

High-voltage materials and electrolytes for Li-ion batteries

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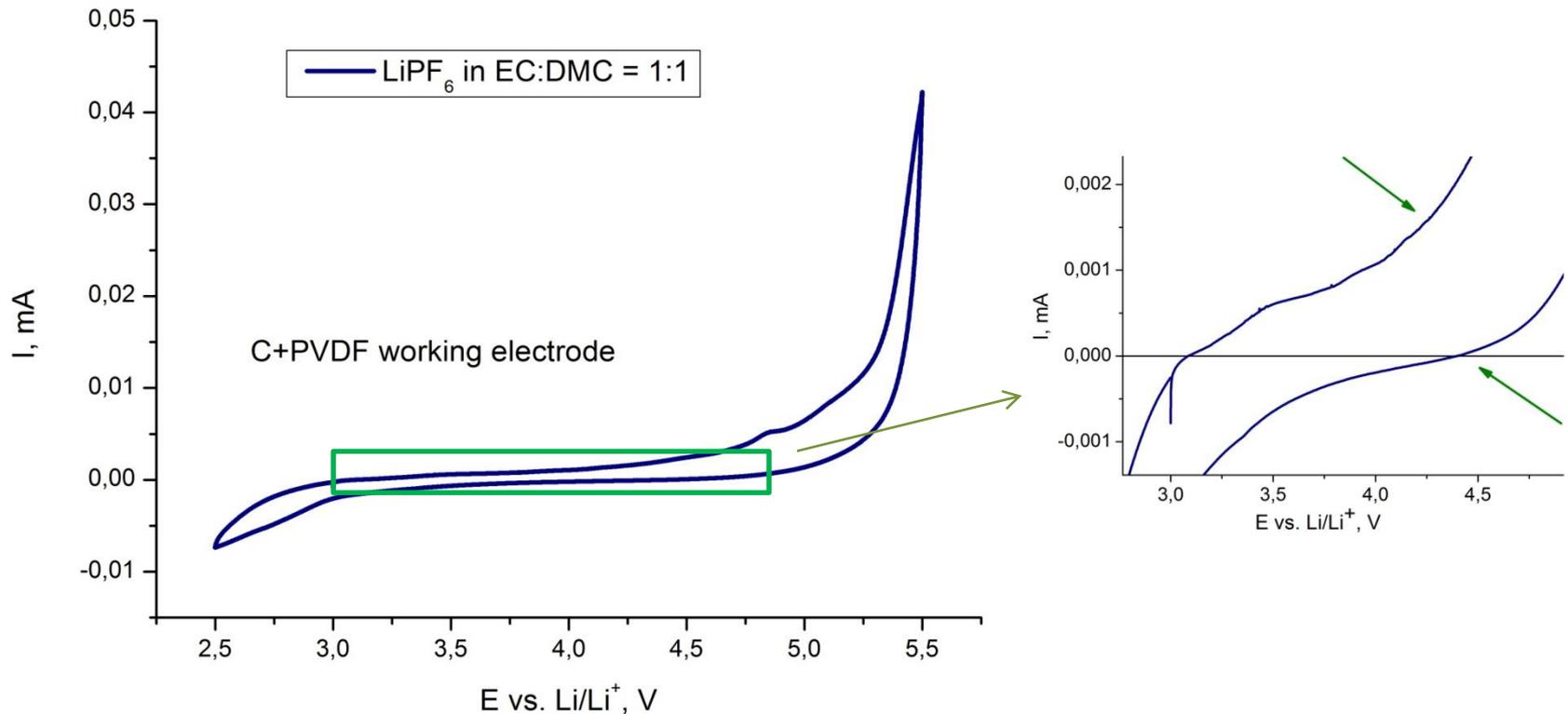
Li-ion batteries: high-voltage inherently

	Average cell voltage, V	Energy density, Wh/kg	Volumetric energy density, Wh/l	Self-discharge, %/month	Lifetime (number of cycles)
Ni-MH	1.2	60-80	~150	10-20	100-1000
Li-Ion	3.7 (LiCoO ₂ + C)	110-250	300-650	1-5	>3000

Replacement of H/H⁺ to Li/Li⁺ and, respectively, H₂O-based electrolytes to organic solvents led to drastic increase of energy density

However, 3.7 V is not a final destination.

What is high-voltage Li-ion battery?



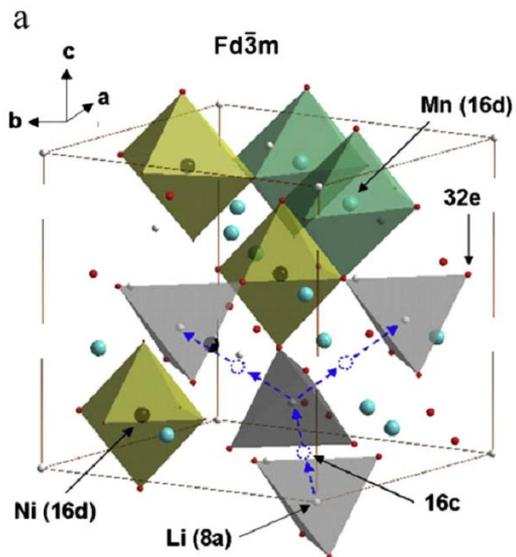
The remarkable oxidation of conventional Li-ion electrolyte starts at ~ 4.5 V vs. Li/Li^+ . The material (and corresponding electrochemical system) with **average** discharge potential > 4.5 V may be considered as high-voltage

Cathode materials

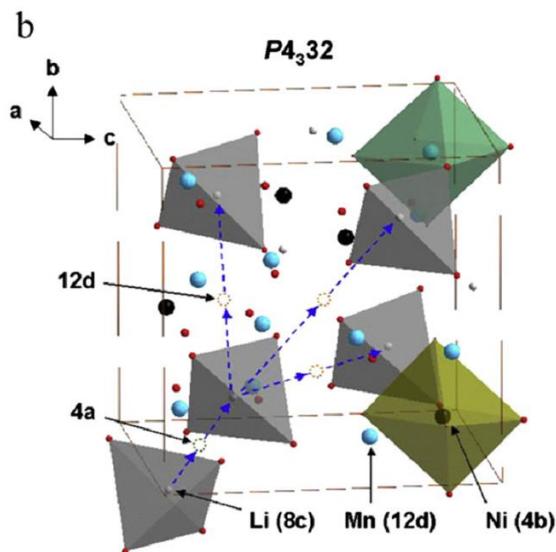
1. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ - average $E \sim 4.6\text{V}$, $C_{\text{theo}} = 146$ mAh/g
2. LiCoPO_4 (LiNiPO_4) - average $E \sim 4.8$ (5.1) V, $C_{\text{theo}} = 167$ mAh/g
3. $\text{Li}_2\text{CoPO}_4\text{F}$ - average $E \sim 4.9$ V, $C_{\text{theo}} = 145$ mAh/g per 1 Li cation
4. $(\text{Na},\text{Li})_2\text{FePO}_4\text{F}$ – possible $2e^-$ transition

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

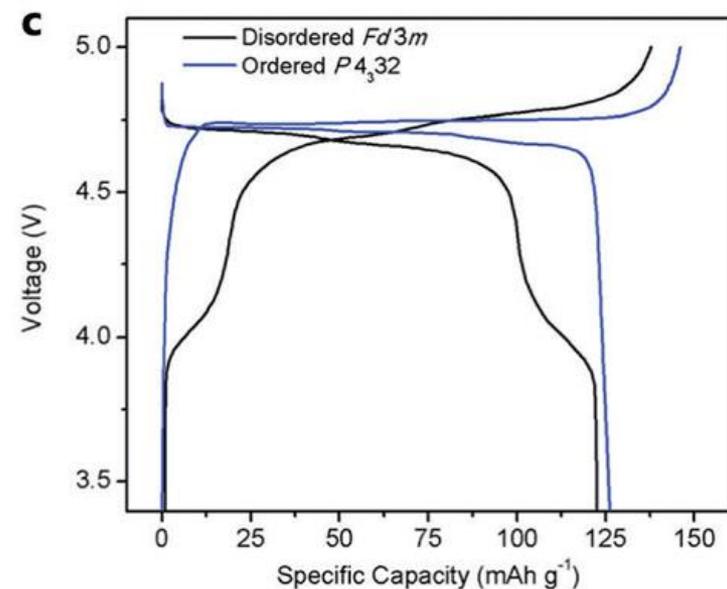
Ni and Mn disordered



Ni and Mn ordered



Charge-discharge curves



Disordered structure demonstrates better conductivity and electrochemical properties

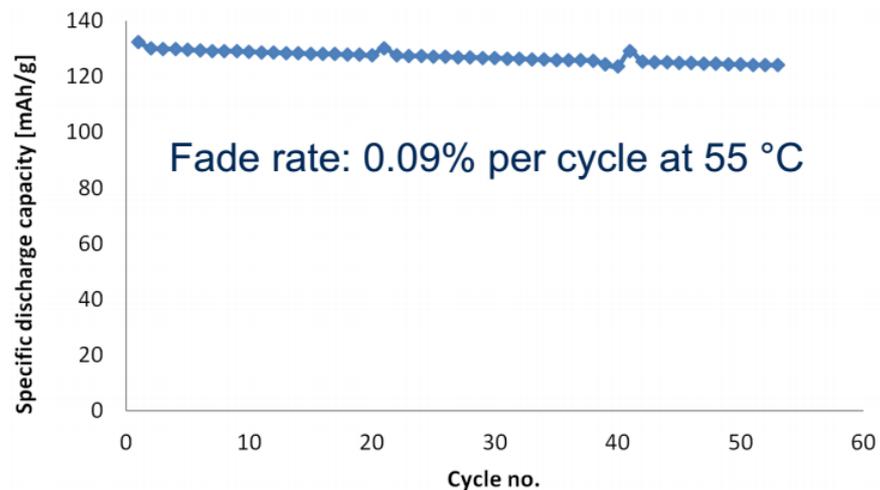
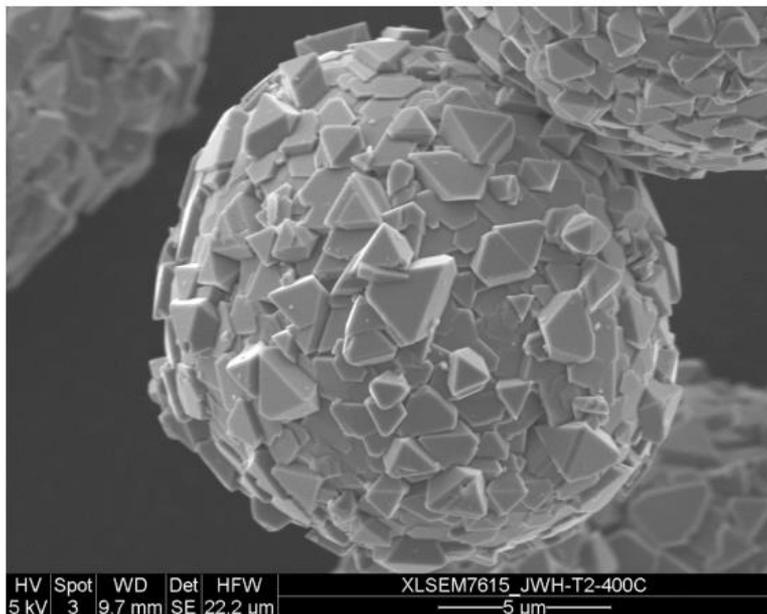
$\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ transitions are realized

Theoretical capacity 146 mAh/g



The single high-voltage material already developed for large-scale application

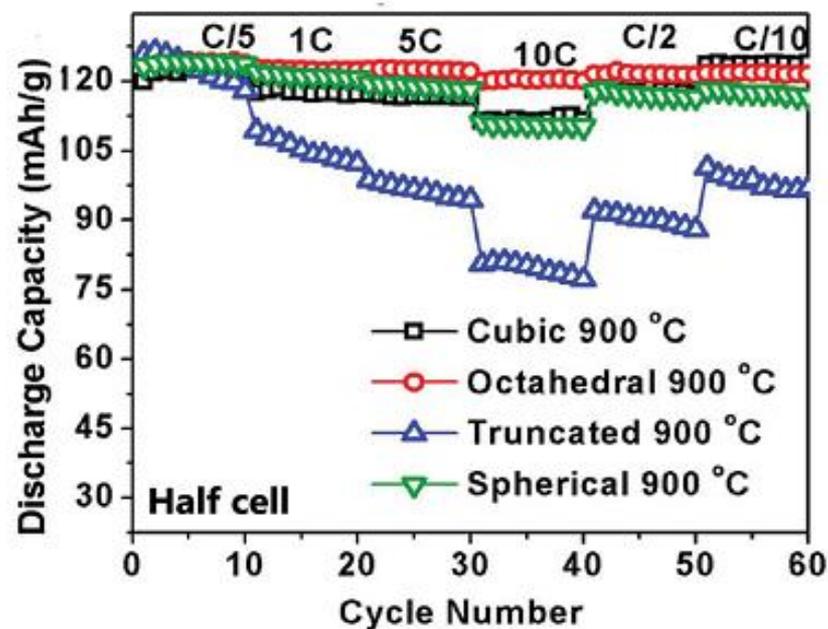
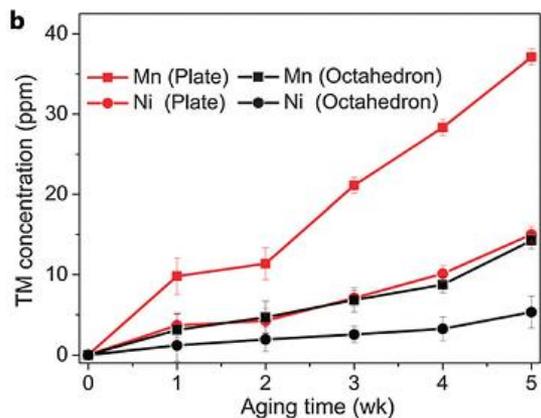
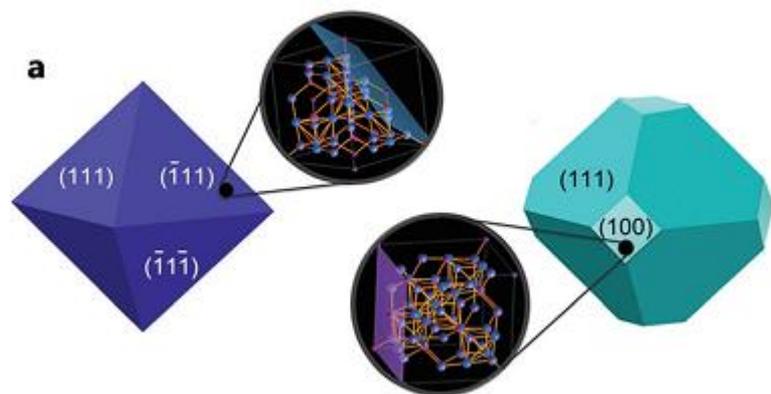
Haldor Topsoe (Denmark):



The form and orientation of the crystallites have large impact on the properties!

