Functional materials in secondary non aqueous Li/Na-batteries

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Li-ion batteries: intro

Portable electronics

Power tools

Can store up 3 times more energy compared to Ni-MeH

Transportation

Performance
(> energy)

Safety
(< hazard)

Smart grid

Scalability
(< costs)
(> calendar life)
(< environmental costs)

Li-ion batteries: intercalation reactions

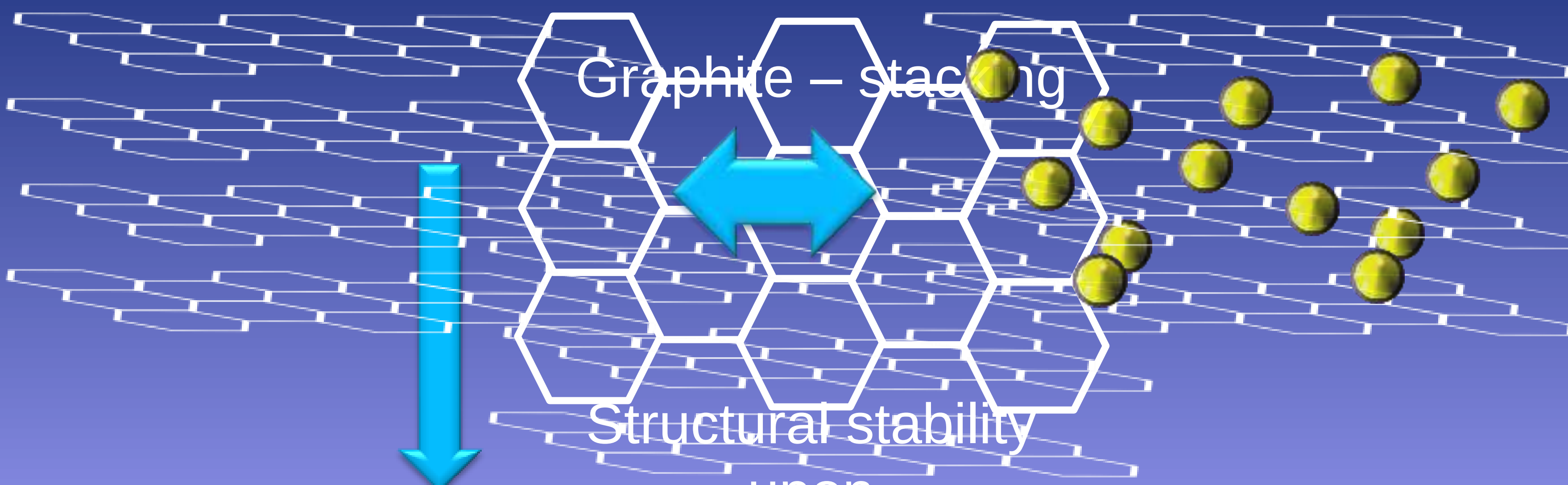
$$\text{Lattice(ox)} + e^- + Li^+ \rightarrow \text{Lattice(red)}$$

Invariant host lattice

Graphite
(oxidized state)

Graphite - layer

LiC_6
(reduced state)



Structural stability
upon
intercalation/deintercalation

Graphite intercalation: theoretical capacity

C (ox) + (1/6) e⁻ + (1/6) Li⁺ → (1/6) LiC₆(red)

$$Q(C, 1\,mol) = \frac{1}{6} \cdot F/\text{Coulomb}$$

$$Q_{th} = \frac{Q(C{,}1\,mol))}{AW(C)} \cdot \frac{1000}{3600} = \frac{(1/6)\cdot F}{12mol/g\cdot 3.6} = 372\ \text{mAg}^{-1}$$

Lattice(ox) + e⁻ + Li⁺ → Lattice(red)

Theoretical specific capacity

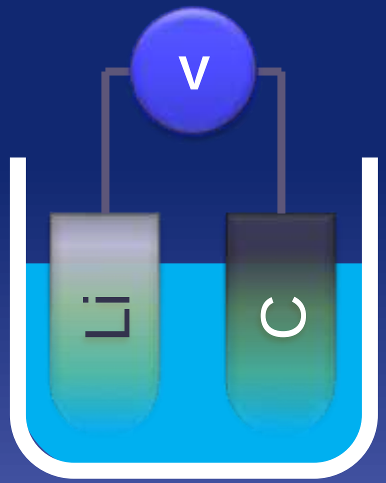
$(Host^{ox}) + xLi^{+} + xe^{-} \rightarrow Li(Host^{red})$

$$\left\{Q_{th} = {}^{x\cdot F}\!/_{(3.6\cdot MW_{Host})}\right\} / \text{mAg}^{-1}$$

Graphite intercalation: redox potential

C (ox) + (1/6) e^- + (1/6) Li^+ → (1/6) LiC_6(red)

e^- + Li^+(ox) → Li(red) Plating reaction of metallic lithium



C / liquid electrolyte (solvent & Li^+ salt) / Li

$$\left\{ C + \frac{1}{6}e^- + \frac{1}{6}Li^+ \rightarrow \frac{1}{6}LiC_6 \right\} \times 6 +$$

$$Li \rightarrow Li^+ + e^- \quad =$$

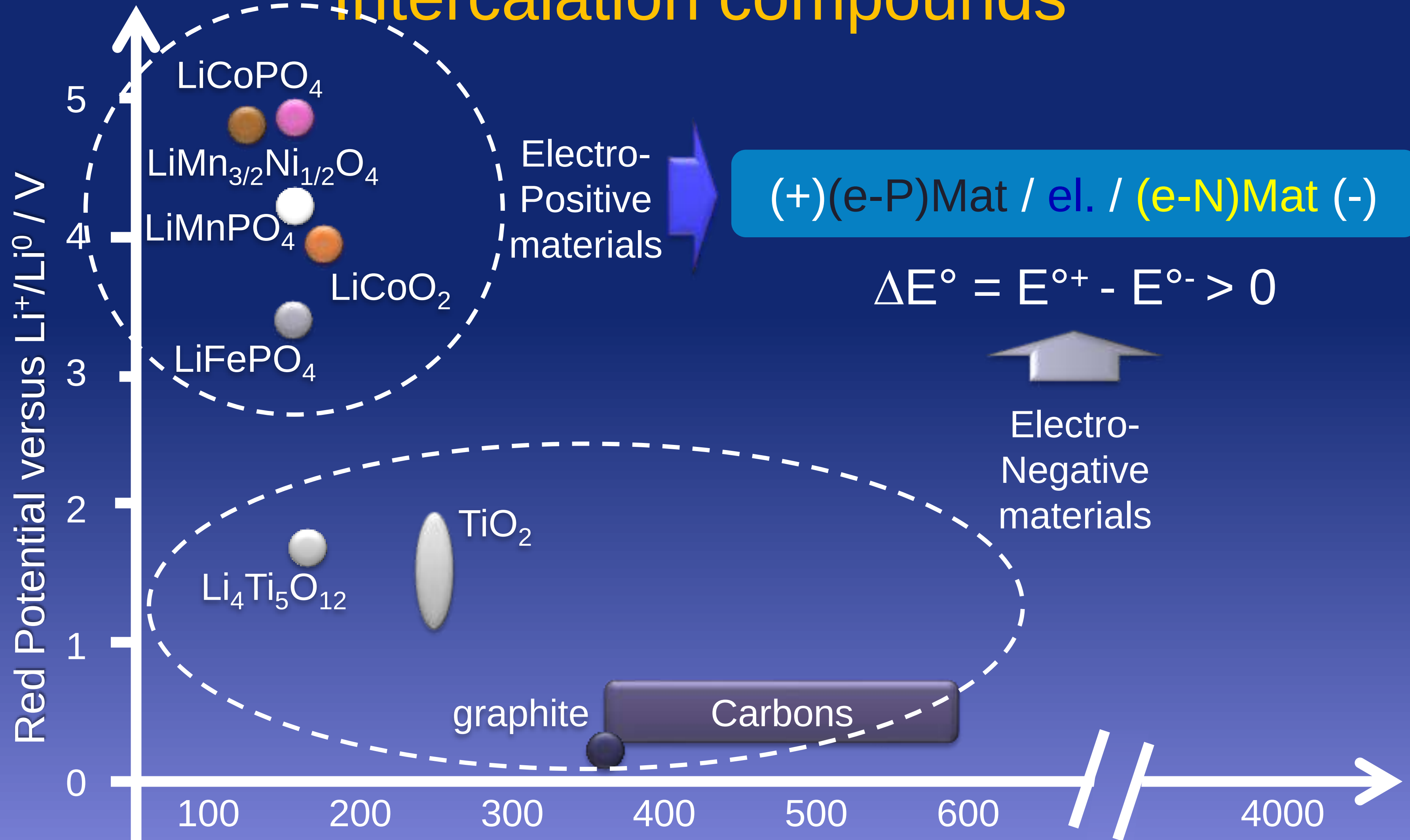
$$6\,C + Li \rightarrow LiC_6$$

Fem?

$$\Delta_r G^o = \Delta_f G^o\,(LiC_6)$$
$$\Delta_f G^o\,(LiC_6) = -n \cdot F \cdot \Delta E^o$$

$$E^o(C/LiC_6) = -\frac{\Delta_f G^o\,(LiC_6)}{n \cdot F} = -\frac{-15.1\,\frac{kJ}{mol}}{1 \cdot 96485} = 0.156\,V\ vs.\,Li^+/Li$$

Intercalation compounds



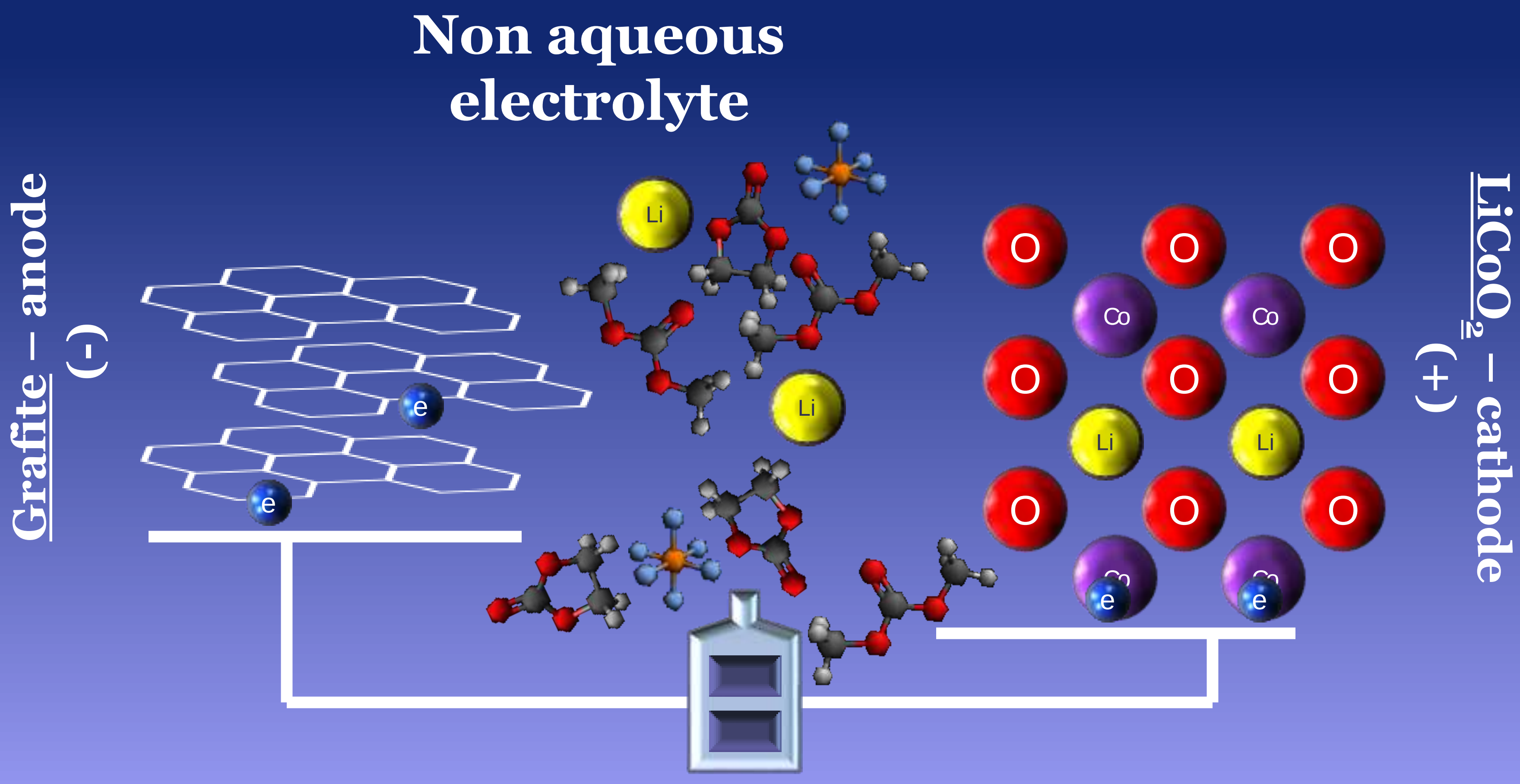
Theoretical specific capacity $\left\{Q_{th} = {}^{x\cdot F}/_{MW_{Host}}\right\}$ / mAg^{-1}

