Armand research directions have been opened for new classes of materials**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BASTA

DFG Deutsche Forschungsgemeinschaft

"Funktionsmaterialien und Materialanalytik zu Lithium–Hochleistungsbatterien" WO882/4–1

CLARIANT

Thank you for your attention!

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Widderstall
Solar test-field

Ulm
Electrochemical Energy
Technologies

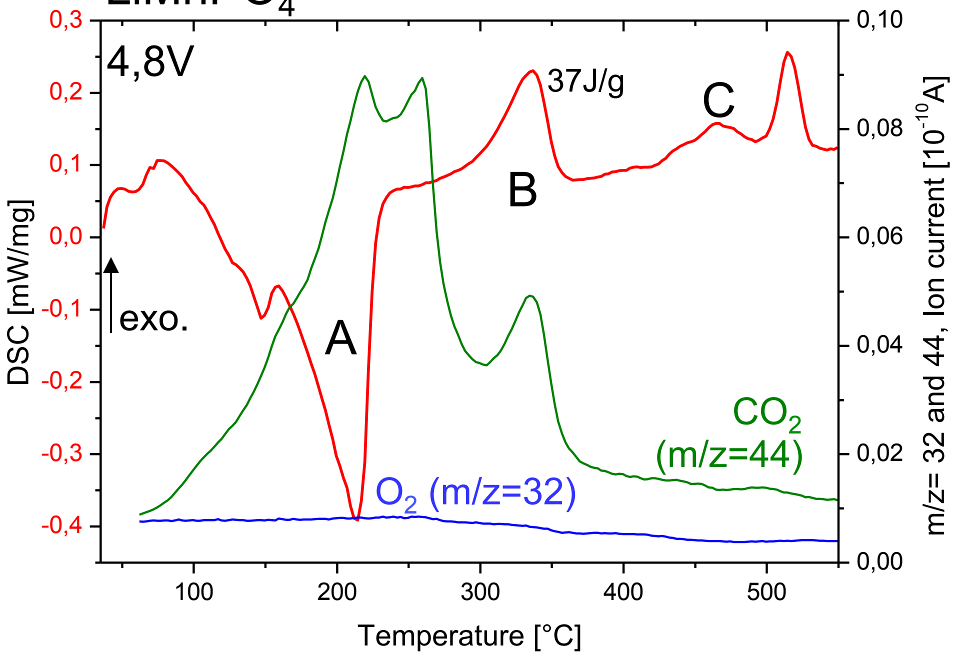
Ulm
eLab
Center for battery research

High-Voltage $LiMnPO_4$: Effect of Doping

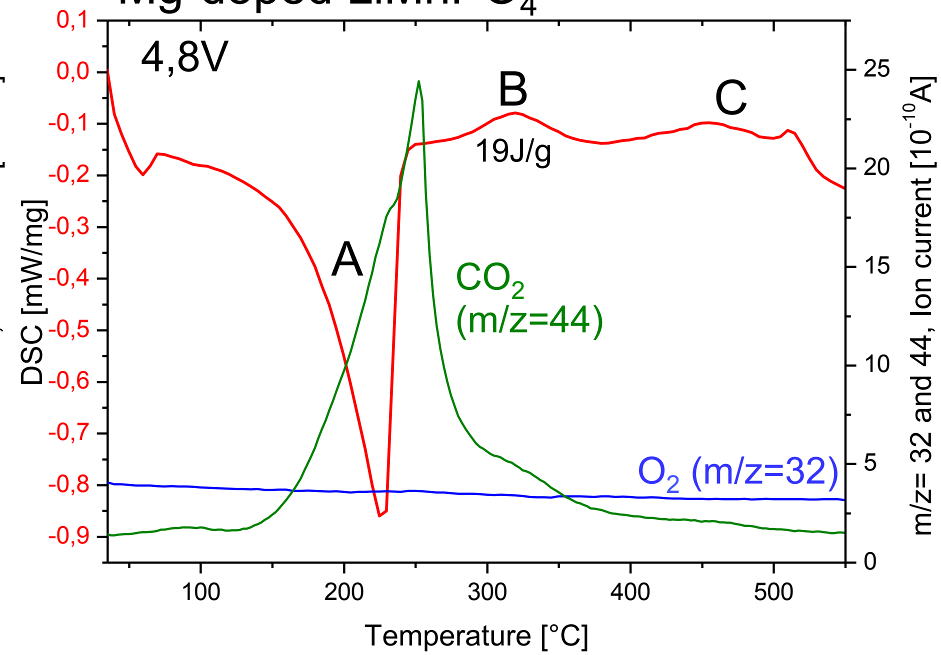
- Chemical composition
- Crystal structure
- Doping
- SEI stability