LiNi_{0.5}Mn_{1.5}O₄

Crystallites with different grain facets demonstrate different degradation rates

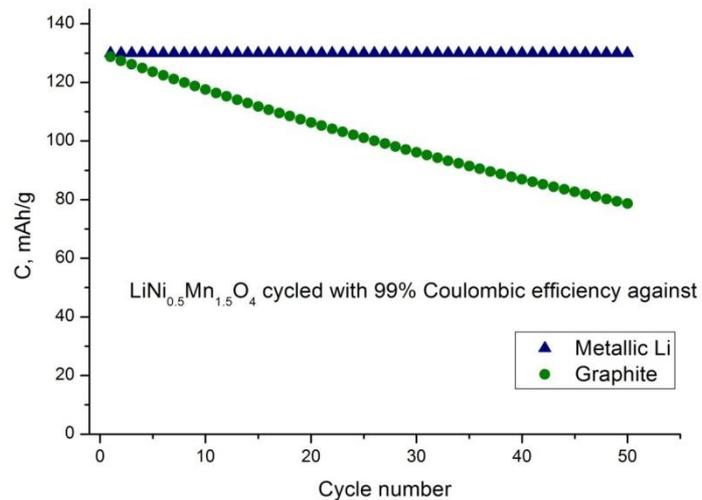


(111) facets are considered as preferable for enhanced Li⁺ transport and better passivation from parasitic processes

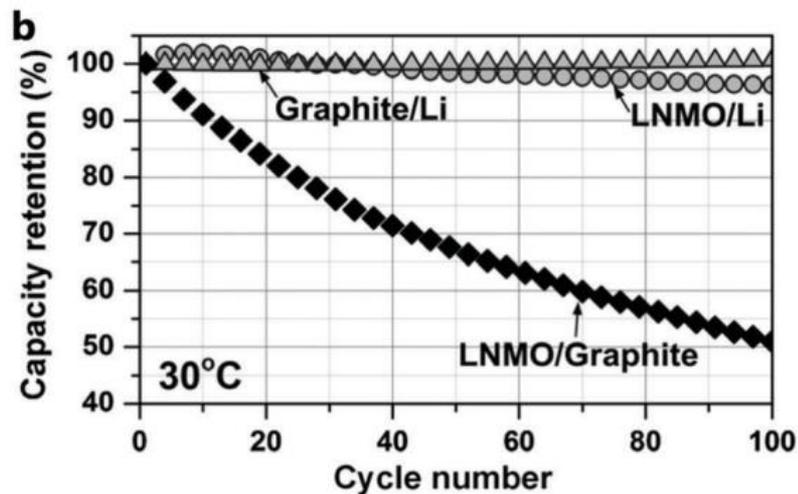


Main problem: Coulombic efficiency in conventional electrolytes is still not high enough

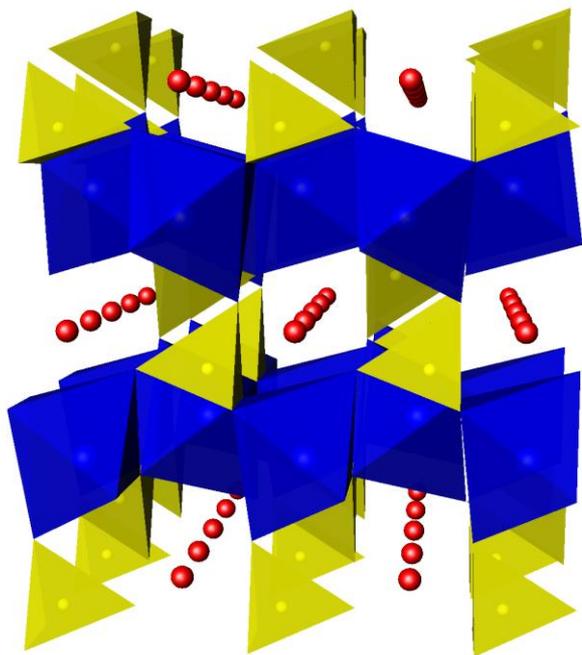
Thought experiment



Real experiment



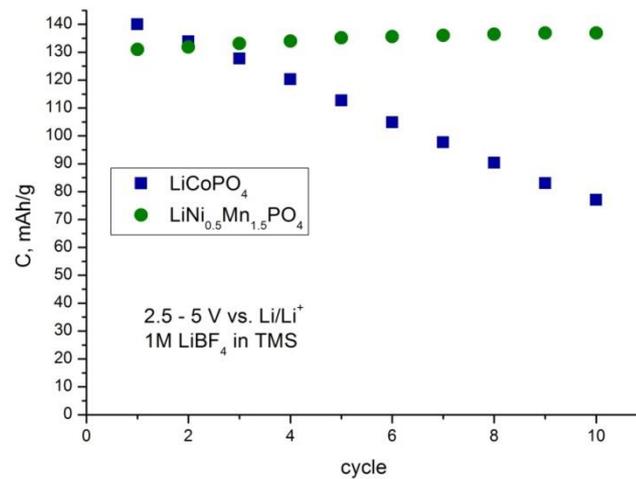
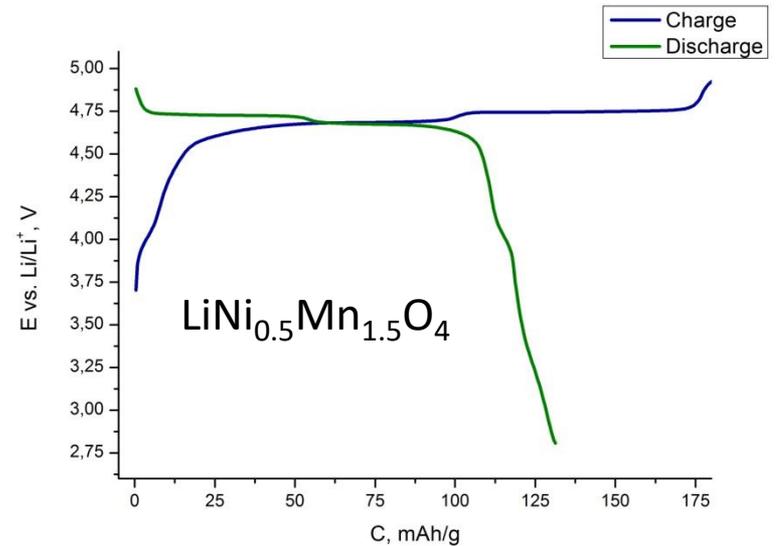
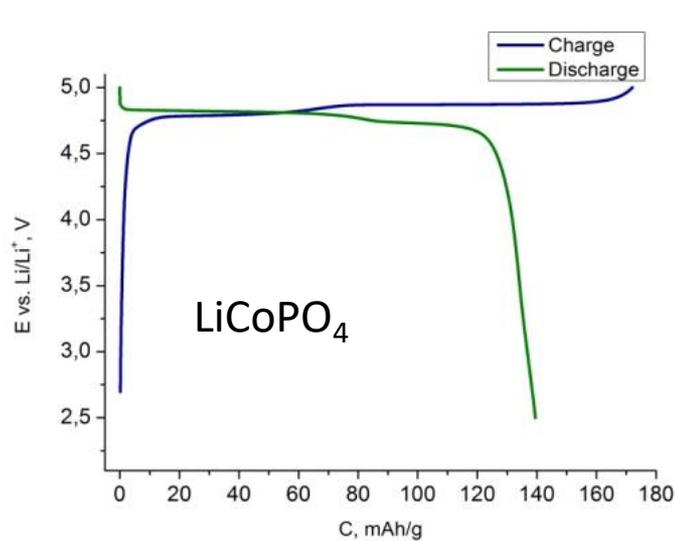
Olivine-type structure



	LiFePO ₄	LiMnPO ₄	LiCoPO ₄
E vs. Li/Li ⁺ , V	3.4	4.1	4.8
Theo. specific energy density, Wh/kg	580	700	800
Volume change	6.7%	11%	7%

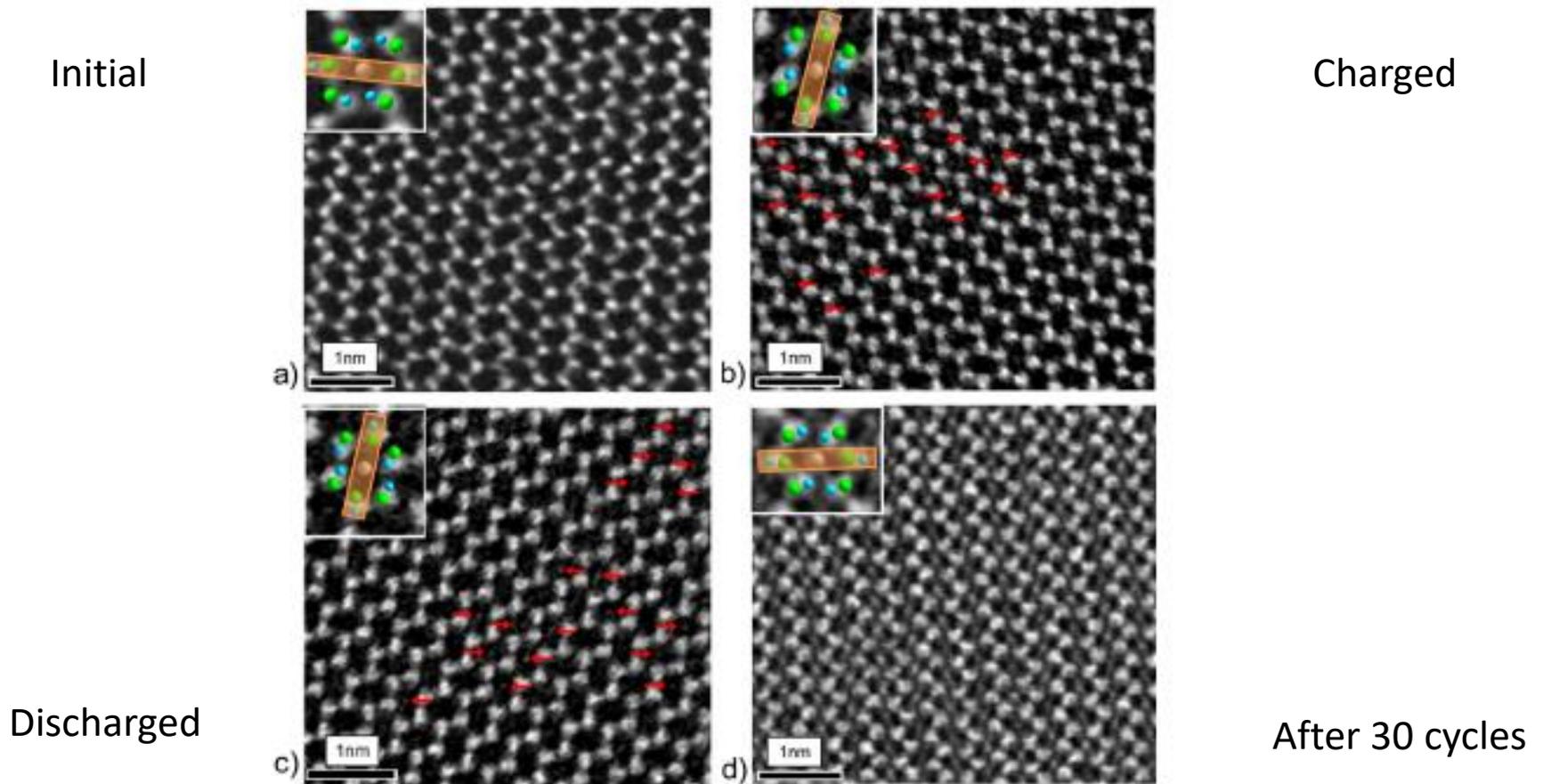
For LiCoPO₄, experimental capacities of 140-150 mAh/g are achieved

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ vs. LiCoPO_4



Similar charge-discharge voltage and curve shape, but LiCoPO_4 degrades much faster

HAADF STEM: electrochemically induced Li-Co anti-site defects

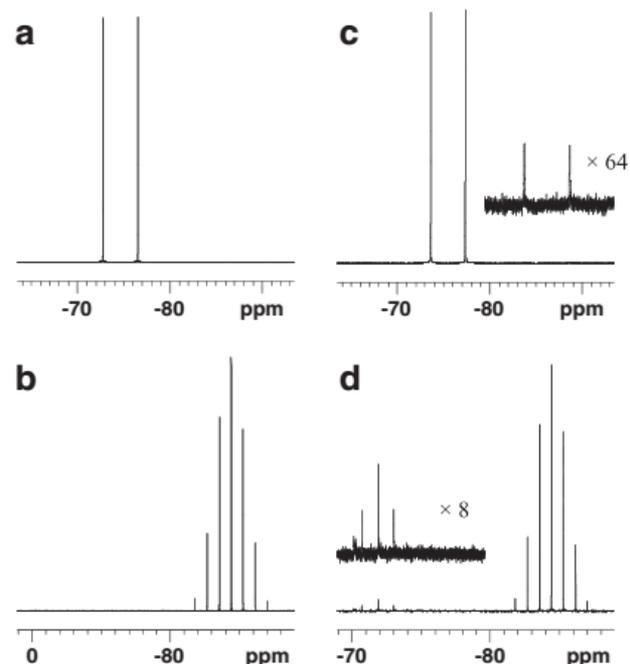
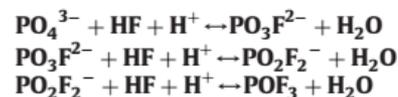


NMR study of LiPF₆-containing electrolyte

PO₂F₂⁻ anions detected in the electrolyte solution after cycling (typical only for cycling, but not for keeping within the same time interval). No traces of PO₂F₂⁻ anions after cycling of LiFePO₄ and LiMnPO₄.

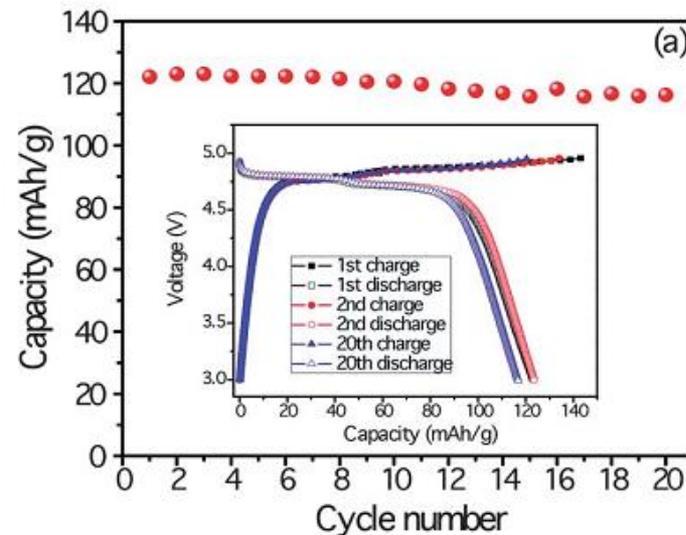
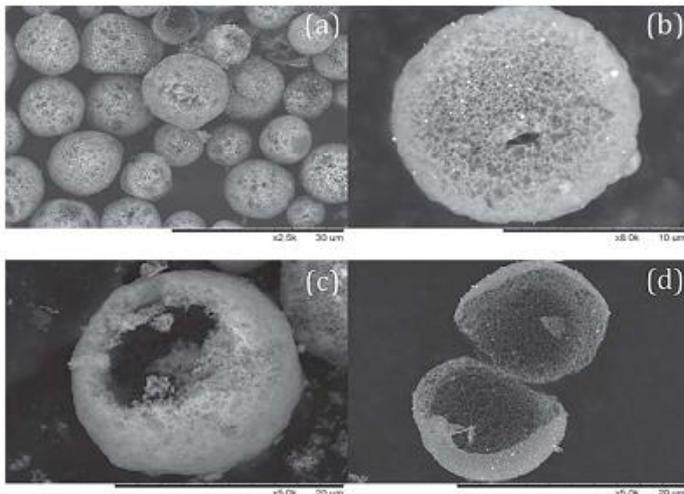


Nucleophilic attack of F⁻ anions on the P atoms, resulting in the breaking of the P—O bonds of the phosphate anions due to instability of delithiated CoPO₄ phase.