$(Host^{ox}) + xLi^+ + xe^- \rightarrow Li(Host^{red})$

Li-ion batteries: fundaments

$$M^{n+}O_{n/2} + e^- + Li^+ \rightarrow LiM^{(n-1)+}O_{n/2}$$

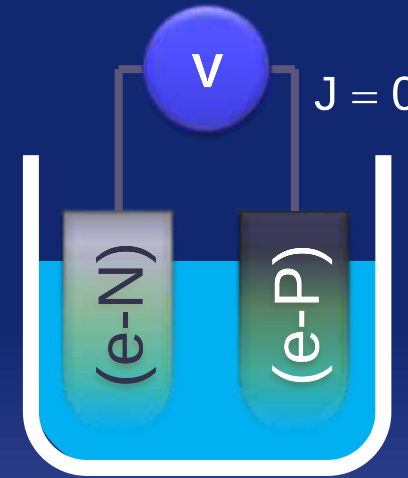
$$C + (1/6)\, e^- + (1/6)\, Li^+ \rightarrow (1/6)\, LiC_6$$

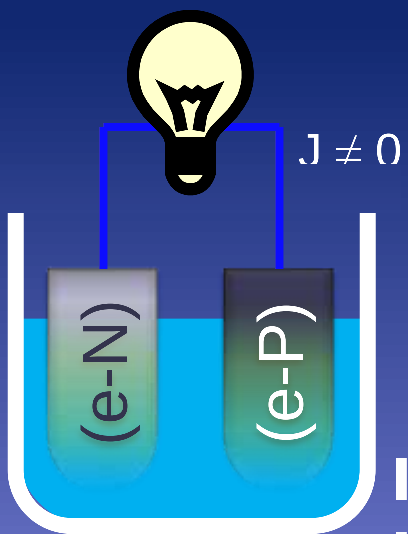


Li-ion batteries: functional properties

(+)(e-P)Mat / electrolyte / (e-N)Mat (-)

$\Delta E° = E°^{+} - E°^{-} > 0$ ➡ $J = 0$ mA/cm^2 ➡ OCV





In discharge

$J > 0$ mA / cm^2

CCV ➡ $\Delta V = \Delta E° - \eta$

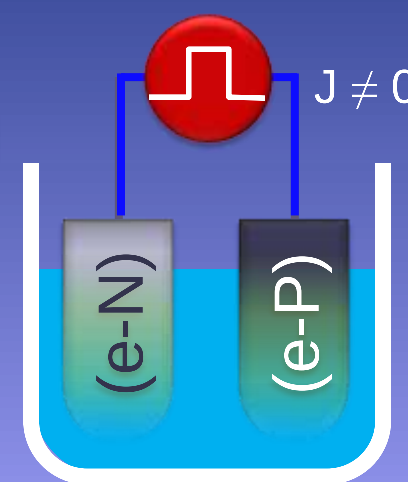
η overpotential

In charge

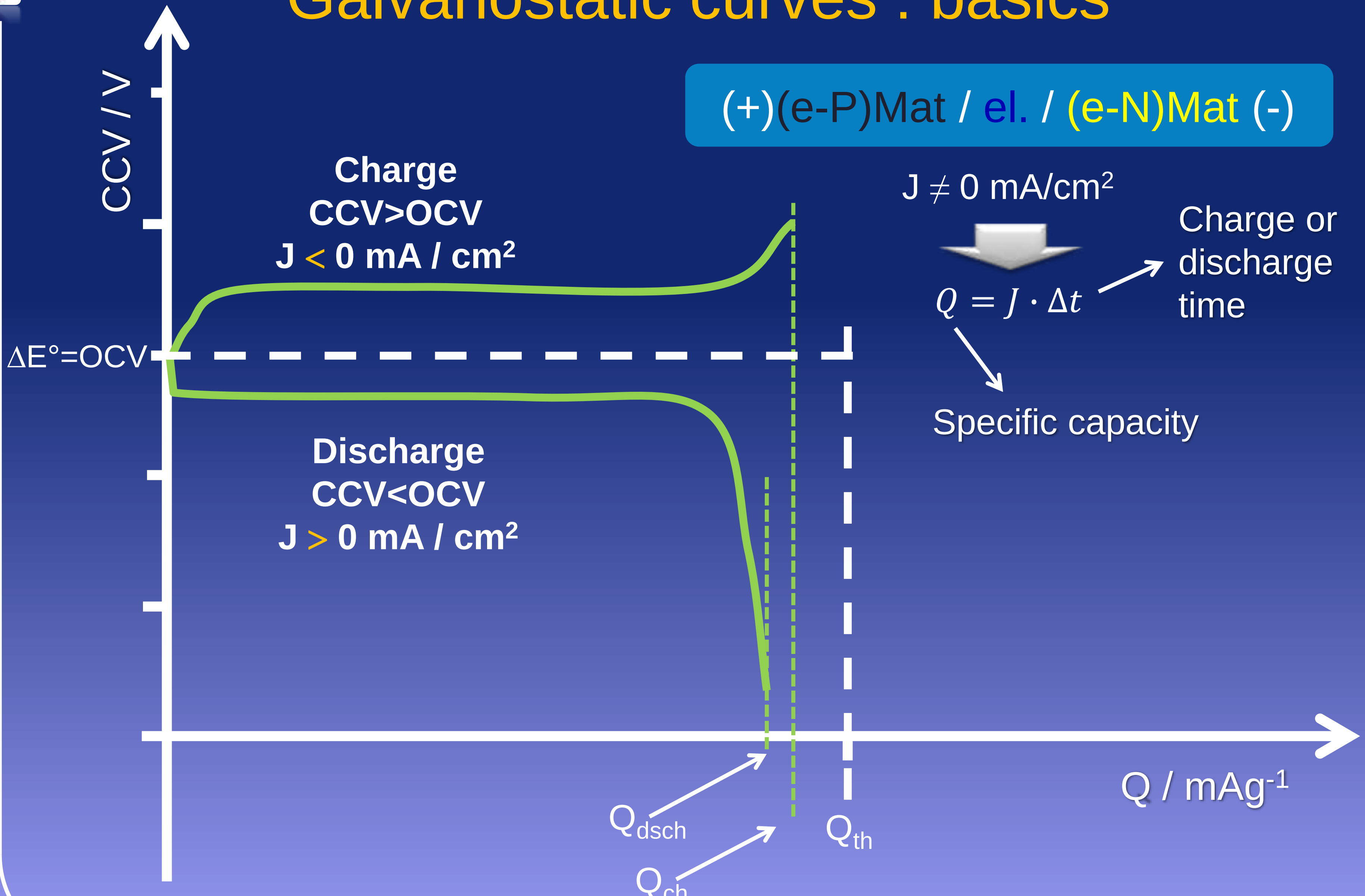
$J < 0$ mA / cm^2

CCV ➡ $\Delta V = \Delta E° + \eta$

η overpotential

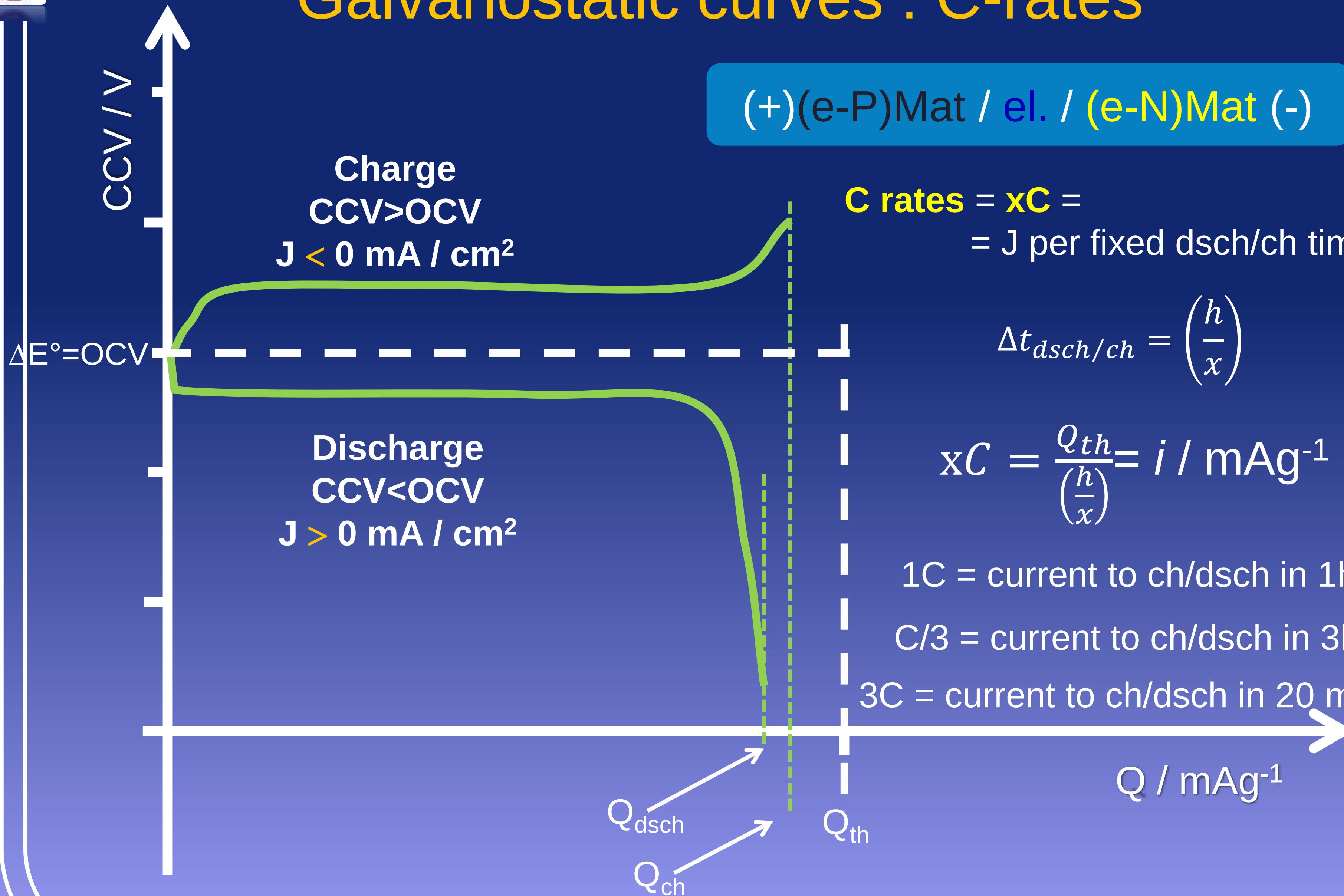


Galvanostatic curves : basics



Galvanostatic curves : C-rates

(+)(e-P)Mat / el. / (e-N)Mat (-)