Electrolyte: 1Mol $LiPF_6$ EC:DMC= 1:1

$LiMnPO_4$



Mg-doped $LiMnPO_4$



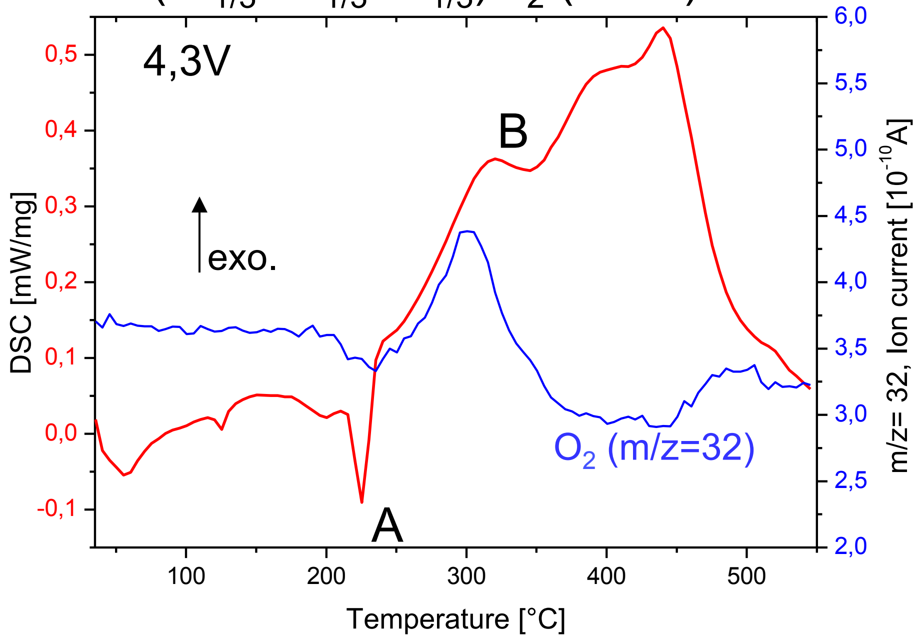
- Exothermic Reaction B: 335°C
- CO_2-Formation: 335°C
- No O_2-Formation

→ Heat formation decreases

Thermal Stability of Fully Charged Cathode Materials From Layered Structure to Olivine

Electrolyte: 1Mol $LiPF_6$ EC:DMC= 1:1

$Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC)

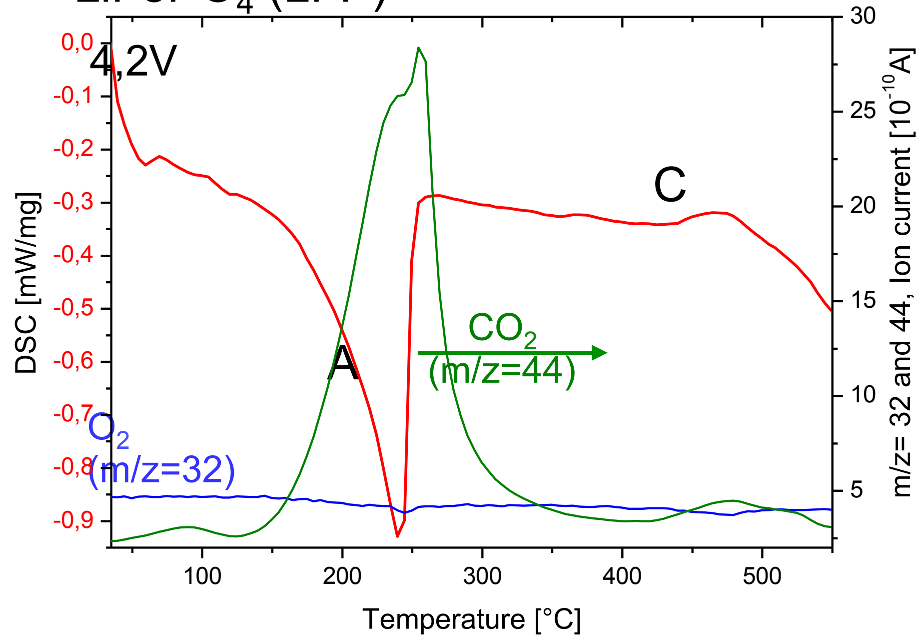


- Exothermic Reaction: 250-500°C
- O_2-Formation: 300°C

Structural changes:

R-3*m*-type → NiO-type + O_2

$LiFePO_4$ (LFP)



- Only small Exothermic Reaction: 470°C
- CO_2-Formation: 470°C (→ binder reaction)
- No O_2-Formation

Excellent Cycling Life
18650 cell Amorphous carbon//LFP
70 Wh/kg