LiCoPO₄: possible improvements

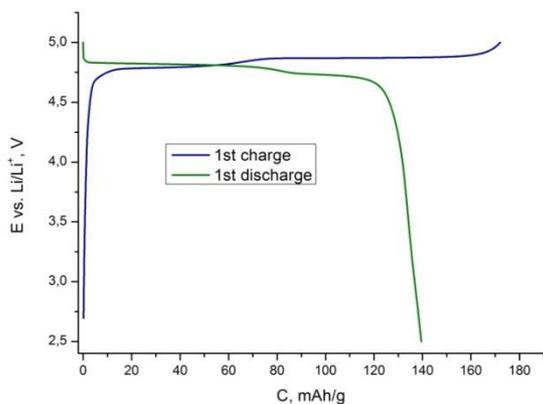
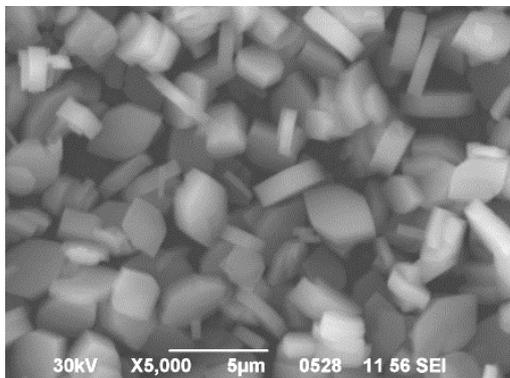
- 1) Reduce F⁻ amount in the electrolyte
- 2) Reduce surface area
- 3) Make a stable coating (an example is given at P. Gamzyukov poster)
- 4) Transform crystal structure - eliminate antisite defects, strengthen framework (see A. Grebenschikova poster)



Porous particle aggregates + LiBOB in electrolyte slow down degradation rate

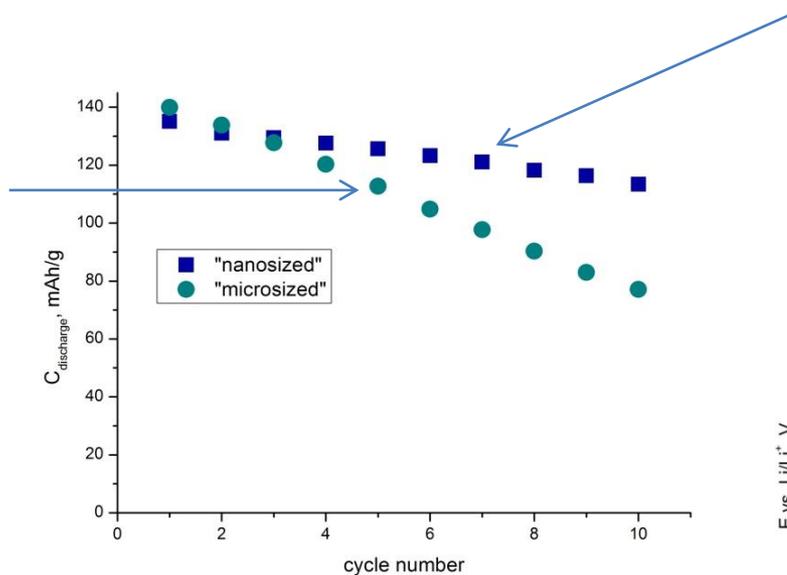
LiCoPO₄: particle size?

0.7-1 μm thickness

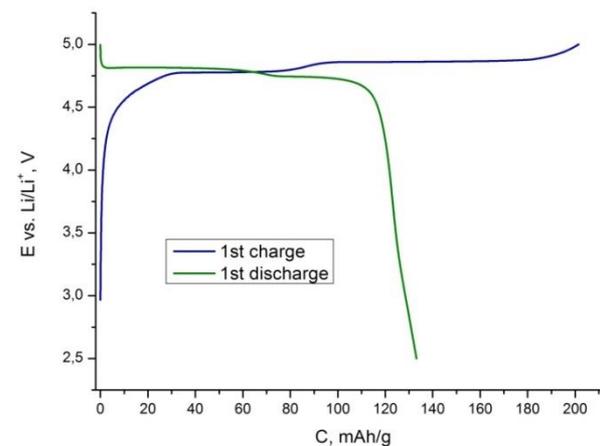
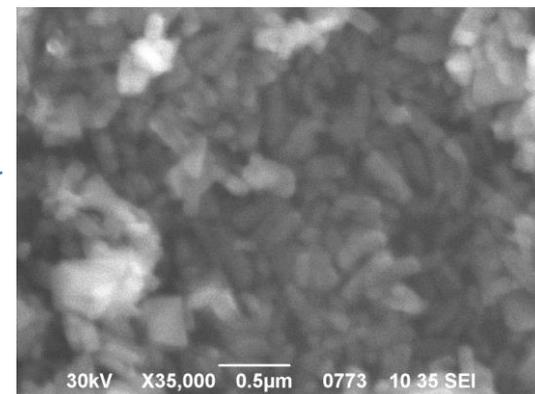


Higher initial capacity,
Coulombic efficiency

Solvothermal synthesis at different temperatures



0.1-0.2 μm thickness

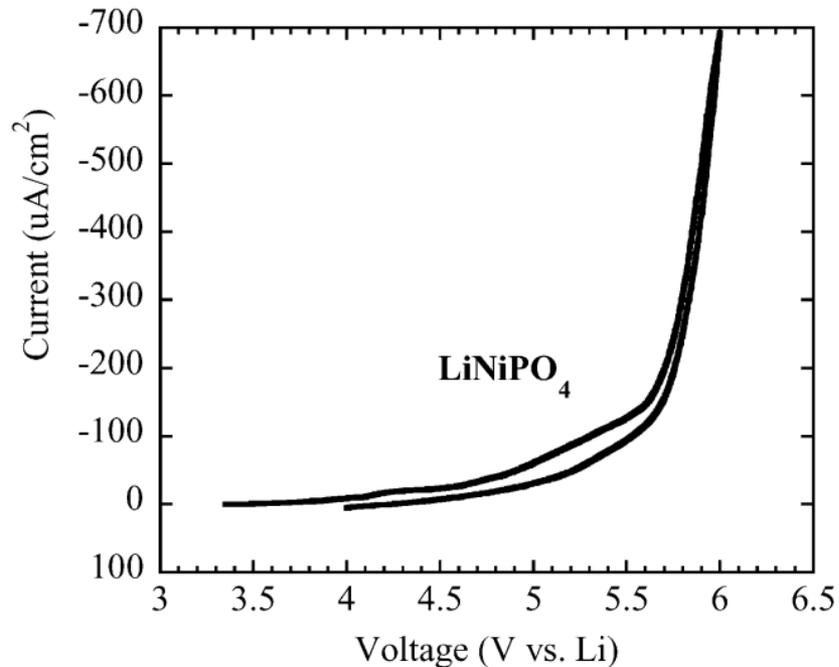


Better capacity retention
during cycling

LiNiPO₄: a “dark horse” among olivines

Theoretical values: capacity 169 mAh/g, voltage 5.1 V, energy density **860 Wh/kg**

No any reliable data on reversible Li⁺ (de)intercalation

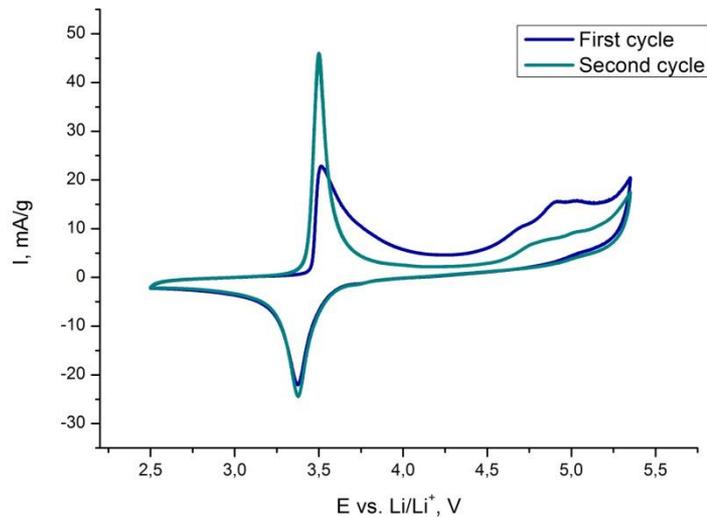
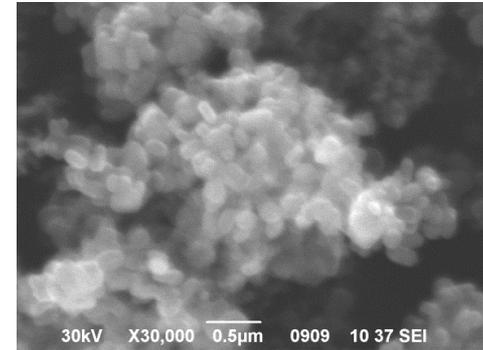


A typical electrochemical behavior of LiNiPO₄

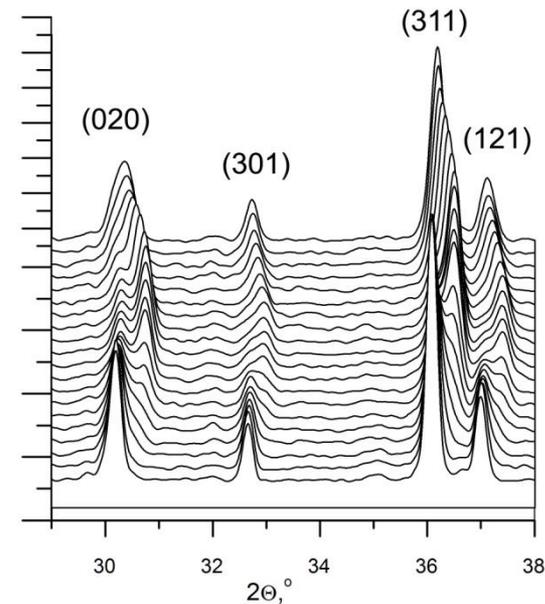
LiNi_{0.5}Fe_{0.5}PO₄: attempt to stabilize crystal structure

Single-phase LiFe_{0.5}Ni_{0.5}PO₄

Pnma, $a = 10.179(2) \text{ \AA}$, $b = 5.935(1) \text{ \AA}$, $c = 4.689(1) \text{ \AA}$, $V = 283.3(1) \text{ \AA}^3$

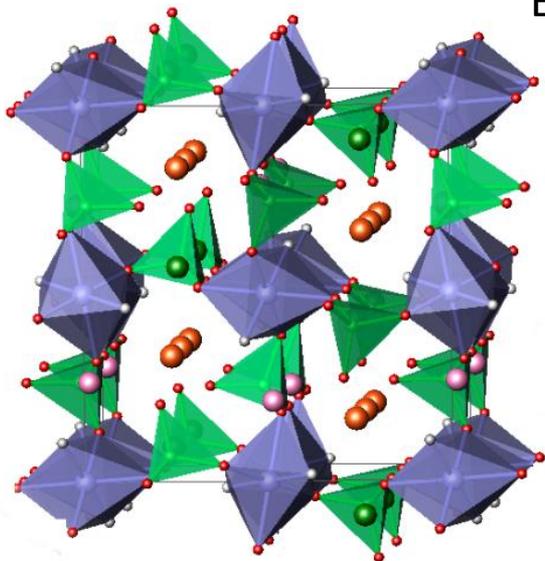


Reversible Fe²⁺/Fe³⁺ peaks, irreversible processes at $E > 4.5$ V. Significant changes after 1st cycle.



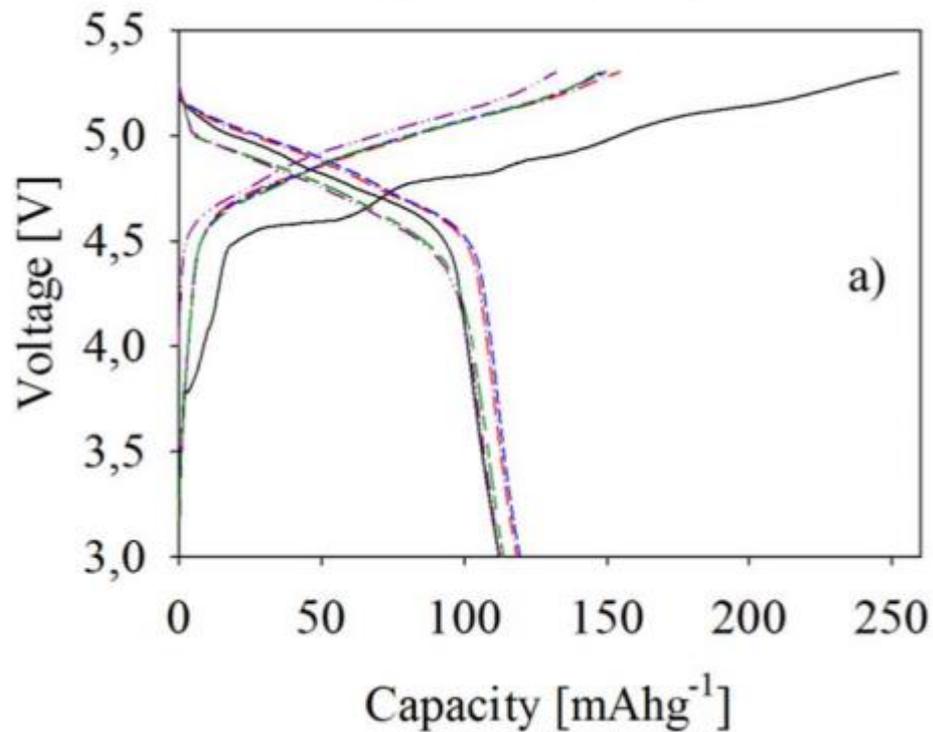
Operando XRD: only one phase transition + single-phase mechanism on discharge

$\text{Li}_2\text{CoPO}_4\text{F}$



Strong inductive effect on Co cations \rightarrow average discharge potential ~ 4.9 V

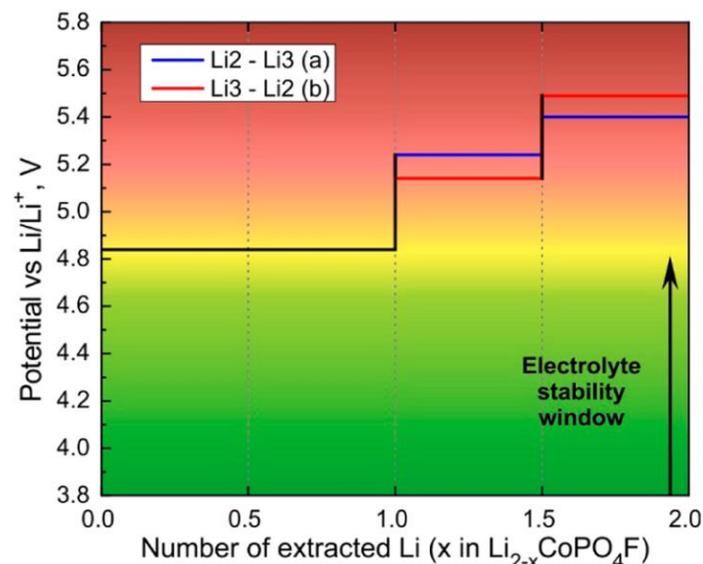
Experimentally achieved reversible capacity ~ 130 - 140 mAh/g



Li₂CoPO₄F

Theoretical capacity 145 mAh/g per 1 Li. Average discharge potential ~ 4.9 V. Three Li sites, Li1-Li1 is the most preferable diffusion path. However, calculated diffusion barriers for other sites are moderate → theoretically, 1.5 or even 2 Li may be extracted – almost **1500 Wh/kg**

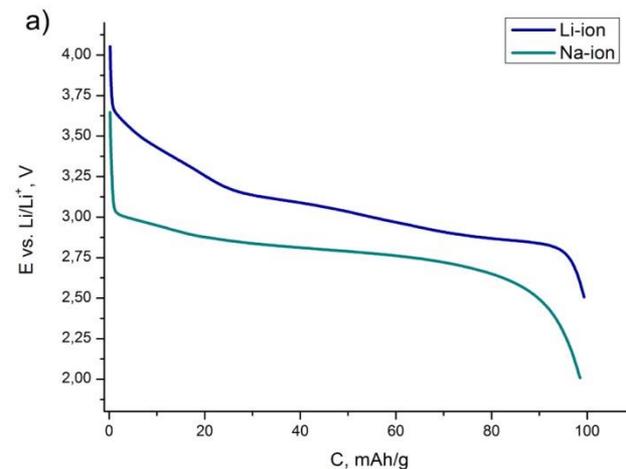
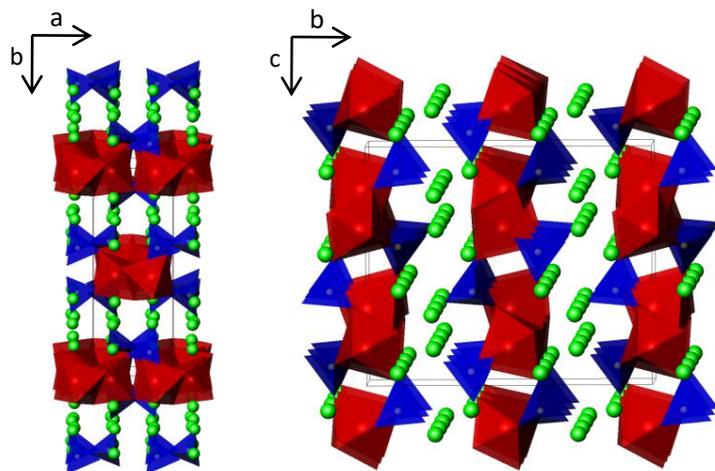
path no.	path length, Å	transition type	E_a , eV
1	3.677	Li1 ↔ Li2	0.35
2	3.330	Li1 ↔ Li1	0.12
3	3.130	Li3 ↔ Li1	0.43
4	3.110	Li3 ↔ Li1	0.34
5	3.167	Li1 ↔ Li1	0.41
6	2.416	Li1 ↔ Li2	0.37