C rates = **xC** =

= J per fixed dsch/ch time

$$\Delta t_{dsch/ch} = \left(\frac{h}{x}\right)$$

$$xC = \frac{Q_{th}}{\left(\frac{h}{x}\right)} = i \,/\, mAg^{-1}$$

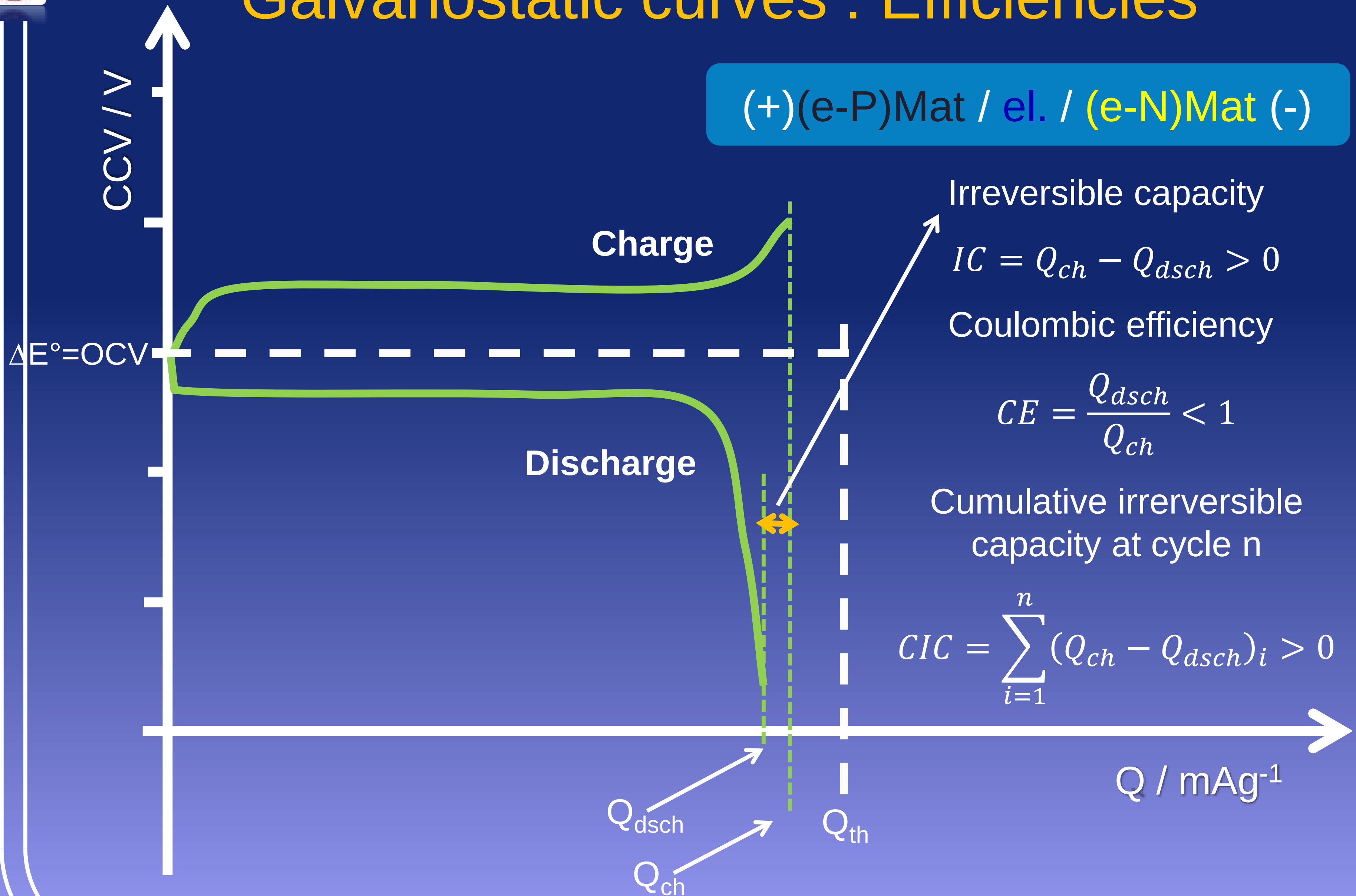
1C = current to ch/dsch in 1h

C/3 = current to ch/dsch in 3h

3C = current to ch/dsch in 20 min

Galvanostatic curves : Efficiencies

(+)(e-P)Mat / el. / (e-N)Mat (-)



Irreversible capacity

$$IC = Q_{ch} - Q_{dsch} > 0$$

Coulombic efficiency

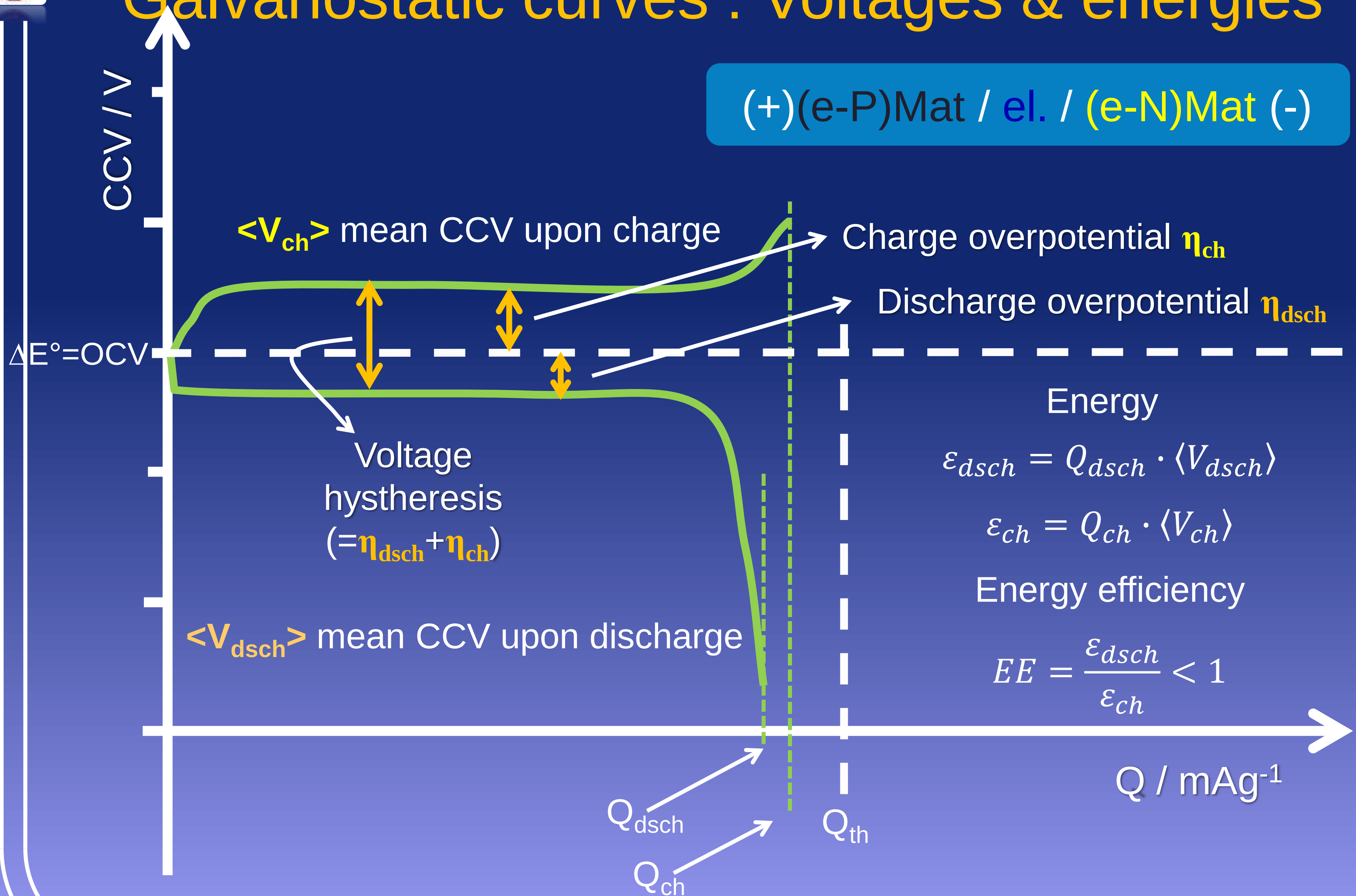
$$CE = \frac{Q_{dsch}}{Q_{ch}} < 1$$

Cumulative irrerversible capacity at cycle n

$$CIC = \sum_{i=1}^{n} (Q_{ch} - Q_{dsch})_i > 0$$

Galvanostatic curves : Voltages & energies

(+)(e-P)Mat / el. / (e-N)Mat (-)



Energy

$$\varepsilon_{dsch} = Q_{dsch} \cdot \langle V_{dsch} \rangle$$

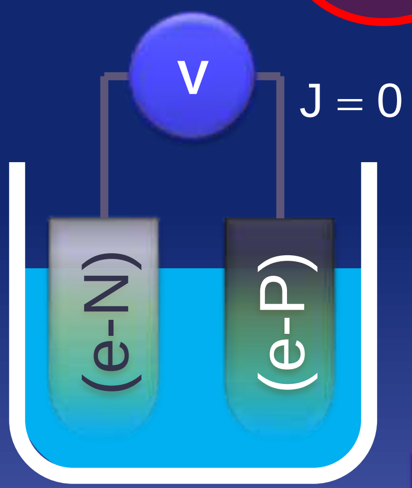
$$\varepsilon_{ch} = Q_{ch} \cdot \langle V_{ch} \rangle$$

Energy efficiency

$$EE = \frac{\varepsilon_{dsch}}{\varepsilon_{ch}} < 1$$

Electrolytes for Li-ion batteries: intro

(+)(e-P)Mat / el. / (e-N)Mat (-)



Electrolyte:
medium for the movement of ions

- e⁻-**insulating**
- easily **transport** Li^+-ions
- electrochemically **inert** at both electrodes

- **Liquid** solution (Li^+ salt and solvent)
- **Gel** electrolyte (Li^+ salt, solvent and polymer)
- **Polymer** electrolyte (Li^+ salt and polymer)
- **Solid** electrolyte (crystalline Li^+ ionic conductor)