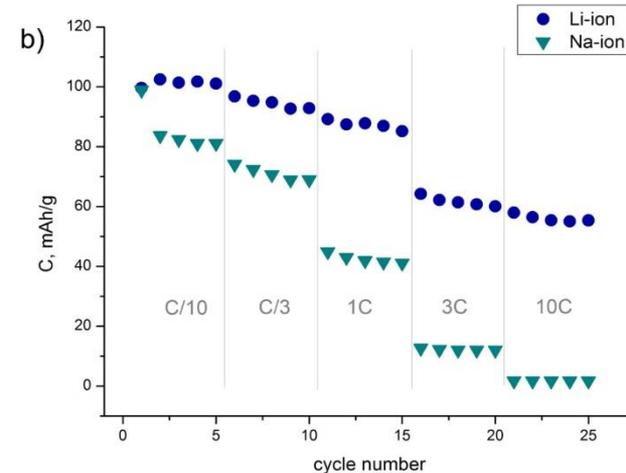
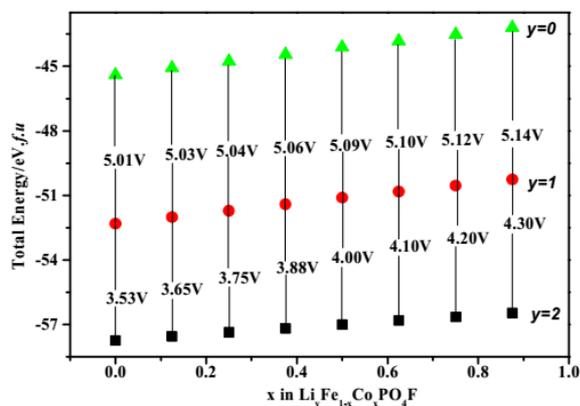
Calculated potentials of Li (de)intercalation from different sites

$(\text{Na,Li})_2\text{FePO}_4\text{F}$: is $\text{Fe}^{3+}/\text{Fe}^{4+}$ possible?

$(\text{Na,Li})_2\text{FePO}_4\text{F}$: 125/145 mAh/g per 1 Na/Li. Low volume change, fast diffusion (see I. Tereshchenko poster)



Ab initio calculations: second Li at ~ 5 V.

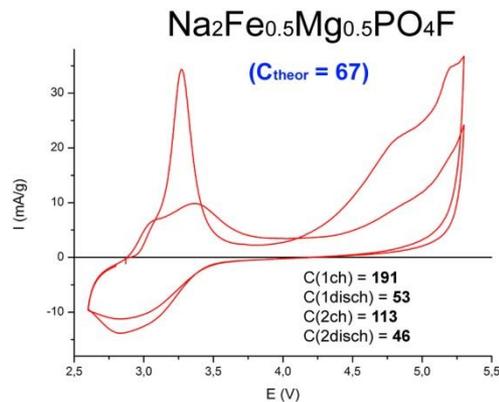
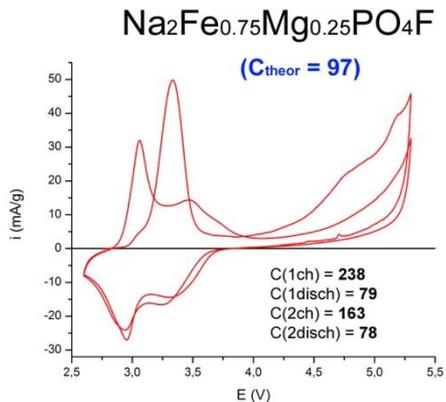
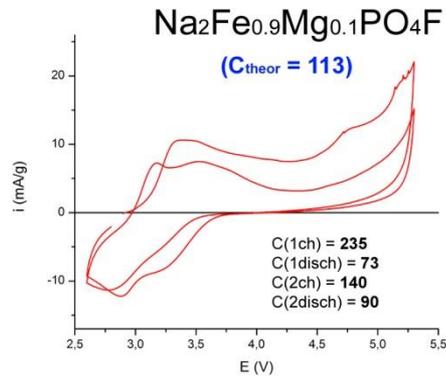
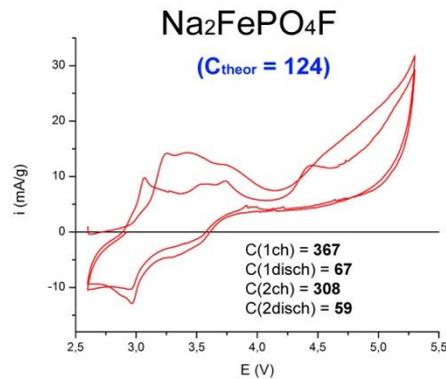


$(\text{Na,Li})_2\text{FePO}_4\text{F}$: is $\text{Fe}^{3+}/\text{Fe}^{4+}$ possible?

Two sites for A-cation in the structure, one is considered to be inactive

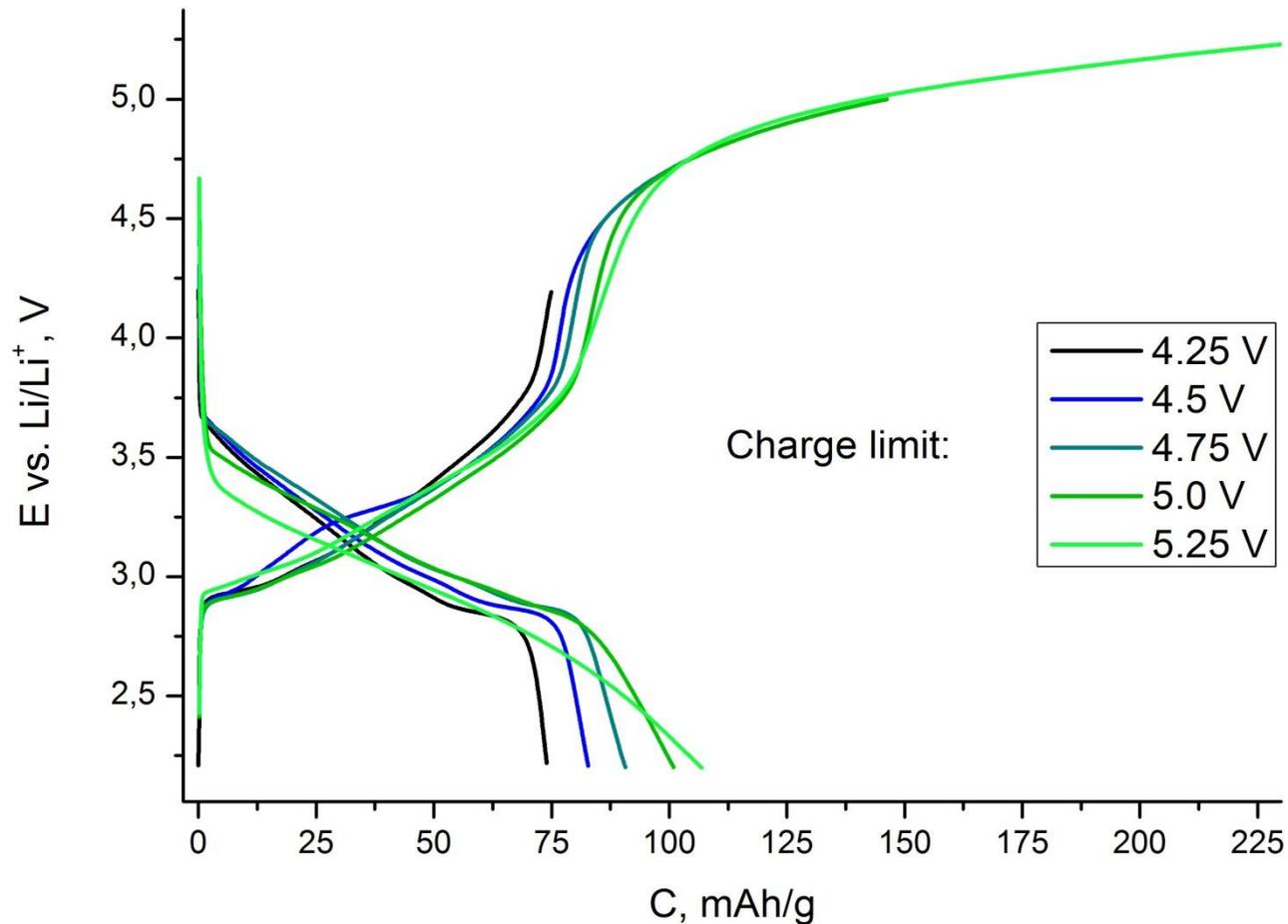


$(\text{Na,Li})_2\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4\text{F}$: only 1 A-cation position is needed to activate $\text{Fe}^{3+}/\text{Fe}^{4+}$



$(\text{Na,Li})_2\text{FePO}_4\text{F}$: is $\text{Fe}^{3+}/\text{Fe}^{4+}$ possible?

$(\text{Na,Li})_2\text{Fe}_{0.75}\text{Mg}_{0.25}\text{PO}_4\text{F}$: $C_{\text{theor}}(\text{Fe}^{2+}/\text{Fe}^{3+}) = 97 \text{ mAh/g}$



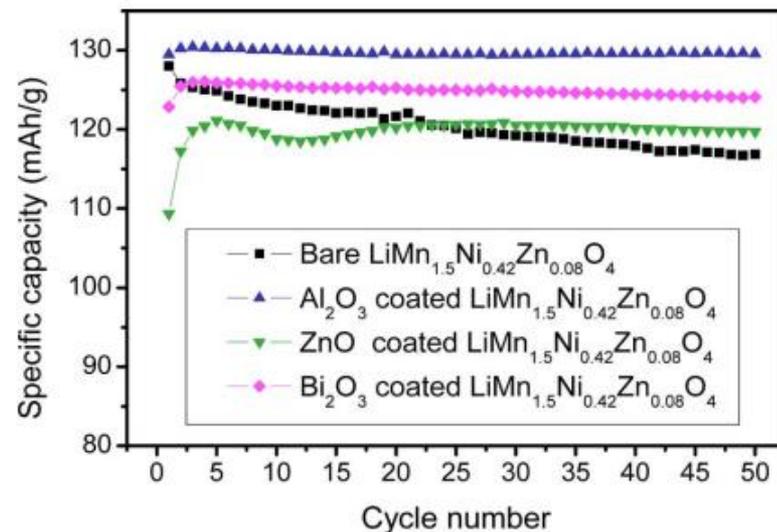
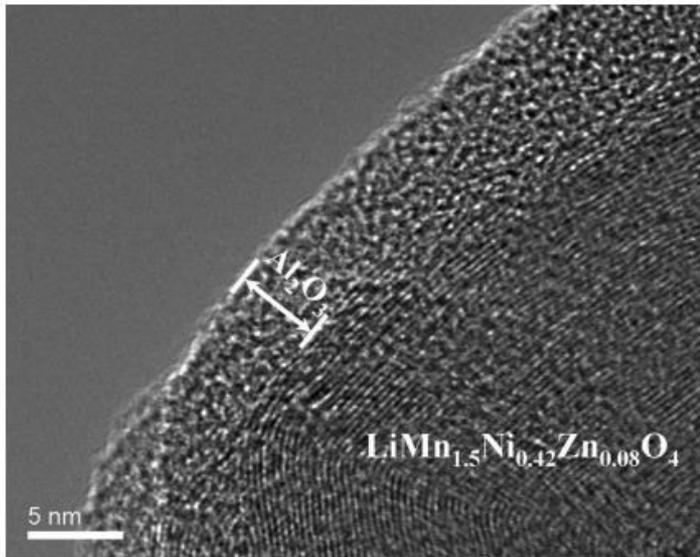
Only small capacity increase upon cycling at elevated potential range

Coatings

Protection against direct contact and electron transfer between cathode material and electrolyte

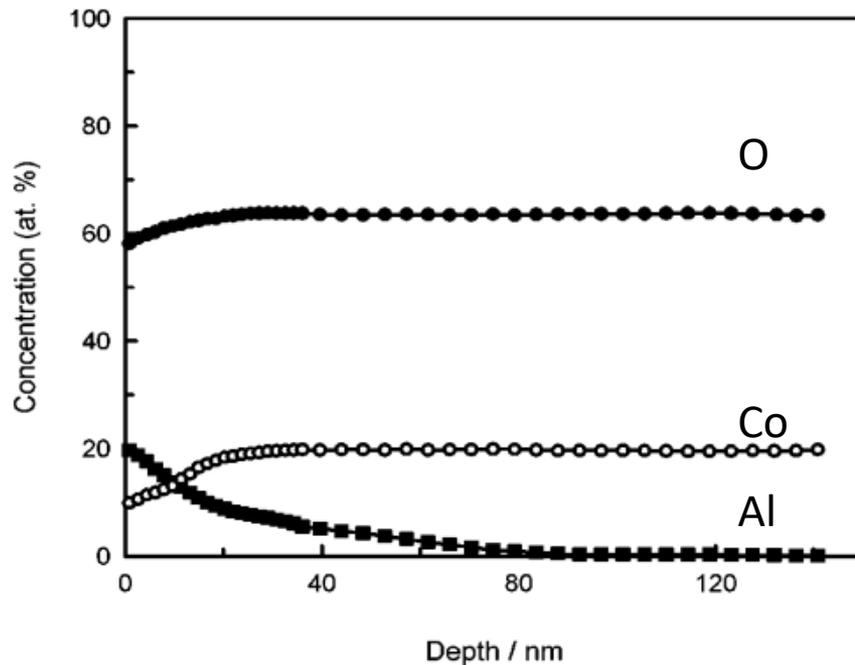
- 1) Oxides (Al_2O_3 , ZrO_2 , CeO_2 , LiAlO_2 etc.)
- 2) Fluorides (AlF_3 , BaF_2 etc.)
- 3) Phosphates (AlPO_4 , Li_3PO_4 etc.)
- 4) Borates (LiBO_2 , $\text{Li}_2\text{B}_4\text{O}_7$ etc.)
- 5) Unstable core – stable shell (e.g. LiCoPO_4 – LiFePO_4)

Typical effect: reduce in initial charge/discharge capacity, increase in cycle life
Main problem: hard to obtain reproducible results for powder materials

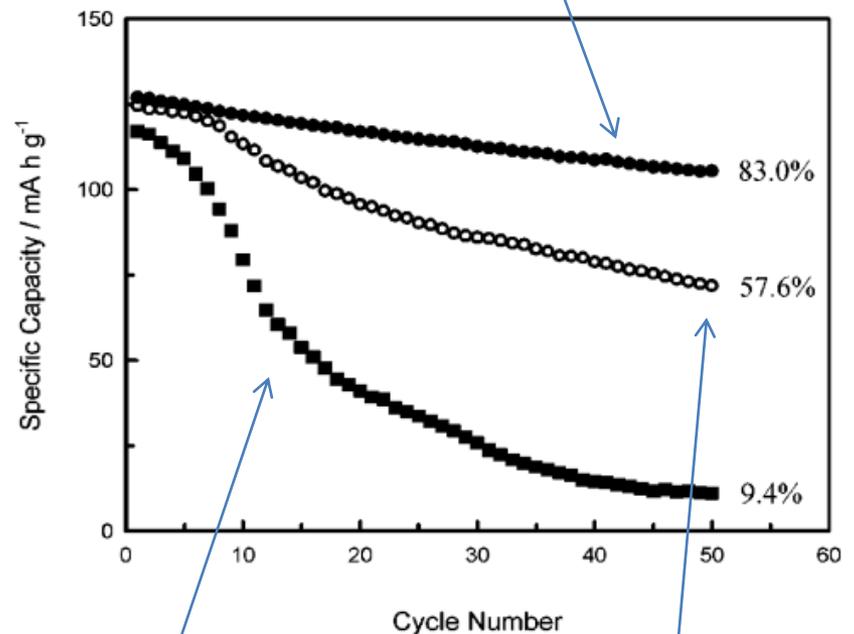


Coatings

Thin-film LiCoPO_4 coated with Al_2O_3 layer



Al_2O_3 -coated LCP in LiBF_4 -based electrolyte

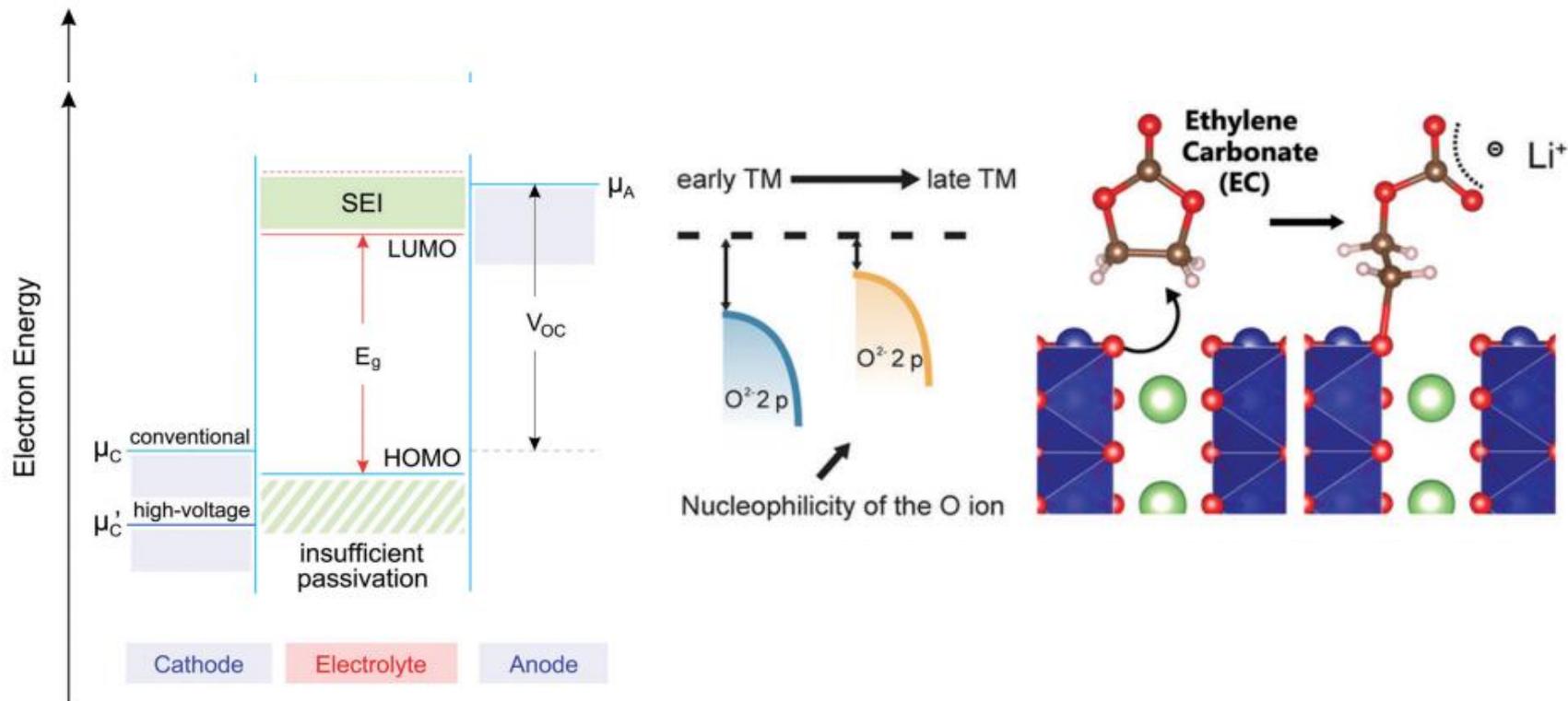


LCP in LiBF_4 -based electrolyte
LCP in LiPF_6 -based electrolyte

It's hard to organize both carbon and protective inorganic coatings

Electrolytes

Voltage window of conventional electrolyte (1M LiPF₆ in EC:DEC = 1.1):



There is no effective passivation in high-voltage region – in contrary with low-voltage (anode) SEI

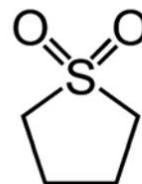
Electrolytes

Possible directions of improving:

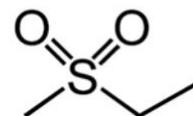
- 1) Stable solvents (sulfones, nitriles, fluorocarbonates)
- 2) SEI-forming additives
- 3) Ionic liquids
- 4) Superconcentrated solutions
- 5) Solid electrolytes

Sulfones

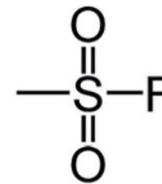
Low cost, wide electrochemical window, good thermal stability



TMS



EMS

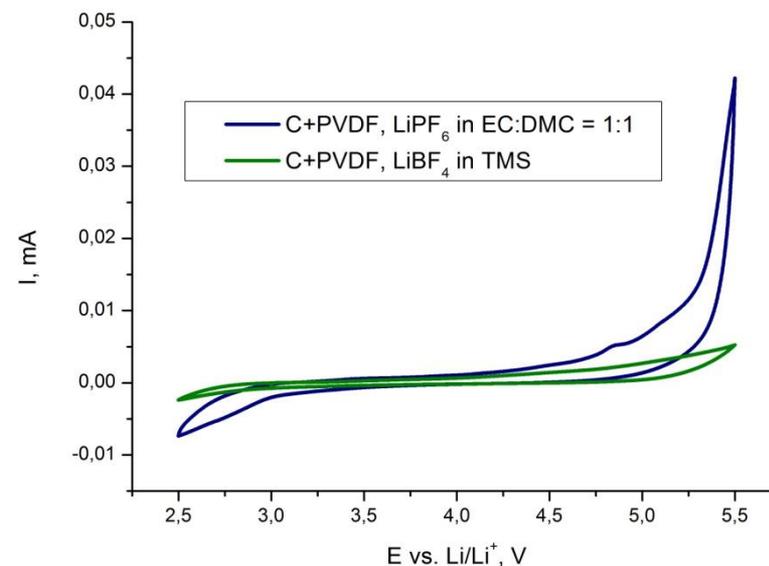


FMS

Table 2. Summary of the physical properties and electrochemical window of sulfone-based electrolytes.^[73,78–80]

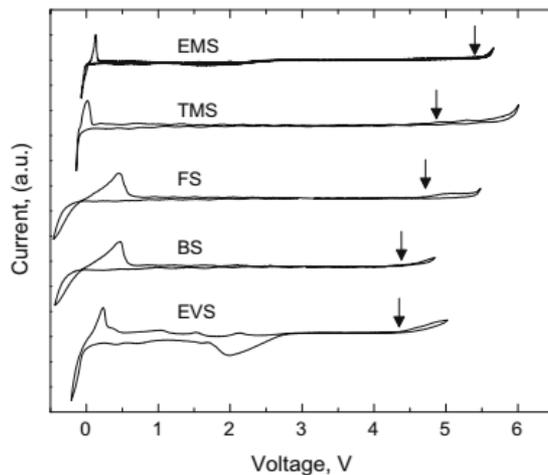
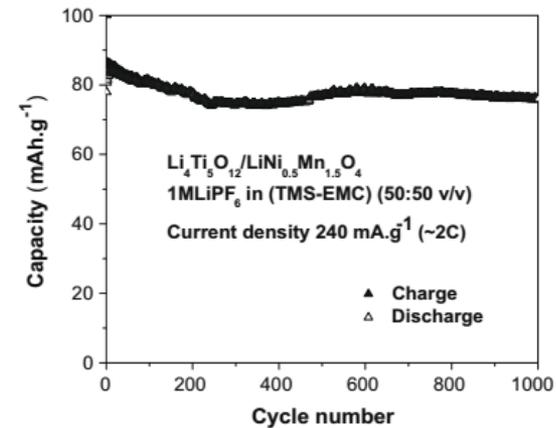
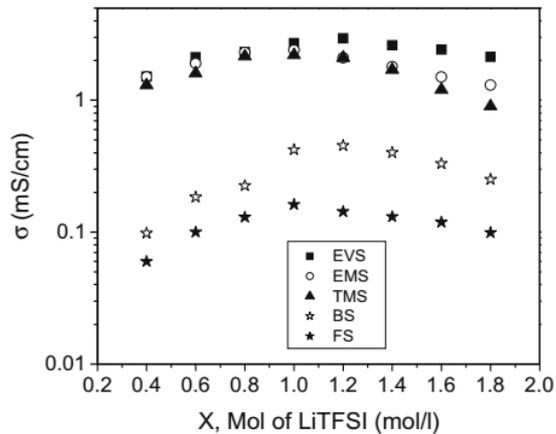
Solvent ^[a]	T_m [°C]	T_b [°C]	σ_{25} [mS cm ⁻¹]	Window (vs. Li ⁺ /Li)
DMS	110	238	/	/
EMS	36.5	240	6.3 (1 M LiTFSI)	5.9
MEMS	15	275	2.8 (1 M LiTFSI)	5.6
EMES	2	286	2.8 (1 M LiTFSI)	5.6
EMEES	< 0	> 290	3.1 (1 M LiTFSI)	5.3
ESCP	38	328	3.2 (1 M LiTFSI)	~5.5
TMS(SL)	27	285	2.5 (1 M LiPF ₆)	5.8
FPMS	56	180	0.035 (1 M LiTFSI)	5.8/LiPF ₆ + DMC

[a] DMS = dimethyl sulfone; EMS = ethyl methyl sulfone; MEMS = methoxyethyl methyl sulfone; EMES = ethyl methoxyethyl sulfone; EMEES = ethyl methoxyethoxyethyl sulfone; ESCP = ethyl sulfonyl cyclopentane; TMS(SL) = tetramethylene sulfone or sulfolane; FPMS = 3,3,3-trifluoropropyl methyl sulfone.



Sulfones

TMS, EMS: excellent oxidative stability, Coulombic efficiency with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material, low volatility and flammability

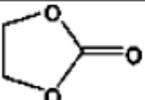
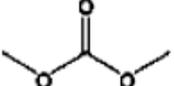
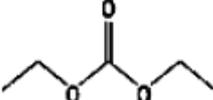


Nitriles

Wide stability window, wide working temperature range.

Low solubility of the conventional salts (LiPF_6 , LiBF_4) \rightarrow using in mixture with carbonates

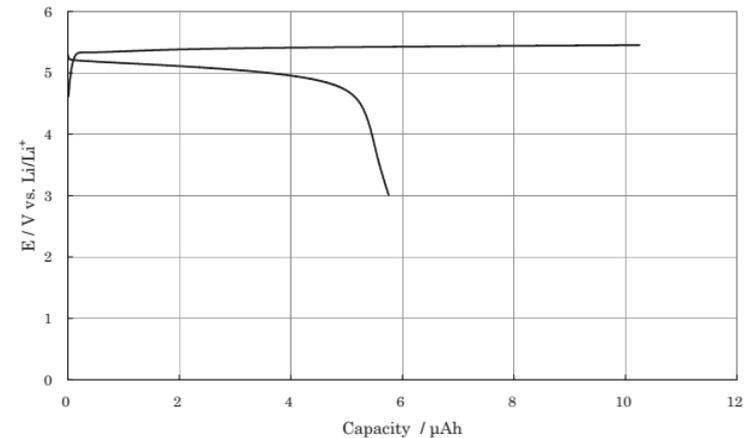
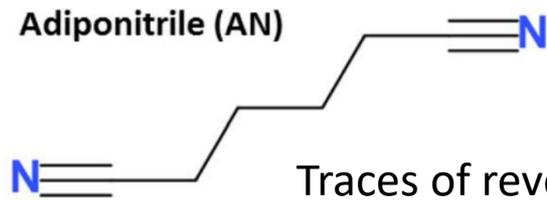
Table 3. List of physical properties and electrochemical windows of dinitrile solvents and common carbon solvents used in lithium electrolytes.^[19]

Solvent	Structure	ϵ ^[a]	η (cp) ^[b]	T_m [°C] ^[c]	T_b [°C] ^[d]	T_f [°C] ^[e]	Window (vs. Li^+/Li)
EC		89	2	35	244	150	5.5
DMC		3	0.7	3	90	18	5.3
DEC		3	0.8	-43	127	25	5.15
dinitriles	$\text{CN}(\text{CH}_2)_n\text{CN}$ n						
malononitrile (MAN)	1	48	solid	31	220	86	-
succinonitrile (SCN)	2	55	2.7	54	266	113	-
glutaronitrile (GLN)	3	37	5.3	-29	287	113	7.3
adiponitrile (ADN)	4	30	6.1	1	295	163	6.9
pimelonitrile (PMN)	5	28	7.6	-31	175	112	7.0
suberonitrile (SUN)	6	25	8.2	-4	325	110	6.8
azelanitrile (AZN)	7	23	8.7	-18	209	> 110	-
sebaconitrile (SEN)	8	22	10.7	8	200	> 113	7.2

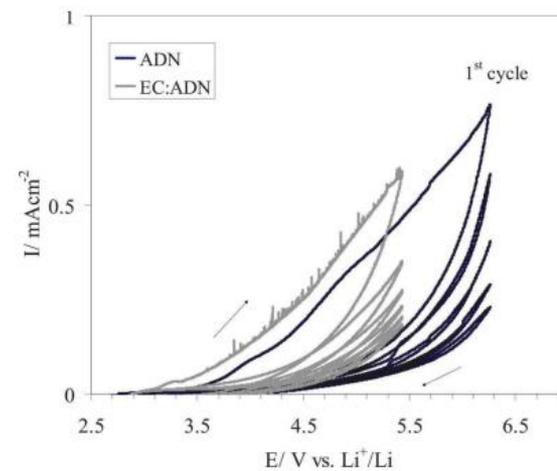
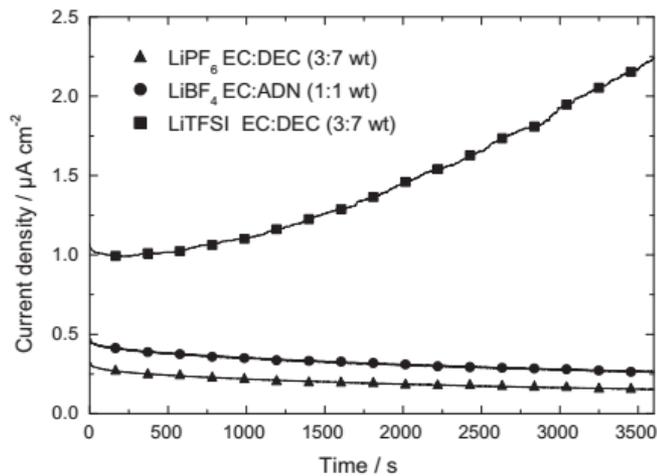
[a] ϵ is the dielectric constant. [b] η is the viscosity. [c] T_m is the melting point. [d] T_b is the boiling point. [e] T_f is the flash temperature; T_{auto} is the auto-ignition temperature.