Li-ion battery: the puzzle challenge

$Li_4Ti_5O_{12}$ e-N

Graphite – e-N | EC:DMC $LiPF_6$ Liquid electrolyte | $LiCoO_2$ – e-P

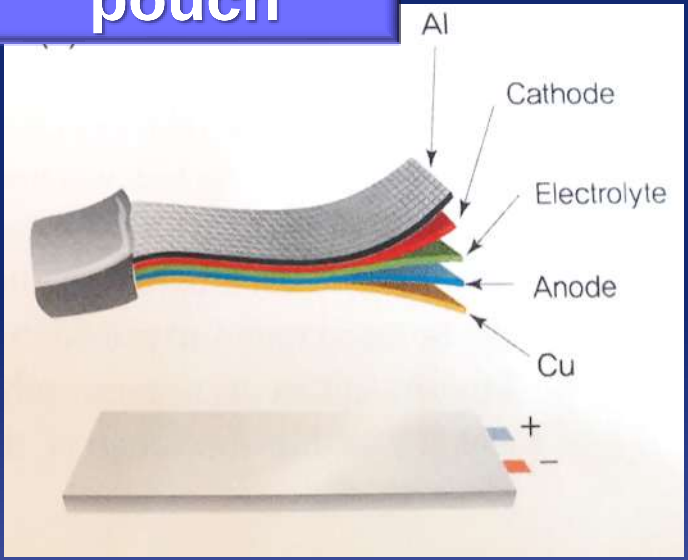
PVDF EC:DMC $LiPF_6$ Gel electrolyte

3.5 V
30 mAh/g_{tot}
95 Wh/kg_{tot}

Transport		Smart grid
Performance (> energy)	> capacity / Co-free	**Scalability** (< costs)
Safety (< hazard)	Non-liquid electrolyte / F-free electrolyte	**Duration** (> calendar life)

Li-ion battery: basic constituents

pouch



Positive electrode

1. ***P-E active material***
2. Conductive agent
3. Polymeric binder
4. Current collector (aluminum)

Negative electrode

1. ***N-E active material***
2. Conductive agent
3. Polymeric binder
4. Current collector (copper)

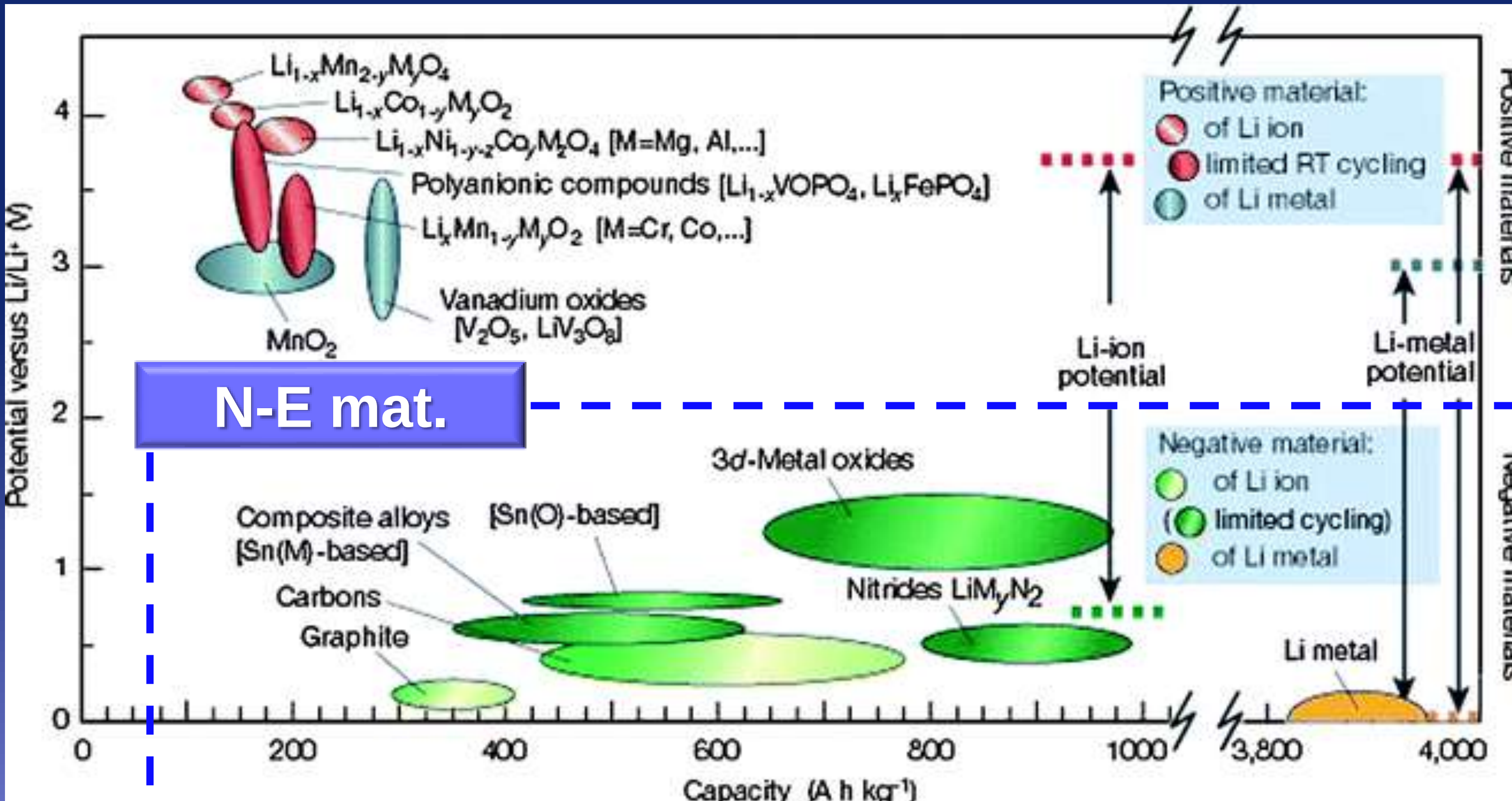
Electrolyte

1. Separator
2. ***Lithium salt***
3. ***Electrolyte solvent***
4. Additives

Others

1. Al tab (+)
2. Ni tab (-)
3. Outer case
4. Safety components (safety vent, thermal shutdown circuit)

Li-ion battery: negative electrodes



Low potential: E° close but above 0 V vs. Li

Invariant lattice: stable structure upon lithiation

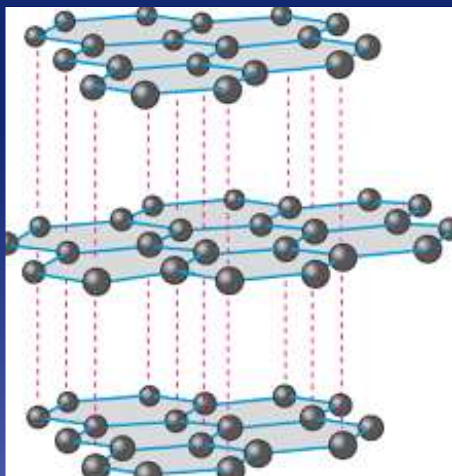
High reversibility: electrochemical reaction in ch/dsch

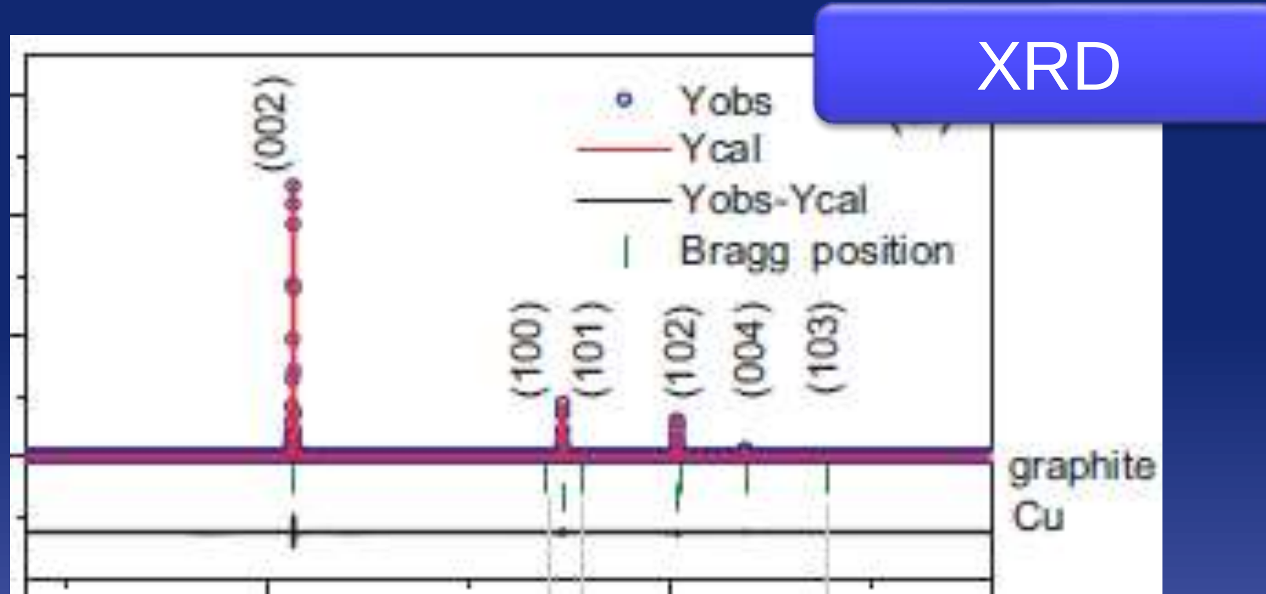
Li-ion battery: negative electrodes families

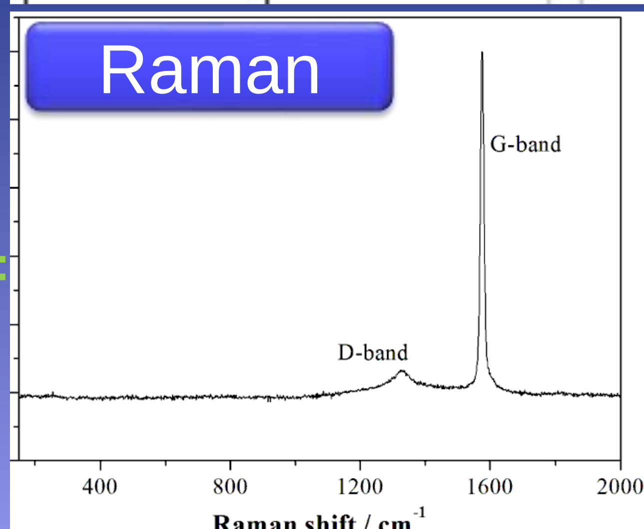
Intercalation chemistry	Conversion chemistry	Alloying chemistry	Lithium
Graphite $6C+Li^{+}+e^{-}\rightarrow LiC_6$	Oxides $CoO+2Li^{+}+2e^{-}\rightarrow Li_2O+Co$	Tin $5Sn+22Li^{+}+22e^{-}\rightarrow Li_{22}Sn_5$	$Li^{+} + e^{-} \rightarrow Li$
Carbons $nC+Li^{+}+e^{-}\rightarrow LiC_n$	Hydrides $MgH_2+2Li^{+}+2e^{-}\rightarrow 2LiH+Mg$	Silicon $4Si+17Li^{+}+17e^{-}\rightarrow Li_{17}Si_4$	
Lithium titanate $Li_4Ti_5O_{12}+3Li^{+}+3e^{-}\rightarrow Li_7Ti_5O_{12}$	Phosphides $Cu_3P+3Li^{+}+3e^{-}\rightarrow Li_3P+3Cu$	Aluminum $4Al+9Li^{+}+9e^{-}\rightarrow Li_9Al_4$	
Titania $TiO_2+Li^{+}+e^{-}\rightarrow LiTiO_2$			