Adiponitrile

Most common:

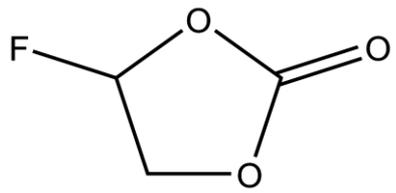


Passivating Al current collector in the presence of ADN and LiTFSI salt:



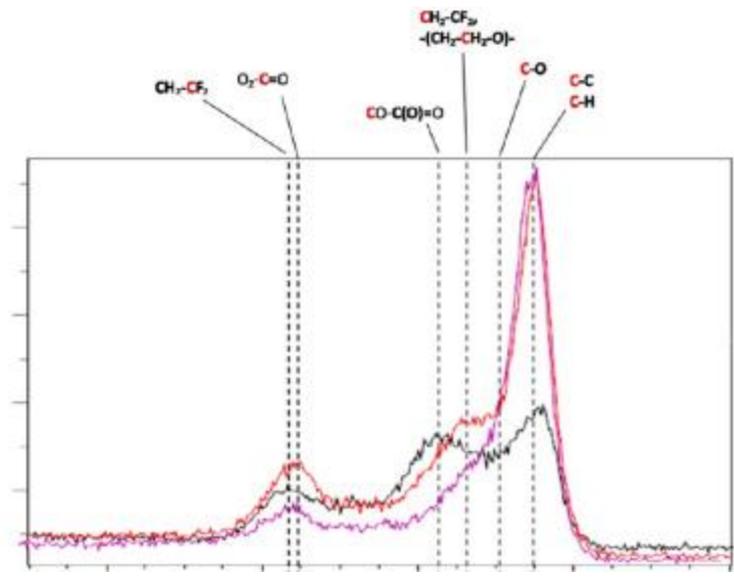
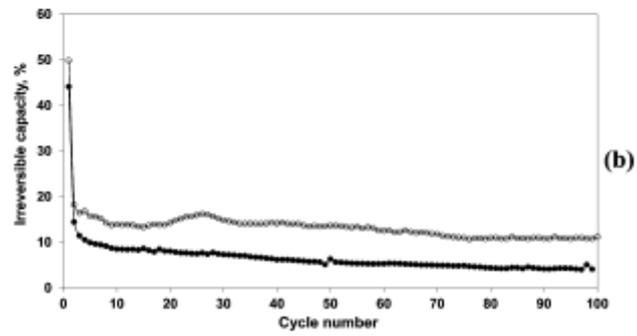
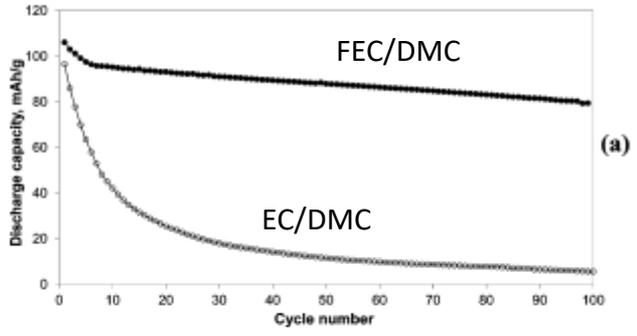
Fluorinated solvents

Fluoroethylene Carbonate:



Sigma-Aldrich:
FEC (99%) 25 g - ~ 50 000 r.

LiCoPO₄:



Initial (magenta), cycled in EC (black), cycled with FEC (red)

FEC: fluorinated species at the surface,
no exfoliation and oxidation of C

Additives: EC or not EC?

Studies of Lithium Intercalation into Carbons Using Nonaqueous Electrochemical Cells

Rosamaría Fong, Ulrich von Sacken, and J. R. Dahn

Moli Energy Limited, Burnaby, British Columbia, Canada V5C 4G2

1990:

ABSTRACT

Li/graphite and Li/petroleum coke cells using a 1M LiAsF₆ in a 50:50 mixture of propylene carbonate (PC) and ethylene carbonate (EC) electrolyte exhibit irreversible reactions only on the first discharge. These irreversible reactions are associated with electrolyte decomposition and cause the formation of a passivating film or solid electrolyte interphase on the surface of the carbon. The amount of electrolyte decomposition is proportional to the specific surface area of the carbon electrode. When all the available surface area is coated with the film of decomposition products, further decomposition reactions stop. In subsequent cycles, these cells exhibit excellent reversibility and can be cycled without capacity loss.

Enabling linear alkyl carbonate electrolytes for high voltage Li-ion cells

Jian Xia^a, Remi Petibon^b, Deijun Xiong^b, Lin Ma^b, J.R. Dahn^{a, b, *}

^a Dept. of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, B3H3J5, Canada

^b Dept. of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H4R2, Canada

2016:

H I G H L I G H T S

- Ethylene carbonate (EC) is actually detrimental for Li-ion cells at high voltages.
- EC-free linear alkyl carbonate electrolytes with various "enablers" were developed.
- Linear alkyl carbonate electrolytes have very good performance at high voltages.

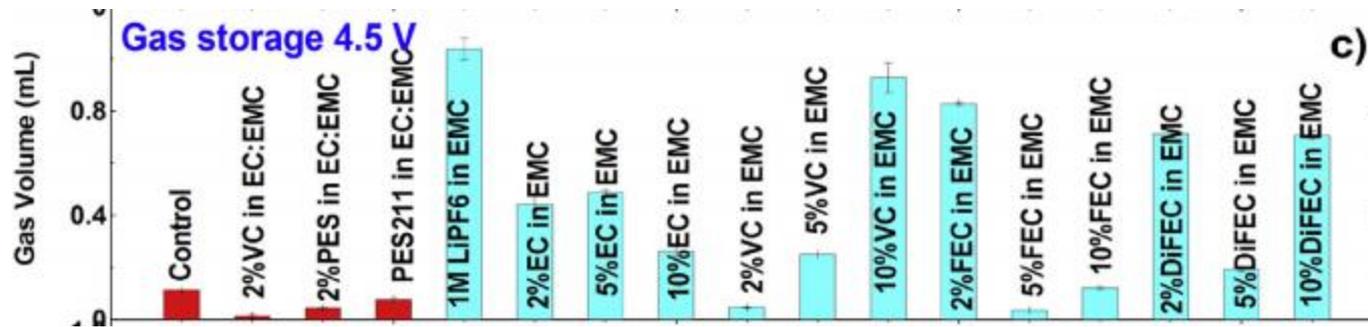
Additives: EC replacement

Table 1

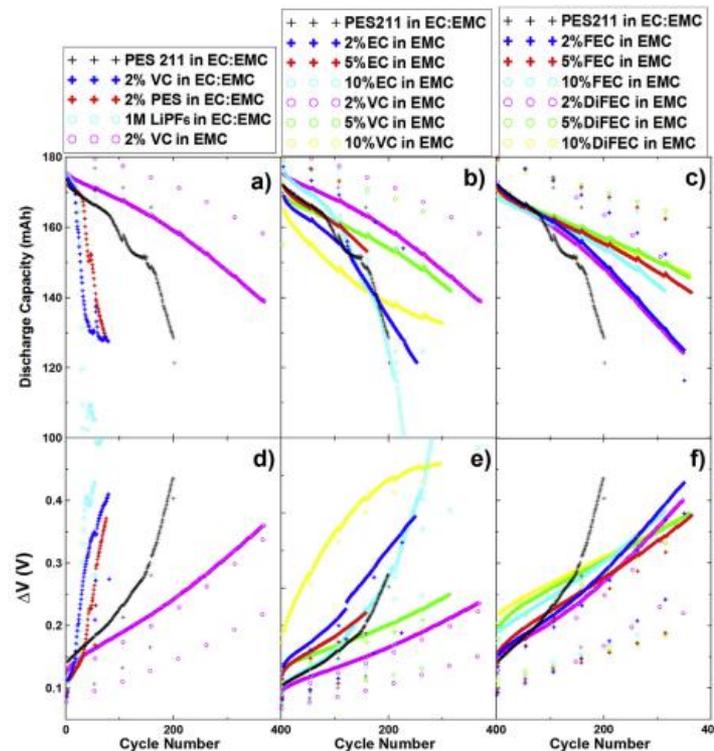
List of abbreviations, additives and their ability to passivate the graphite electrode when used in 1 M LiPF₆ in EMC (no EC).

Additives	Ability to passivate the graphite electrode
EC - ethylene carbonate	Yes
VC - vinylene carbonate	Yes
PES - prop-1-ene,1,3-sultone	Yes
FEC - fluoroethylene carbonate	Yes
DiFEC - (4R,5S)-4,5-Difluoro-1,3-dioxolan-2-one	Yes
MEC - methylene-ethylene carbonate	Yes
SA - succinic anhydride (SA)	Yes
MA - maleic anhydride	No
DPC - diphenyl carbonate	No
VEC – vinyl ethylene carbonate	No

Additives

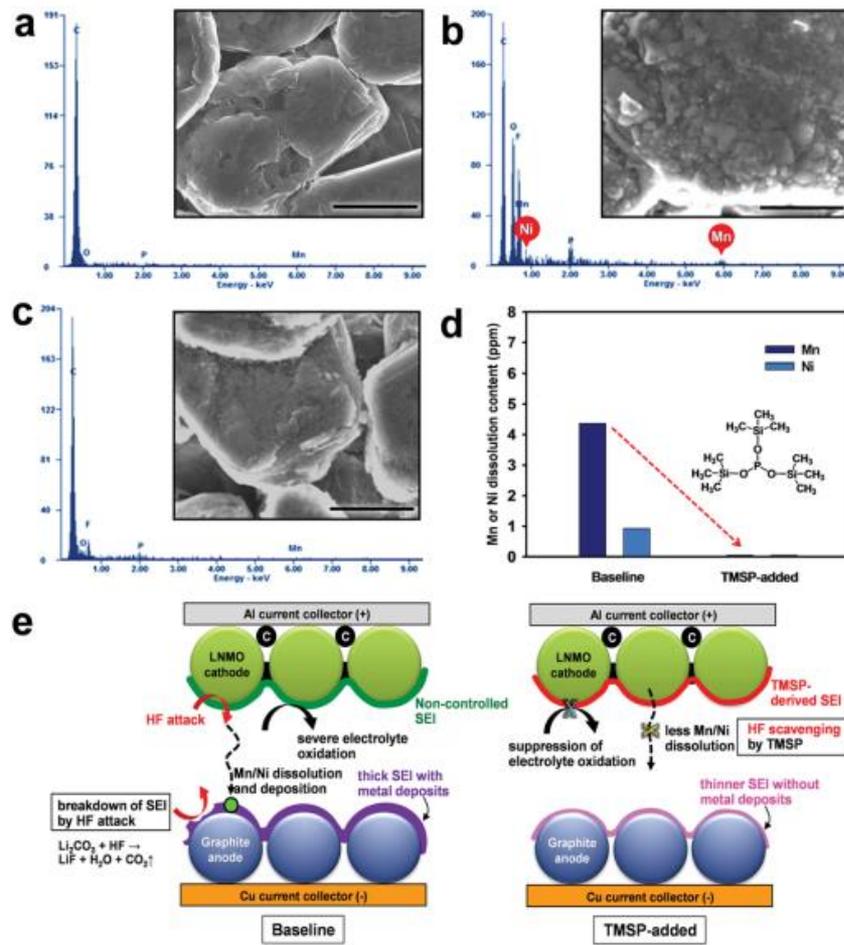
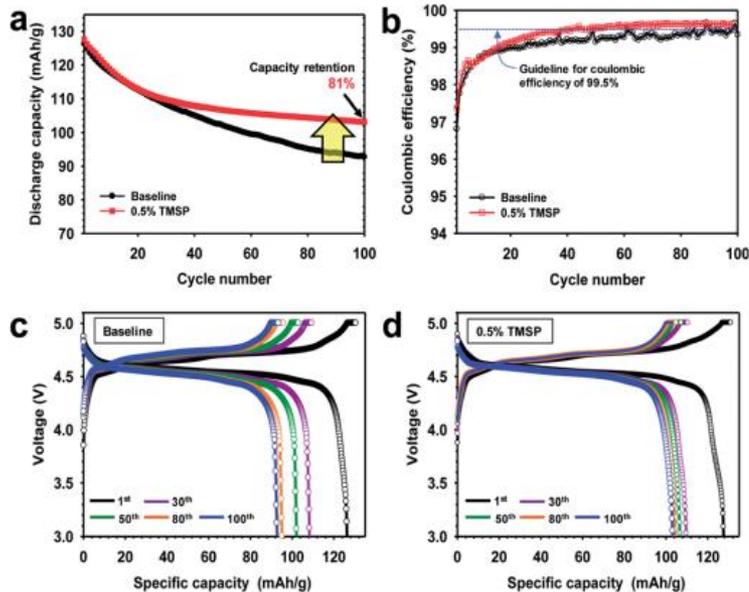
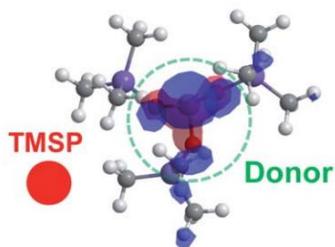


2% VC or 5% FEC additives provide high-quality SEI on both graphite anode and NMC cathode at high (up to 4.5 V) potentials



Additives

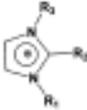
Tris(trimethylsilyl) phosphite (TMSP): reacts with HF traces, prevents d-metal dissolution, forms stable cathode SEI



Ionic liquids

RTIL = liquid salt (anion + cation, without solvents). good thermal stability, non-flammability, low vapor pressure and high oxidation resistance at high voltages. BUT: high cost, high viscosity

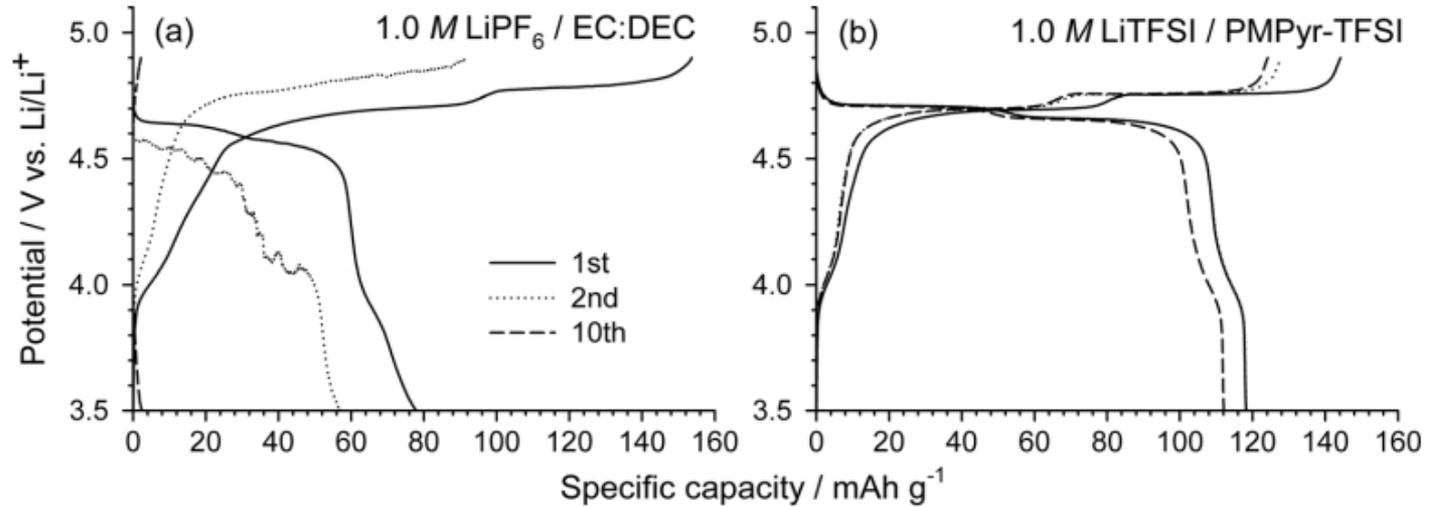
A)