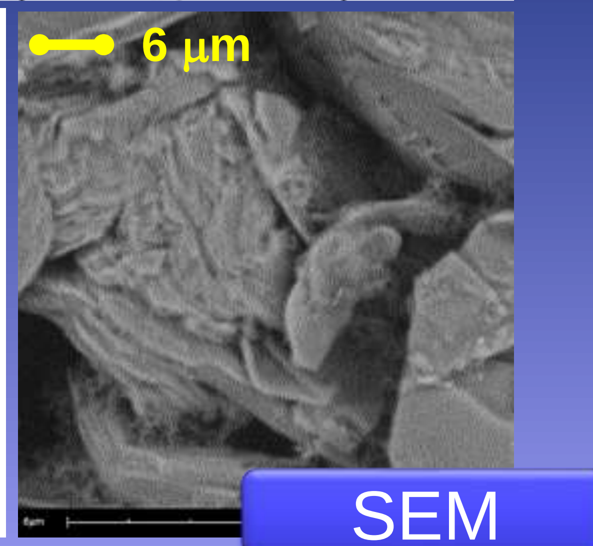
Negative electrodes: graphite

Graphite
hP6 SG 194









Collector: **Cu**

Theoretical capacity:
372 mAh/g

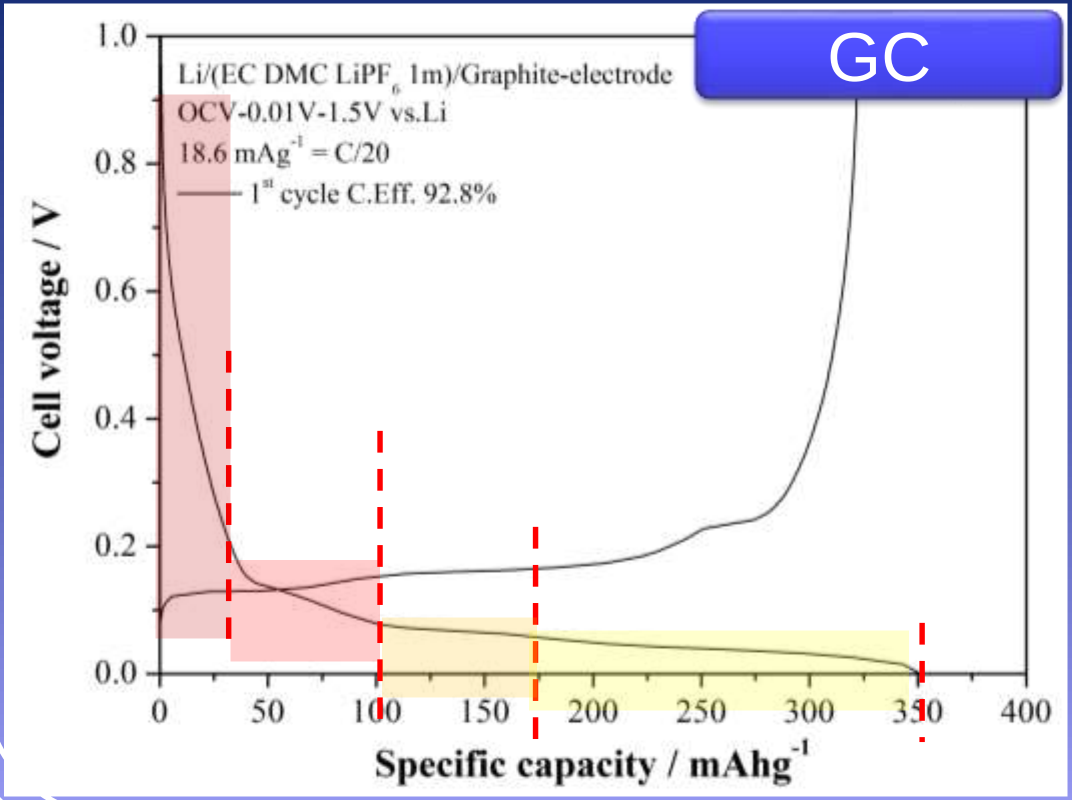
Nominal voltage:
0.1 V vs. Li

Negative electrodes: graphite in Li cells

Graphite
$6C + Li^+ + e^- \rightarrow LiC_6$

(+)Graphite / electrolyte / Lithium (-)

Lithium secondary half cell



Theoretical capacity: 372 mAh/g
Thermodynamic reduction potential:

$$\Delta_r G^o = \Delta_f G^o (LiC_6)$$
$$\Delta_f G^o (LiC_6) = -n \cdot F \cdot \Delta E^o$$
$$E^o = 0.156\, V\ vs\ Li$$

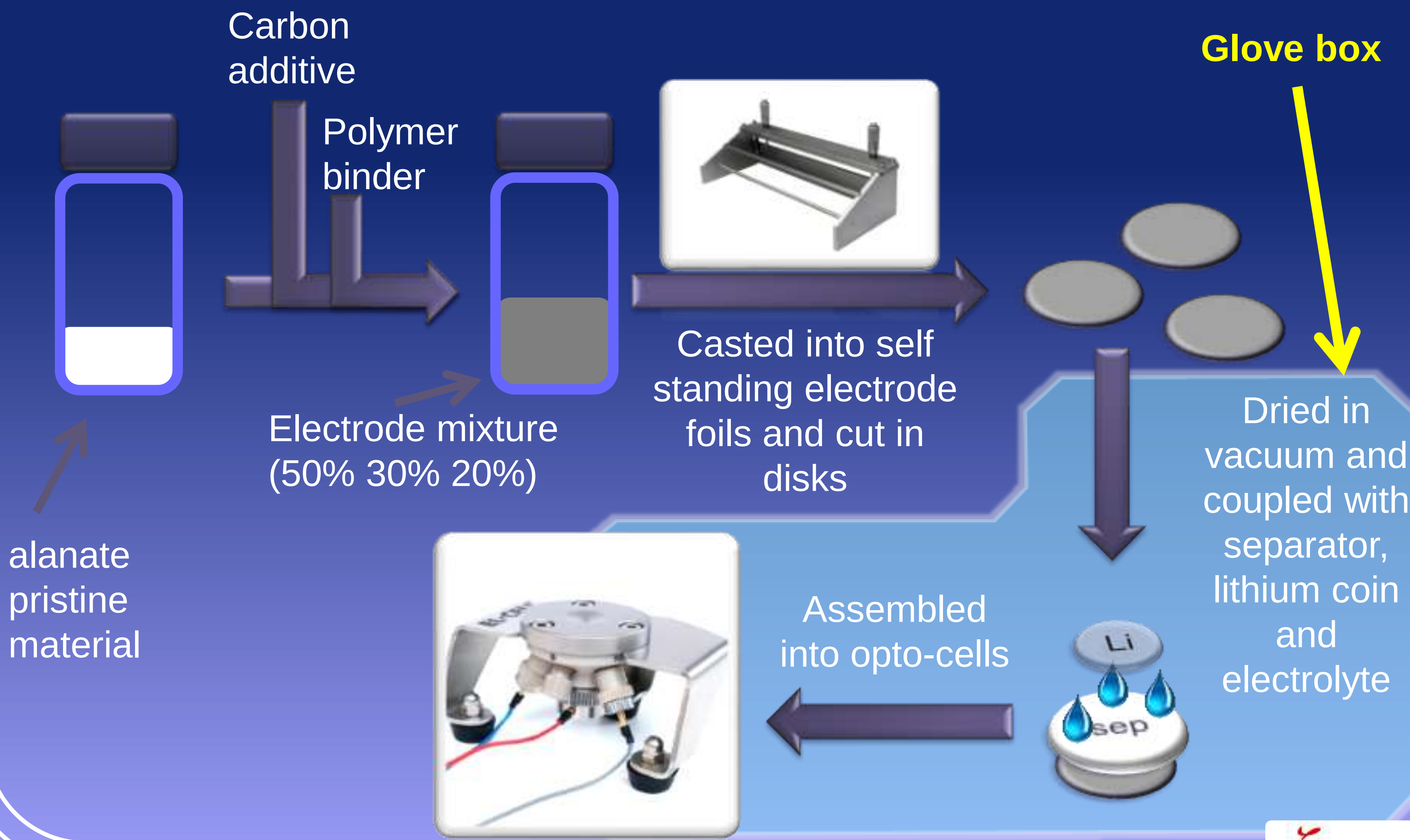
Single potential plateau

Multiple consecutive reactions upon lithiation

Investigation using coupled techniques
e.g. in operando XRD

In operando experiments

The study of the electrochemical lithium incorporation into materials can been carried out by in operando techniques



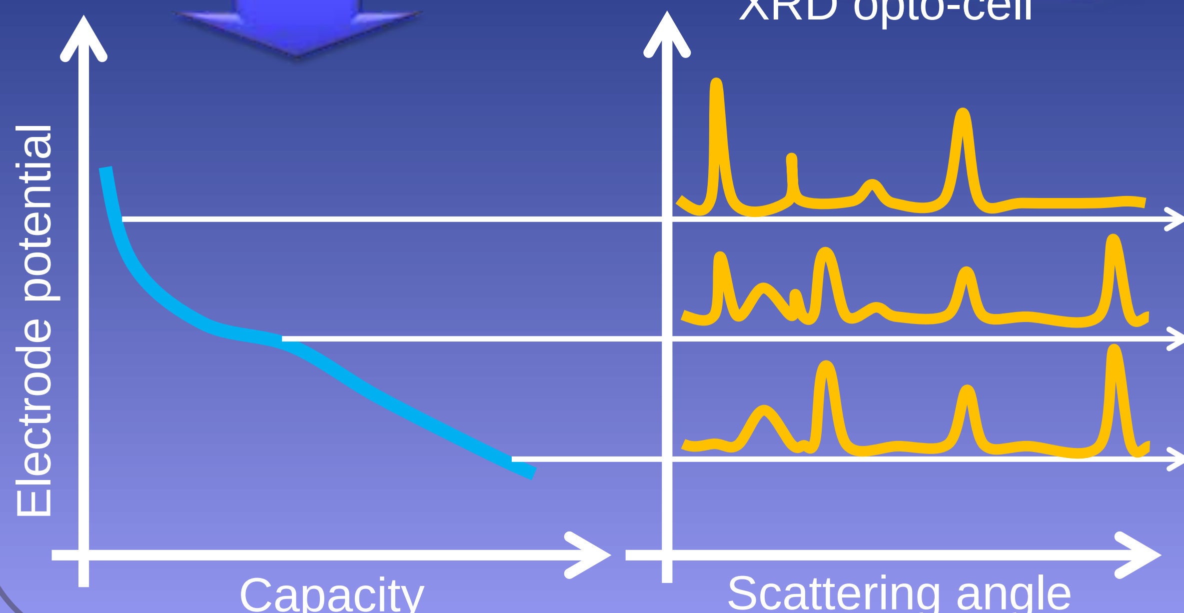
In operando XRD experiments

The in operando analysis implies the simultaneous electrochemical cell discharge/charge and XRD tests

Galvanostat

XRD opto-cell

Alligned into a diffractometer

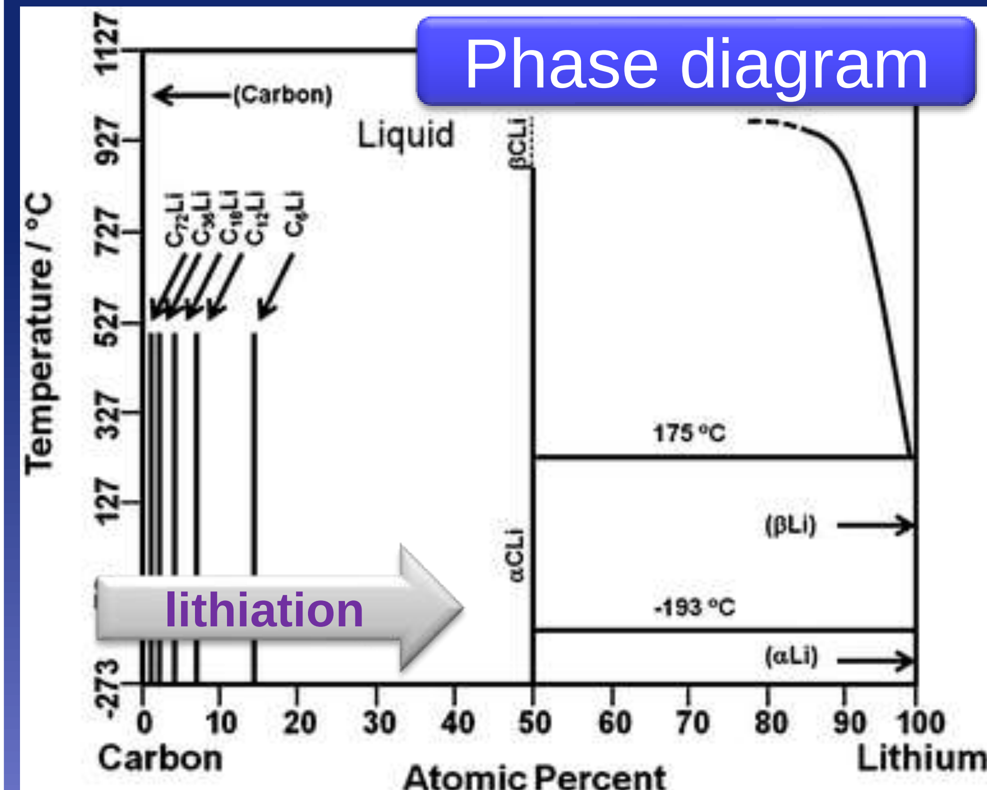


Phase analysis upon cycling

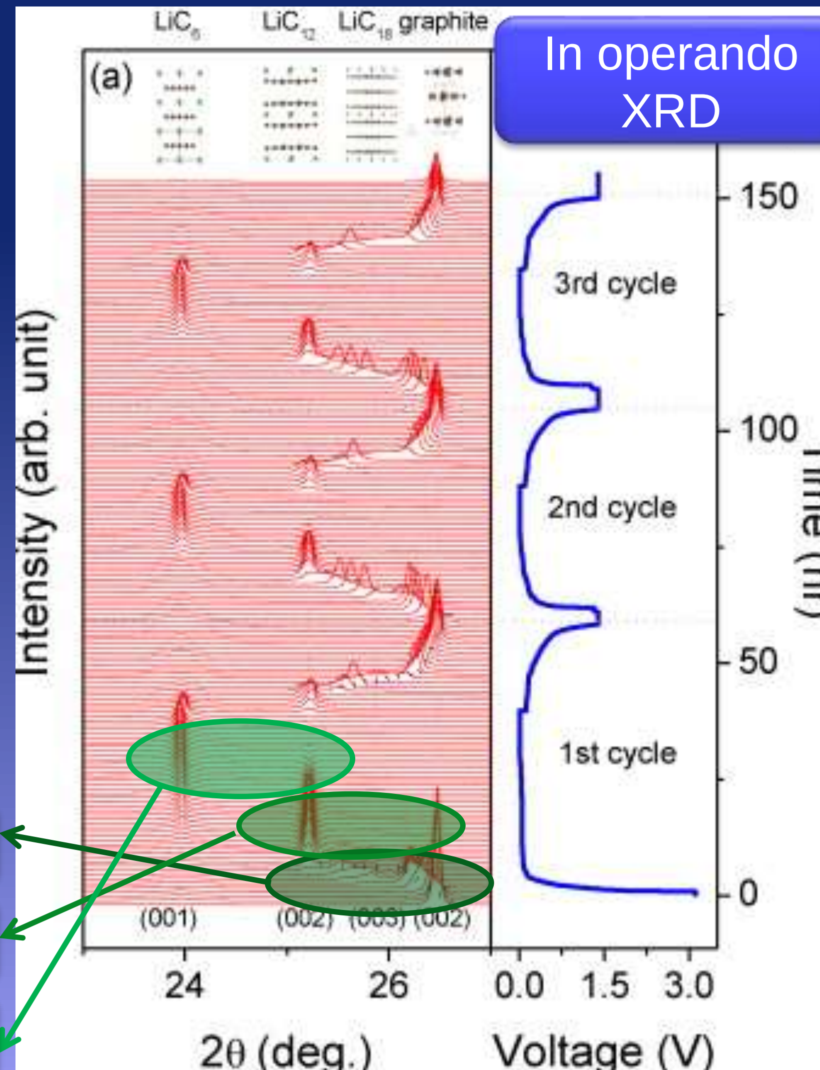
Negative electrodes: graphite in Li cells

Graphite | **(+)Graphite / electrolyte / Lithium (-)**

Phase diagram



In operando XRD



$72C + Li^+ + e^- \rightarrow LiC_{72}$ / $LiC_{72} + 5Li^+ + 5e^- \rightarrow LiC_{12}$

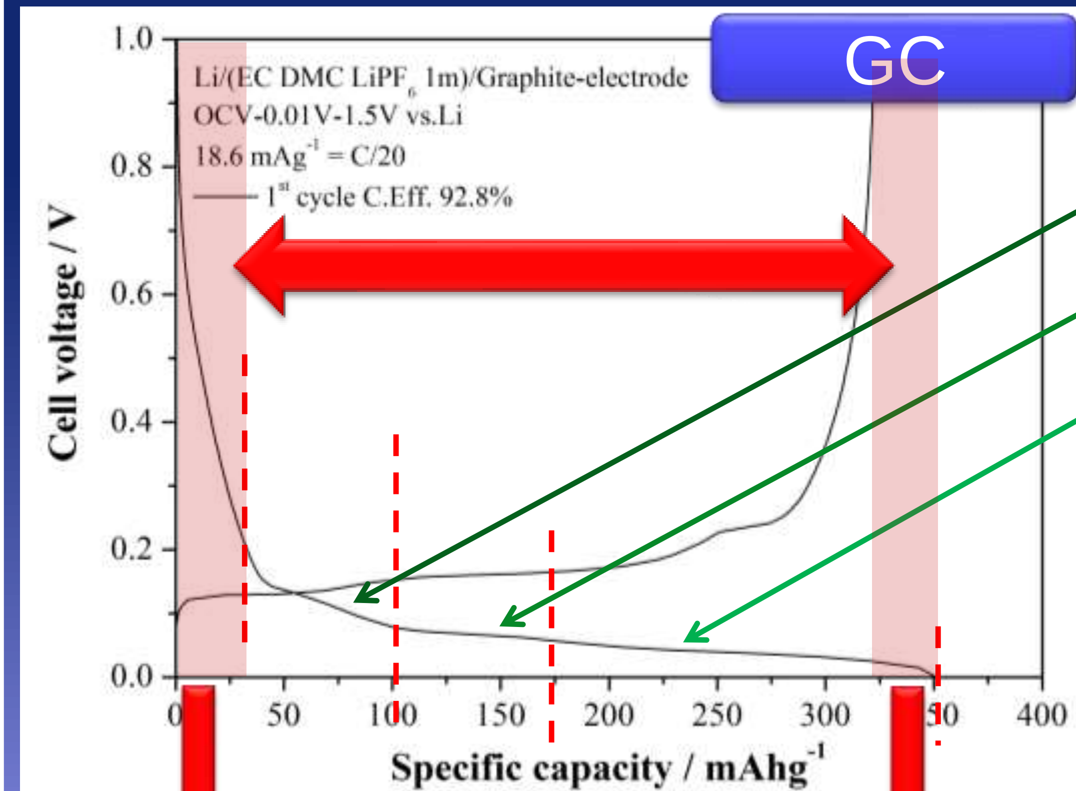
$12C + Li^+ + e^- \rightarrow LiC_{12}$

$LiC_{12} + Li^+ + e^- \rightarrow LiC_6$

Negative electrodes: graphite in Li cells

(+)Graphite / electrolyte / Lithium (-)

Lithium secondary half cell



$72C + Li^{+} + e^{-} \rightarrow LiC_{72}$
$LiC_{72} + 5Li^{+} + 5e^{-} \rightarrow LiC_{12}$

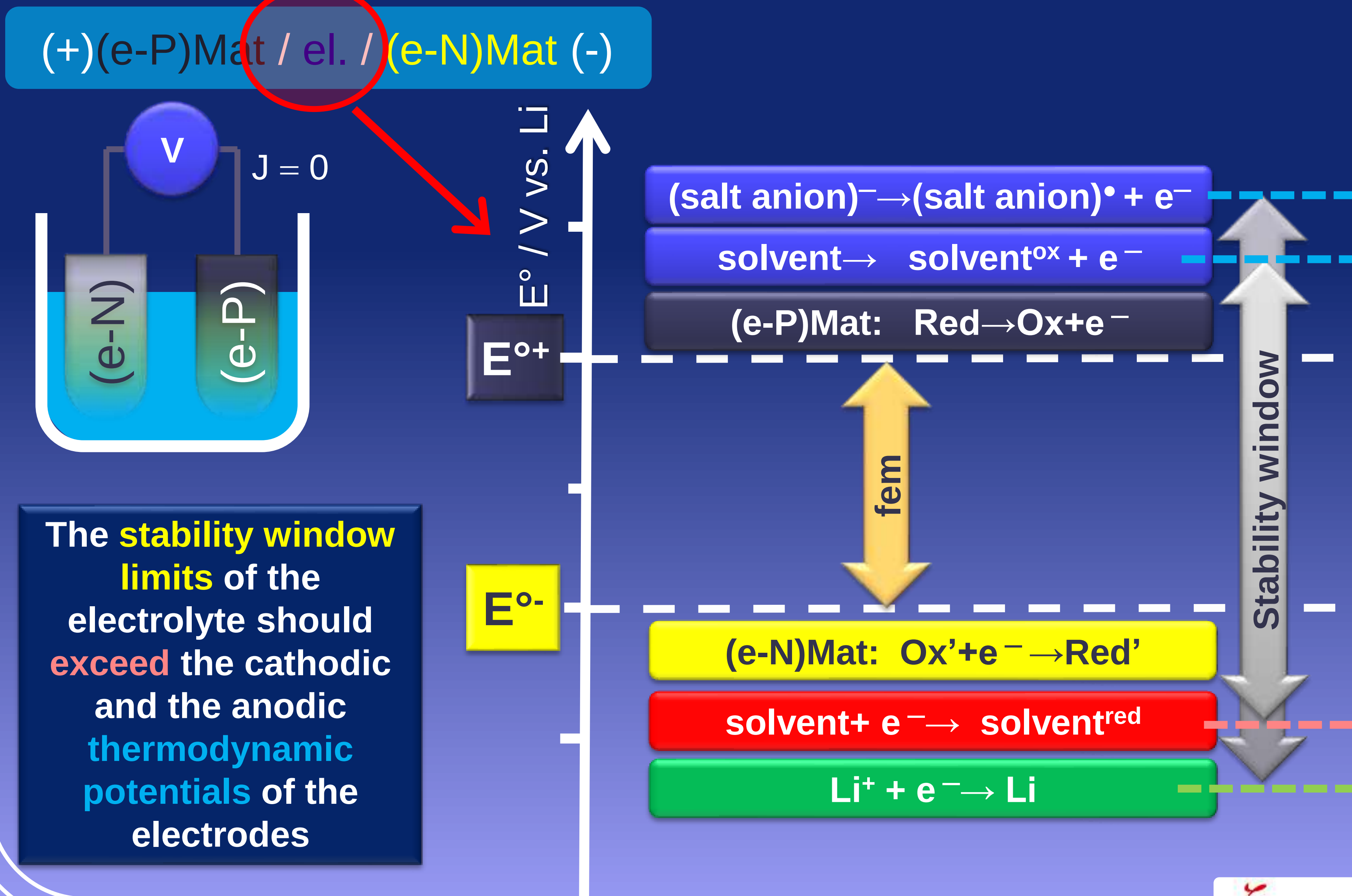
$12C + Li^{+} + e^{-} \rightarrow LiC_{12}$