Cation	Anion	T_m (°C)	E_{red} (V vs. Li)	E_{ox} (V vs. Li)
 imidazolium	TFSI	0.8 ($R_1=Me$; $R_2=H, R_3=Et$)	1.0 ($R_1=Me$; $R_2=H, R_3=Et$)	5.3 ($R_1=Me$; $R_2=H, R_3=Et$)
	BF_4^-	15 ($R_{1,3}=Me$)		
	PF_6^-	58–62 ($R_{1,3}=Me$)		
	TFSI	15 ($R_{1,2}=Me$; $R_3=Pr$)	0.64 ($R_1=Me$; $R_2=H, R_3=Hex$)	5.73 ($R_1=Me$; $R_2=H, R_3=Hex$)
	FSI	-12 ($R_1=Me$; $R_2=H, R_3=Et$)	0.7	5.3
	$B(CN)_4^-$	12.6 ($R_1=Me$; $R_2=H, R_3=Et$)		
 pyrrolidinium	TFSI		0.2 ($R_1=Me$; $R_2=Pr$)	5.6 ($R_1=Me$; $R_2=Pr$)
	FSI	-9 ($R_1=Me$; $R_2=Pr$)		
		-18 ($R_1=Me$; $R_2=Bu$)		
	TFSI	-7.9 ($R_1=Et$; $R_2=Bu$)		

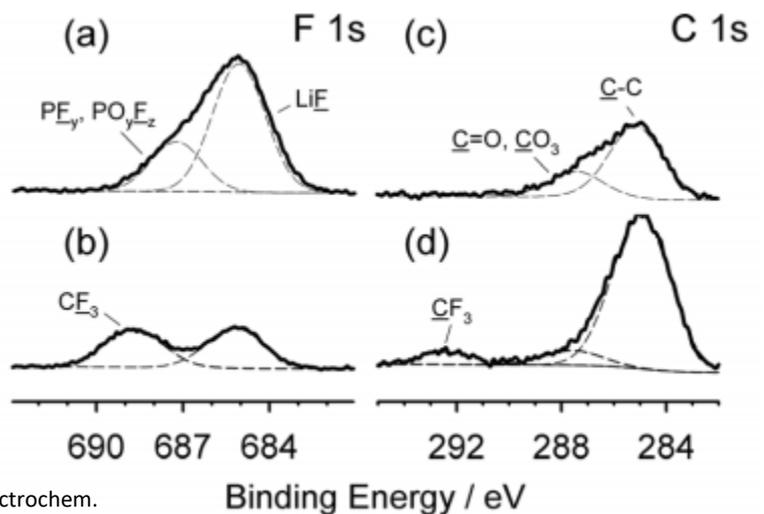
Ionic liquids

Propylmethylpyrrolidinium bis(trifluoromethylsulfonyl)imide:

50°C:



Conventional electrolyte: LiF-containing surface film grows with cycling, increasing R_{ct}
 PMPyr-TFSI: more organic C-C and C-F species, thickness is much lower.

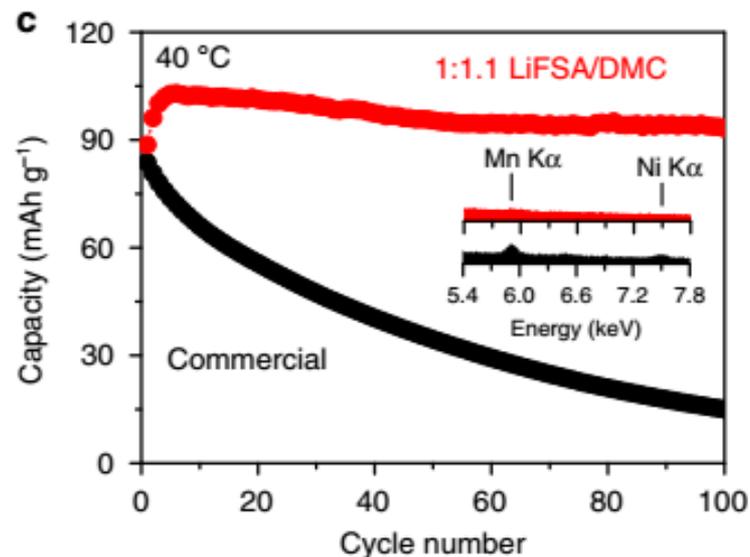
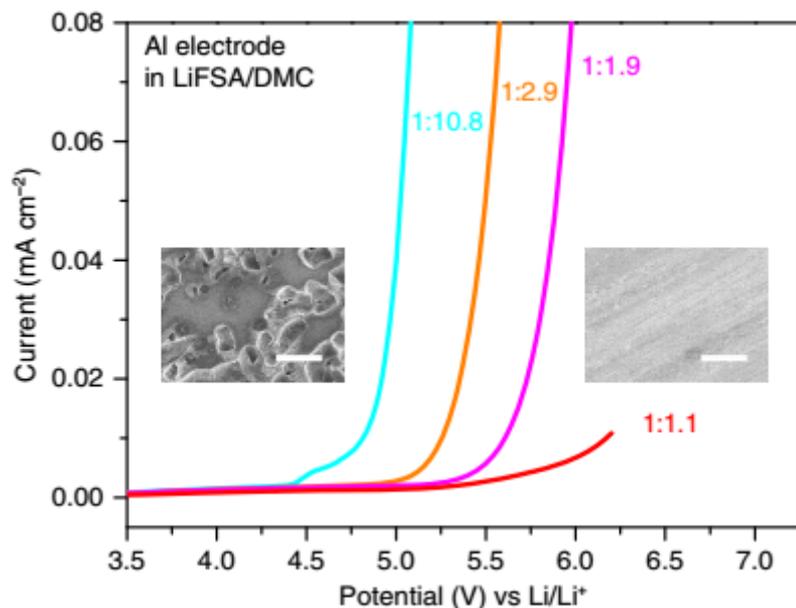


Junyoung Mun, Taeun Yim, Kyungjin Park, Ji Heon Ryu, Young Gyu Kim, and Seung M. Oh, J. Electrochem. Society, 158 (5) A453-A457 (2011)

Concentrated electrolytes

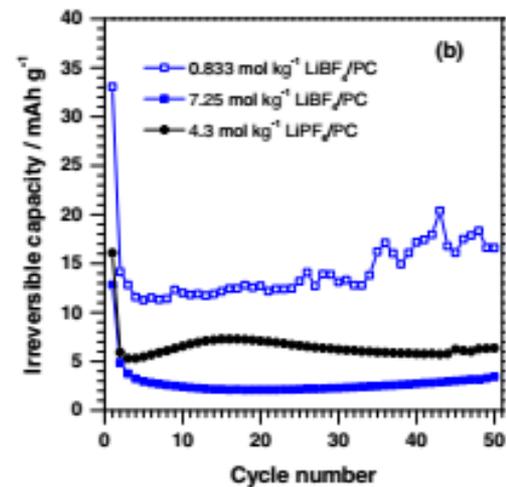
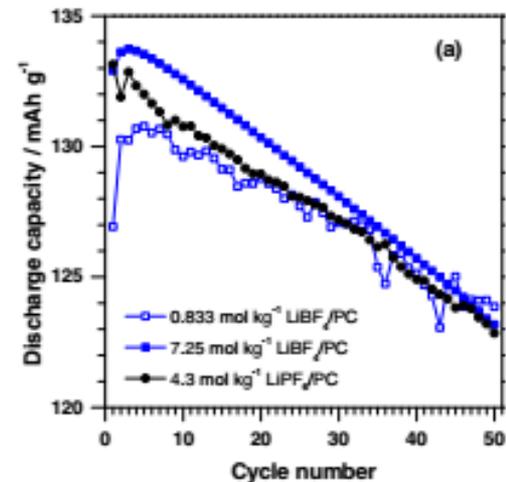
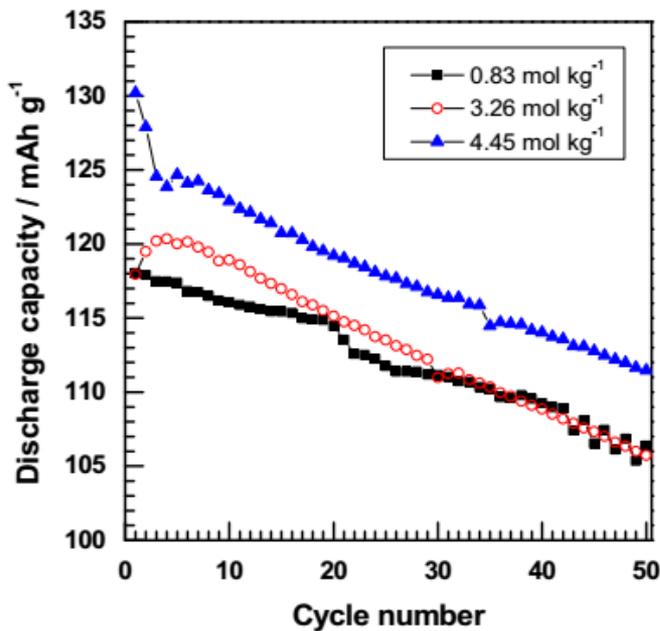
Unique properties in comparison with 1M solutions: stable Li metal cycling, stable graphite cycling without EC additive, enhanced interfacial Li⁺ transport, low volatility and flammability etc.

Since 2016: application as high-voltage electrolytes. LiN(SO₂F)₂ (LiFSA) + DMC:



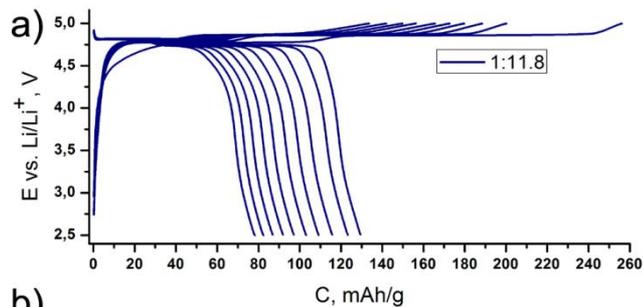
Concentrated electrolytes

Concentrated LiPF_6 and LiBF_4 – PC solutions: better Coulombic efficiency but insufficient wetting properties

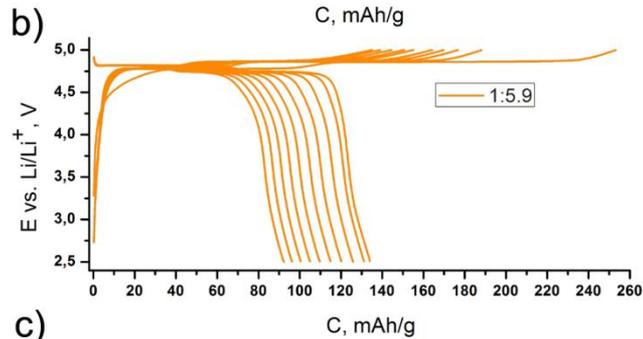


Concentrated electrolytes

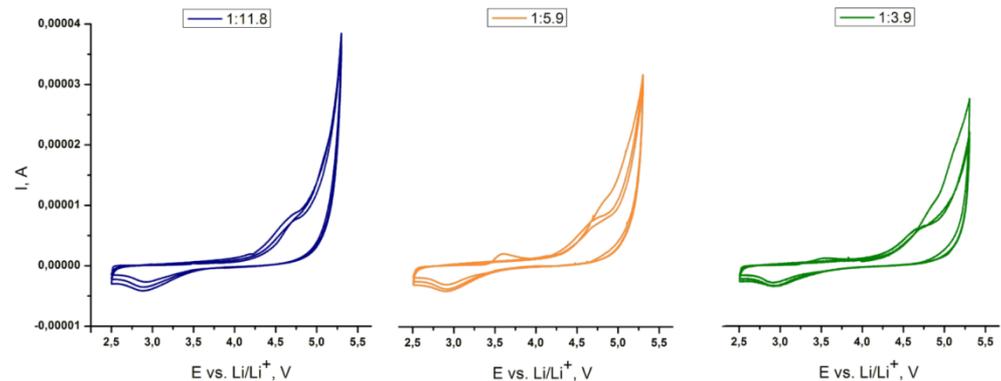
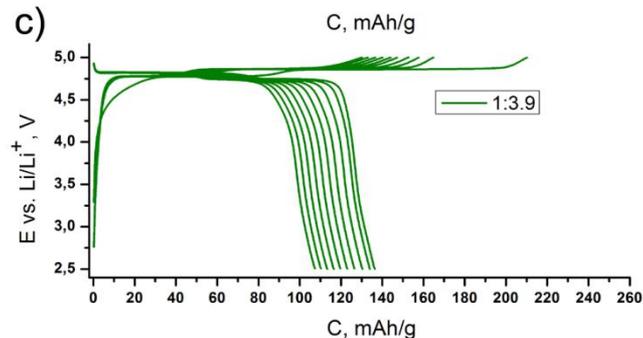
Semi-concentrated solutions ($\sim 2\text{M}$ and 3M) of LiBF_4 in PC: elevated high-voltage stability, no problem with wettability (see V. Shevchenko poster)



LiCoPO_4

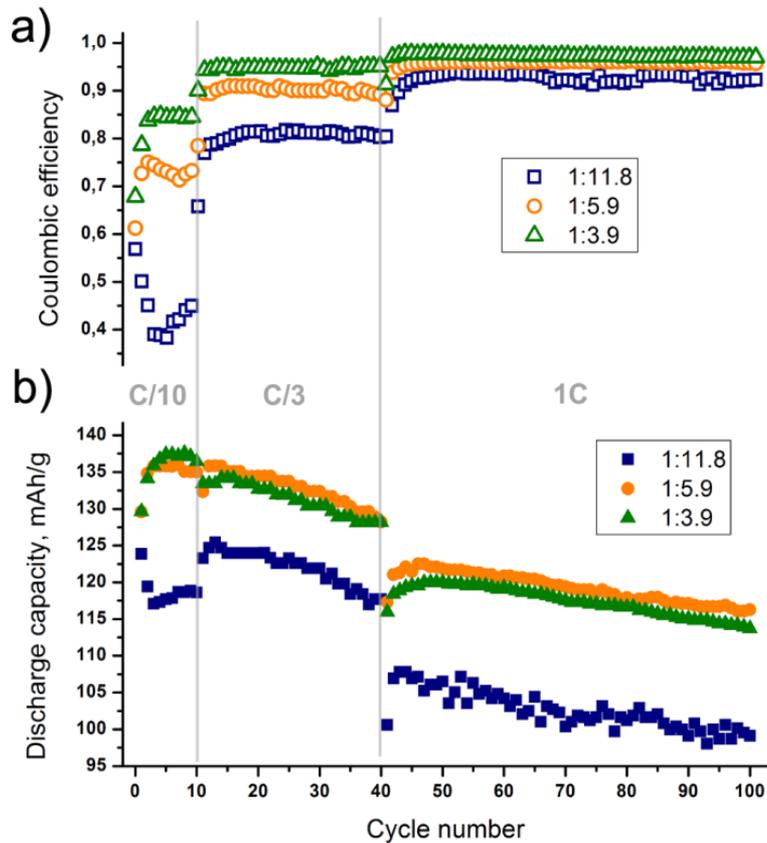


C+ PVDF

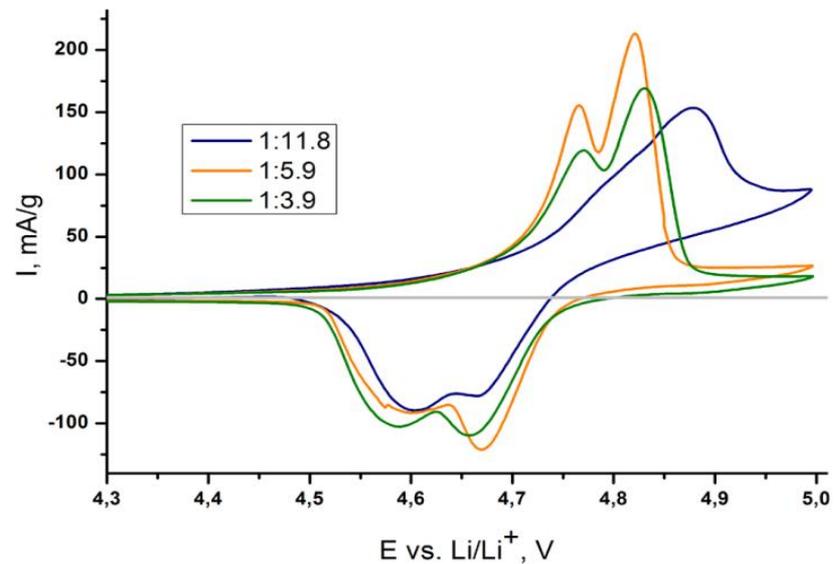


Concentrated electrolytes

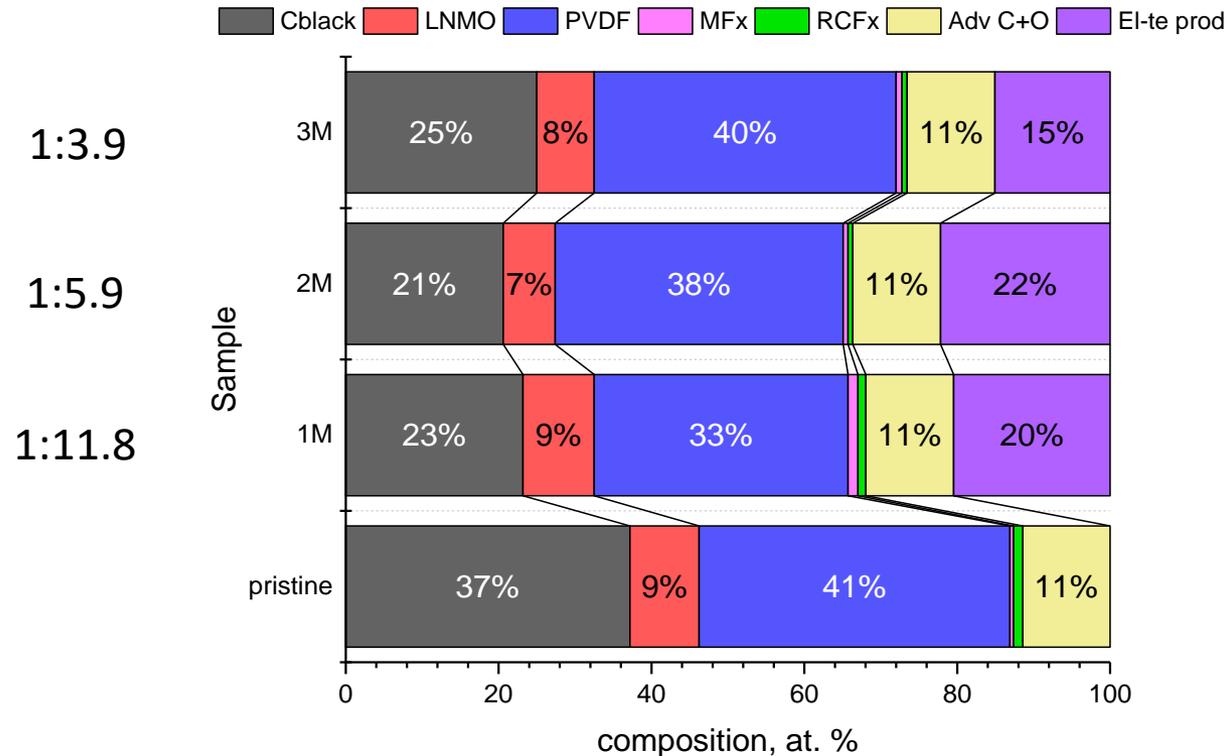
LiNi_{0.5}Mn_{1.5}O₄ galvanostatic cycling:



LiNi_{0.5}Mn_{1.5}O₄ CV after cycling:



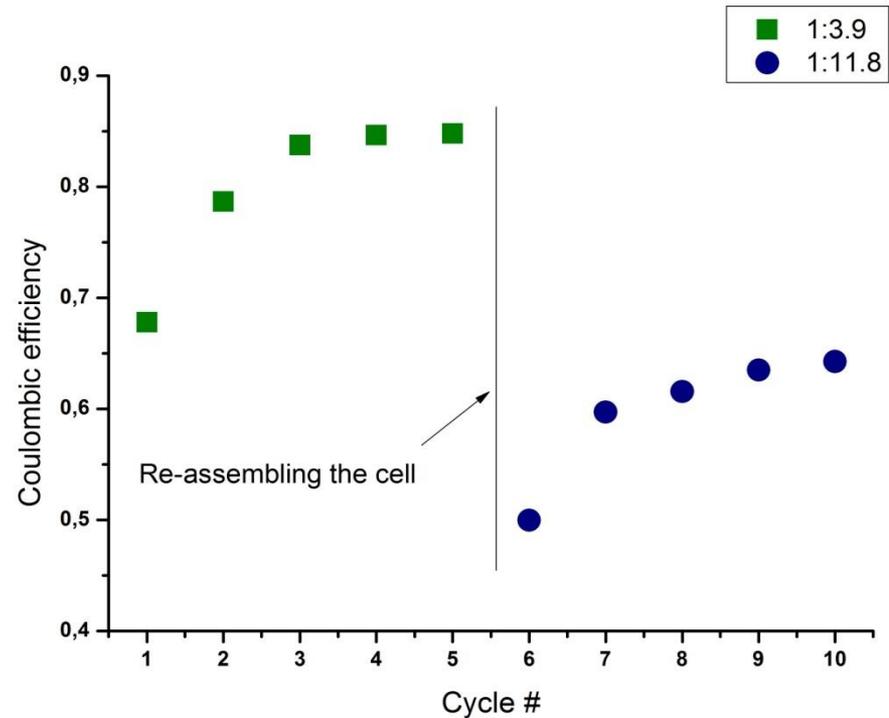
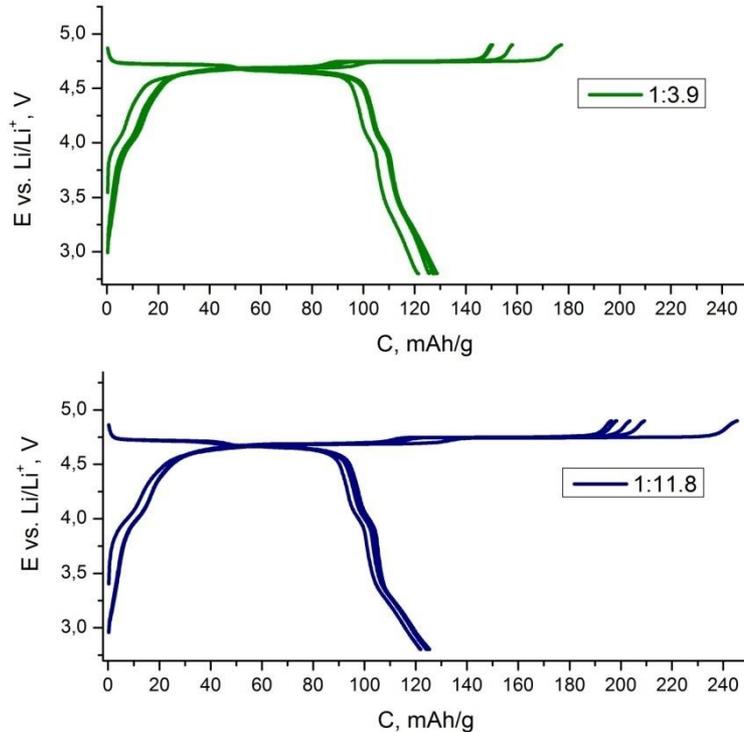
Concentrated electrolytes



XPS analysis of electrodes after cycling: no considerable difference in composition or binding energies

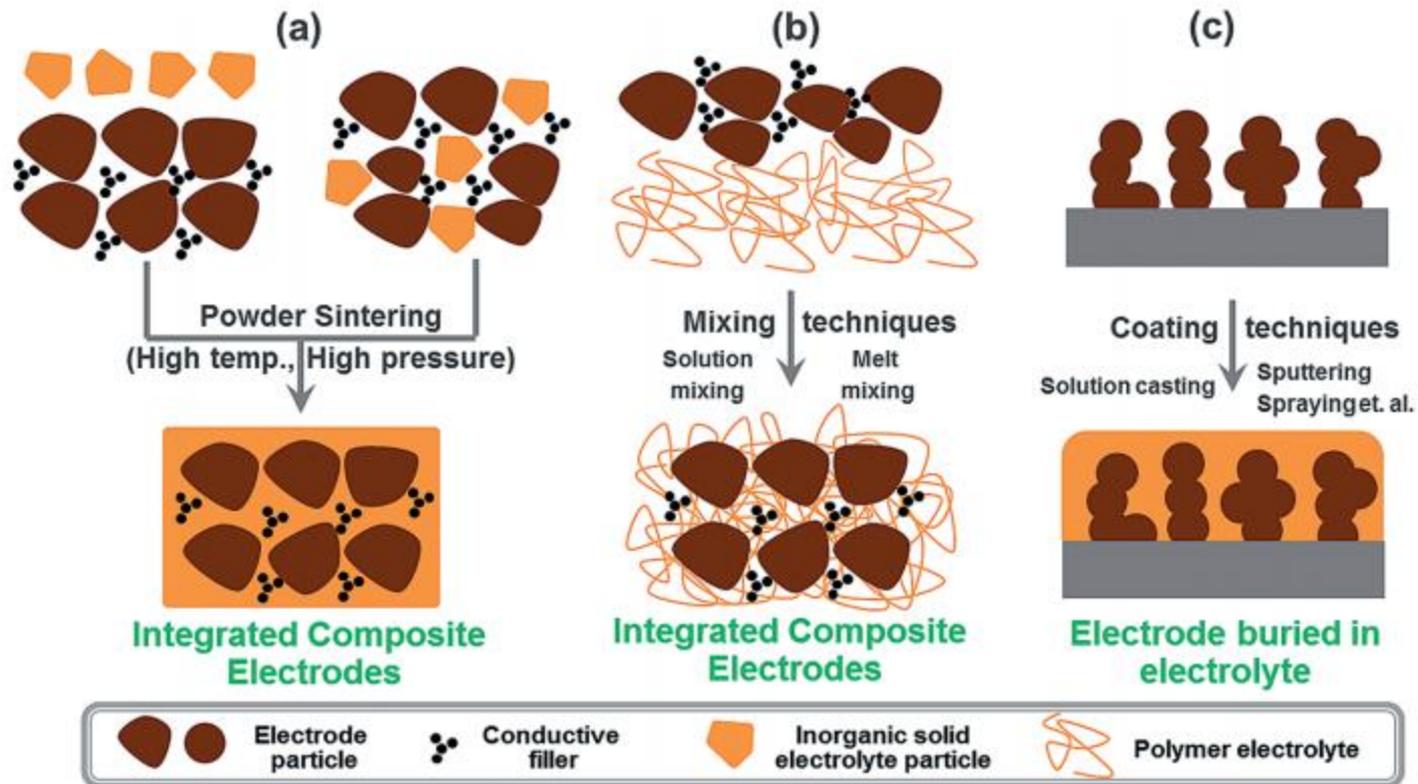
Concentrated electrolytes

5 cycles in concentrated electrolyte (1:3.9), re-assembling, 5 cycles in dilute electrolyte (1:11.8)



No considerable influence of “SEI pre-formation” on the electrochemical behavior in dilute electrolyte

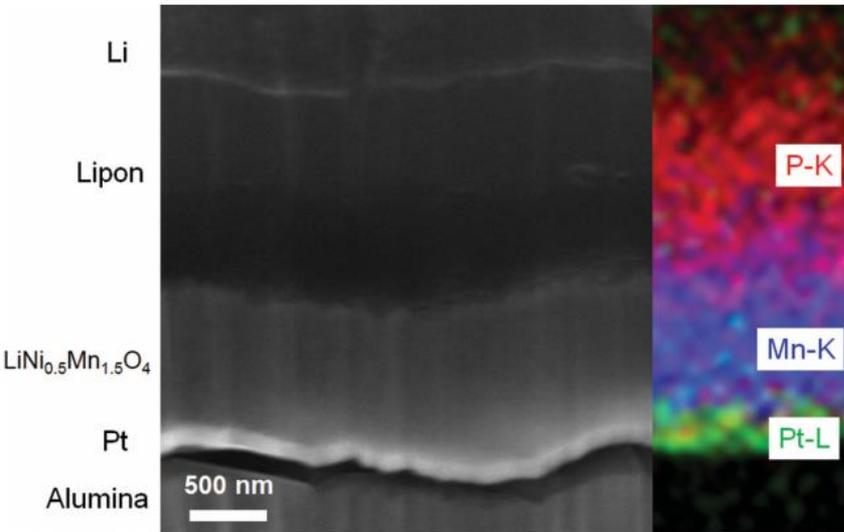
Solid electrolytes



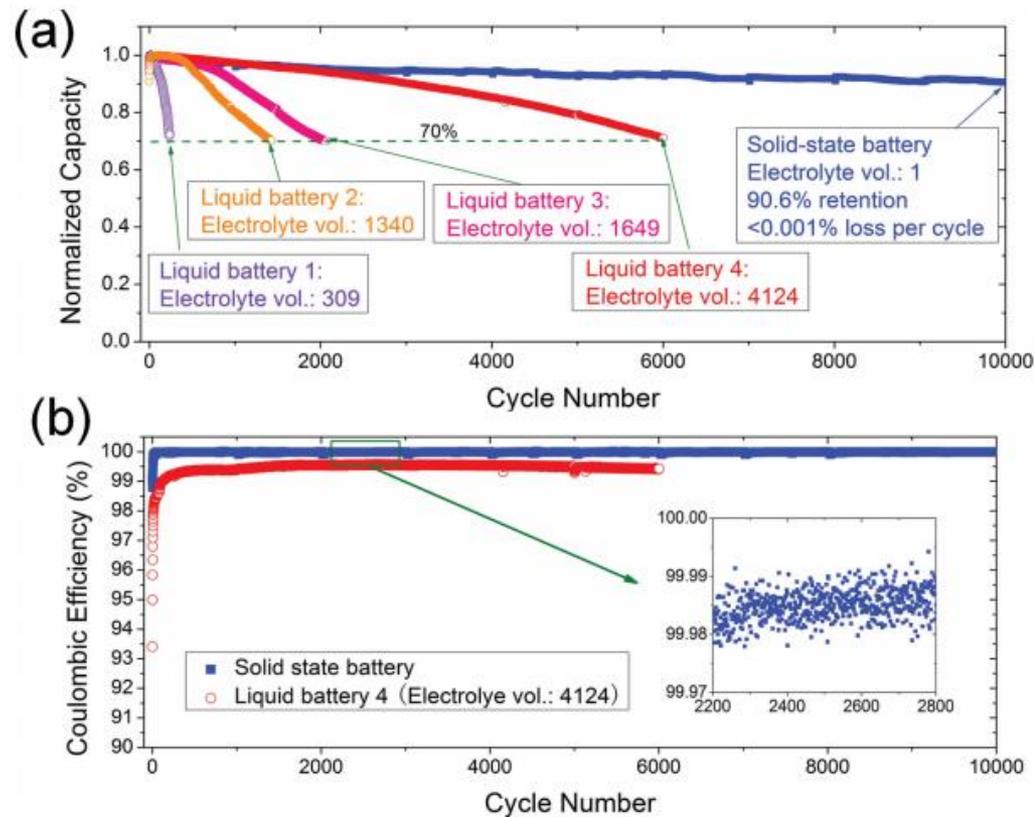
Most common solid electrolytes: Li_3N , LiPON, Li_2S -based glass, NaSICON-type oxides, $\text{Li}_{0.5-3x}\text{La}_{0.5+x}\text{TiO}_3$, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ etc.

Solid electrolytes

LiNi_{0.5}Mn_{1.5}O₄/LiPON/Li thin film battery:



10 000 cycles at 5C rate



However, “bulk” electrodes still need improvements – problems with the interface

Concluding remarks

Most of the efforts in the field of high-voltage batteries are aimed at optimizing Li-ion chemistry which was founded **26 years ago**. However, average discharge voltage of the majority of the cells is still 3.7 V.

Change the way of thinking or continue with optimization?

Thank you for the attention and for
your future ideas!