$LiC_{12} + Li^{+} + e^{-} \rightarrow LiC_{6}$

CCP>0.25 & irreversible capacity

Solid electrolyte interphase formation

Electrolytes for Li-ion batteries: stability



The stability window limits of the electrolyte should exceed the cathodic and the anodic thermodynamic potentials of the electrodes

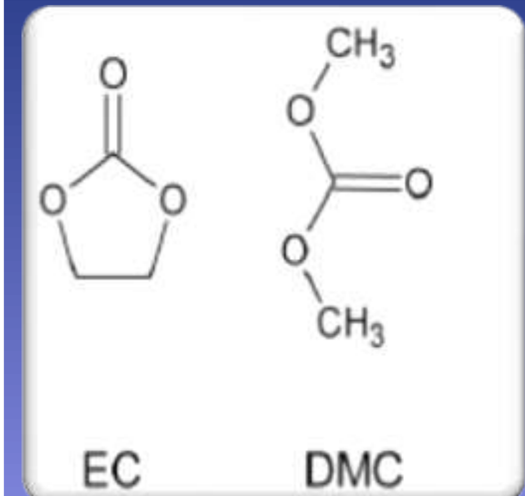
Irreversible degradation of electrolytes

Electrolyte: medium for the movement of ions

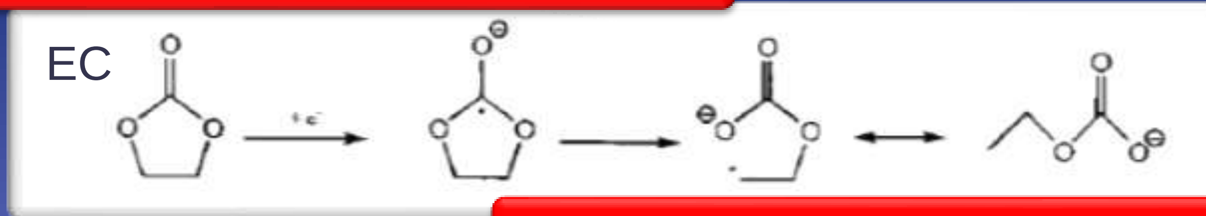
Liquid solution (Li^+ salt and solvent)

Salts: inorganic salts/complex organic salts

Solvents: organic carbonates (cyclic/linear)

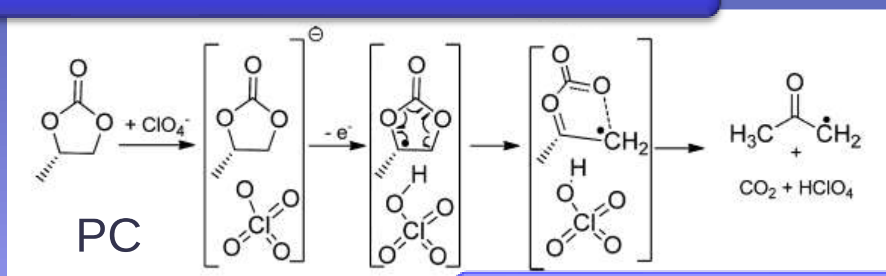


solvent+ e$^-$→ solvent^{red}



E°=1.3 vs Li (exp, CV on Pt)

solvent→ solvent^{ox} + e$^-$

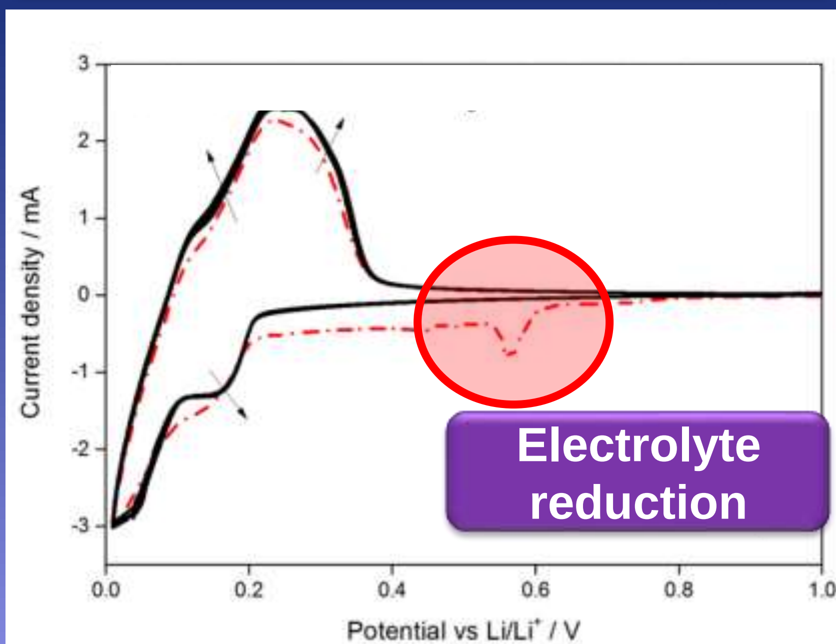


E°=5.2 vs Li (DFT & CV on Pt)

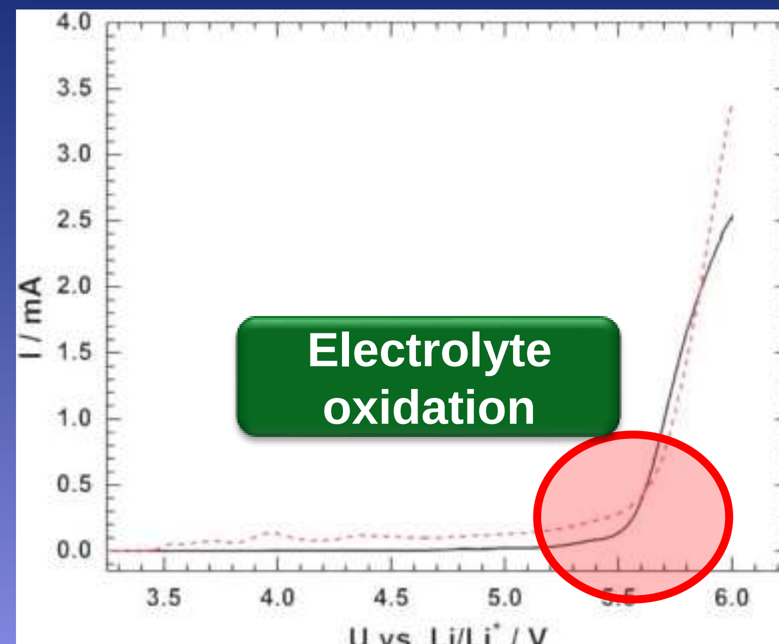
Electrochemical stability window of an electrolyte

(+) Carbon/ electrolyte / Lithium (-)

Cathodic polarization (Cyclic voltammetry)



Anodic polarization (linear sweep voltammetry)



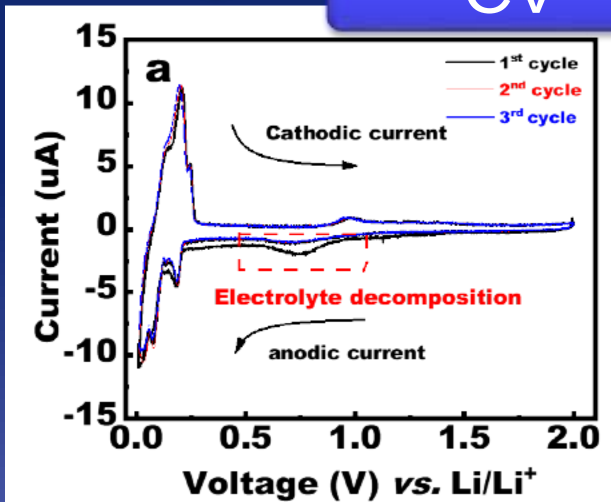
Only in the first cycle then the interface becomes inert

Electrolyte decomposition over graphite

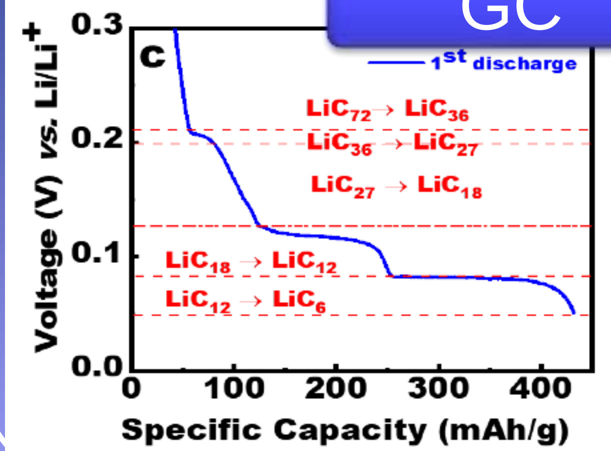
(+)Graphite / electrolyte / Lithium (-)

SEI formation analysis

CV



GC

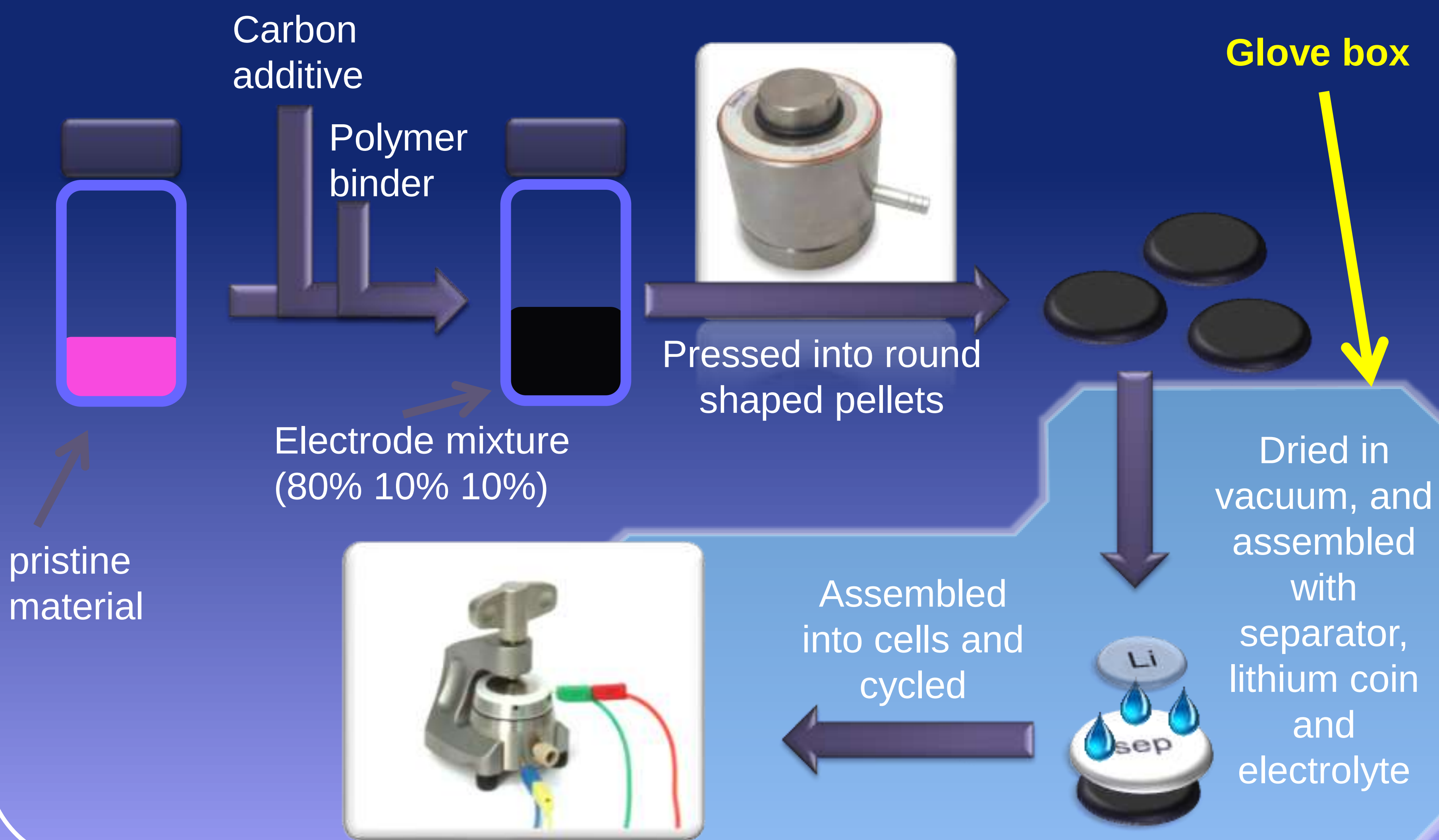


1. The electrolyte decomposes at 0.8-0.7 V vs. Li
2. The decomposition occurs only in the first cycle
3. This irreversible reaction leads to capacity loss
4. This irreversible reaction does not alter the lithium intercalation into the graphite lattice

Ex situ investigation of the graphite surface

Post-mortem sample preparation procedure

The preparation of the samples analysed ex situ requires a multistep procedure



Post-mortem TEM sample preparation procedure

The preparation of the samples analysed by TEM requires a multistep procedure

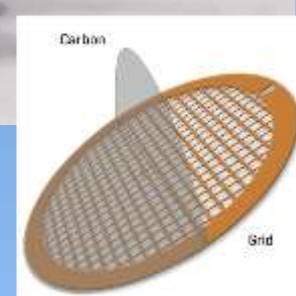
Electrodes recuperated from cells in glove box

Washed with DME/THF and dried in vacuum

Post mortem electrode materials

Spread over carbon mesh grids for TEM

Glove box



Transferred to TEM chamber

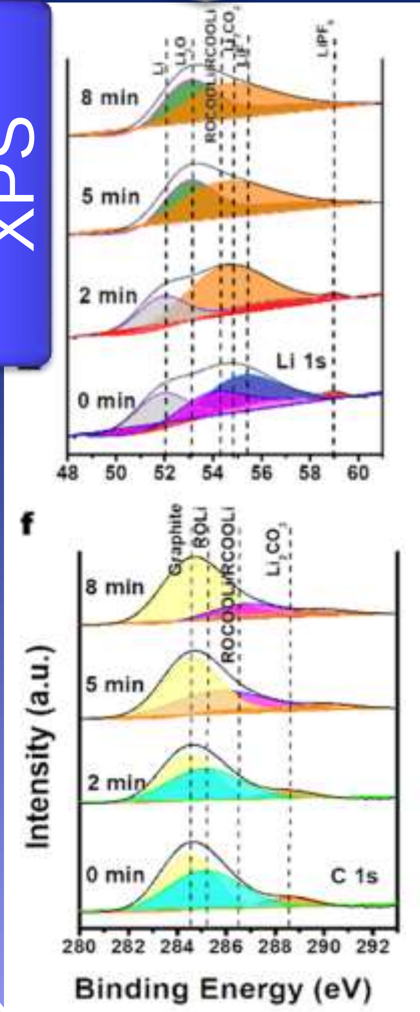
Morphology after cycling

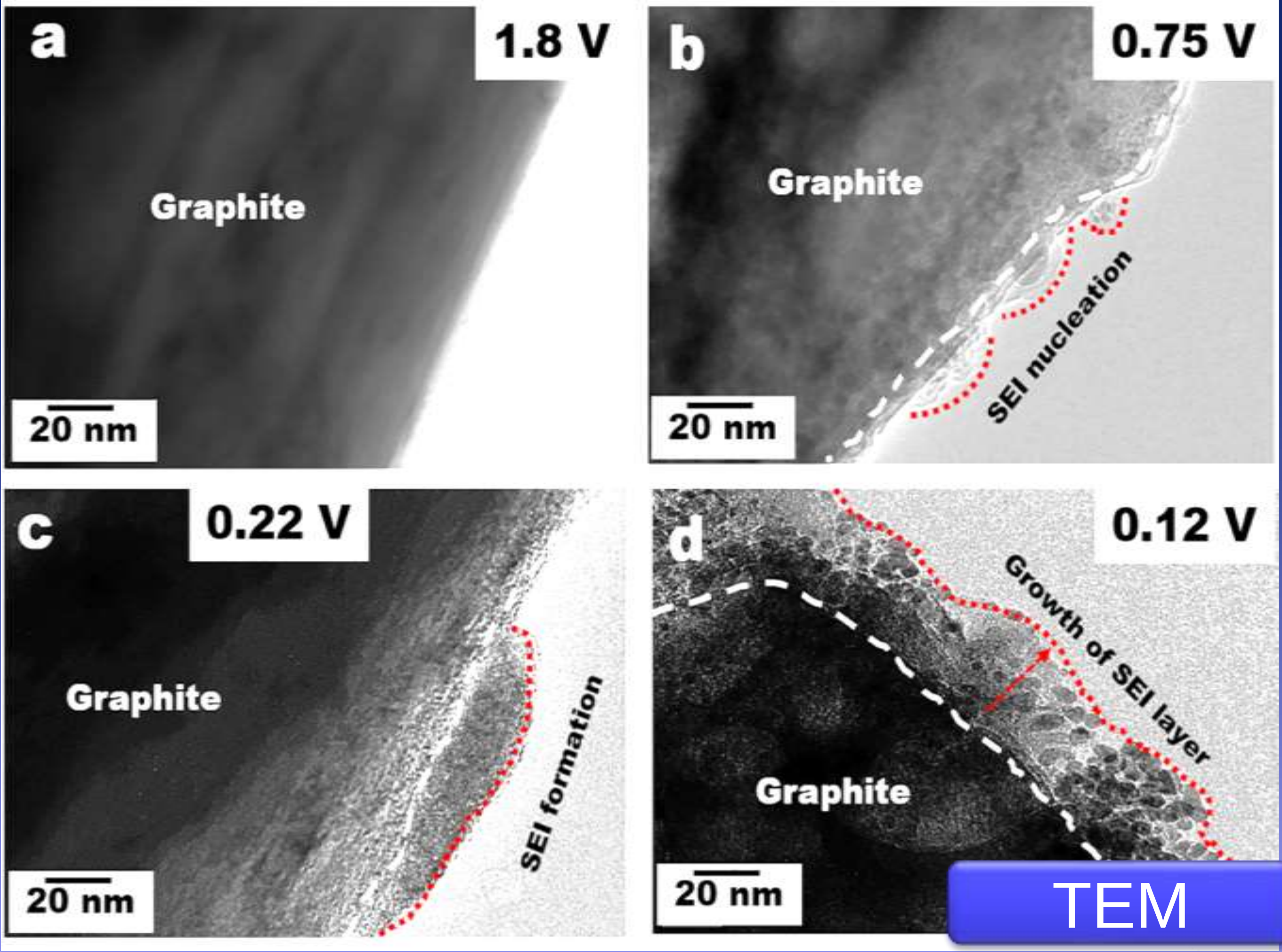
Electrolyte decomposition over graphite

(+)Graphite / electrolyte / Lithium (-)

Ex situ analysis

XPS

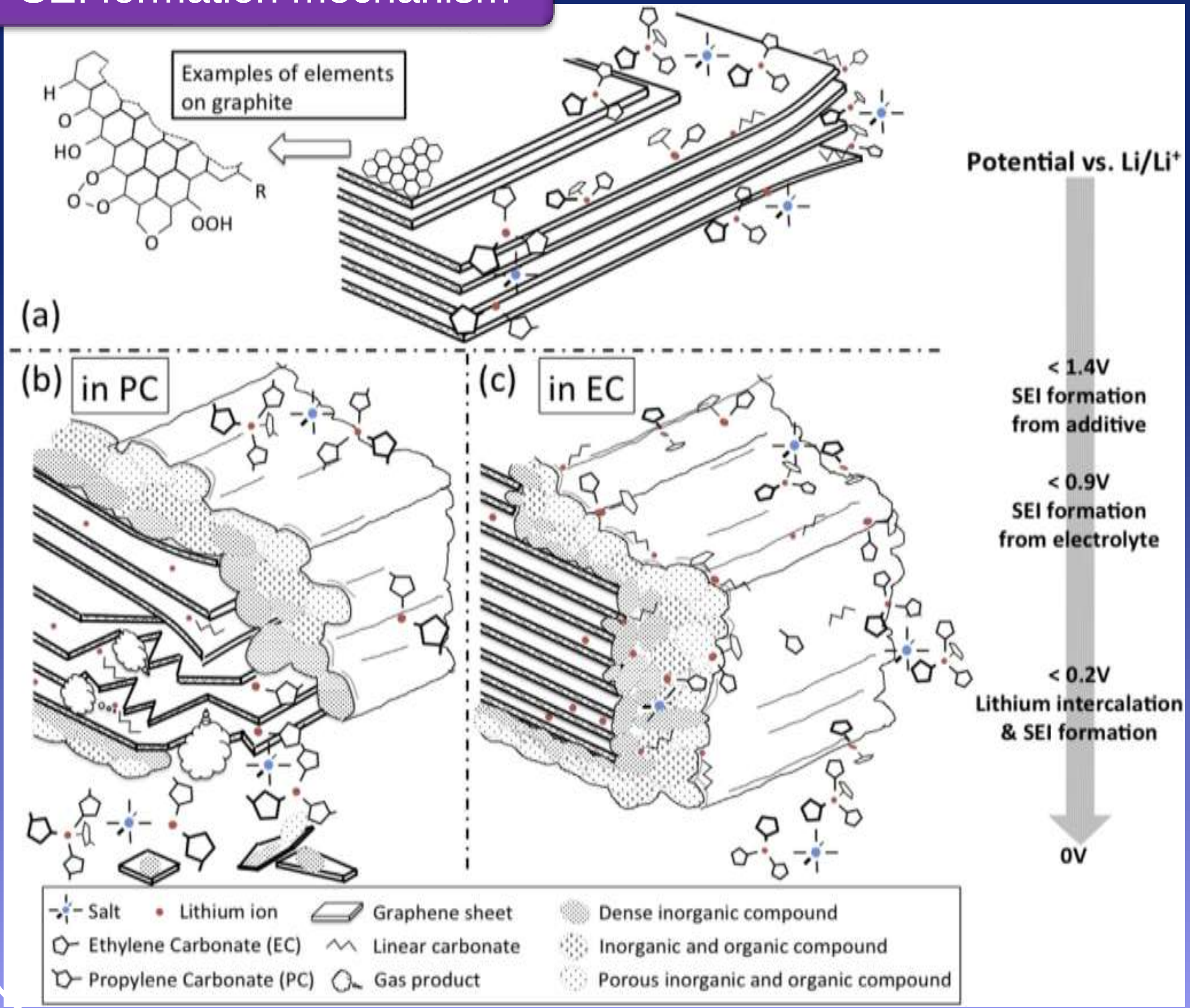




TEM

Solid electrolyte interphase over graphite

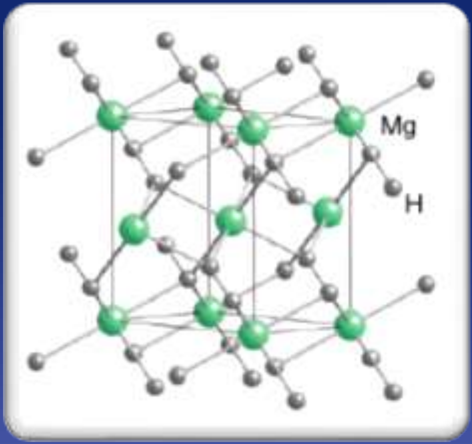
SEI formation mechanism

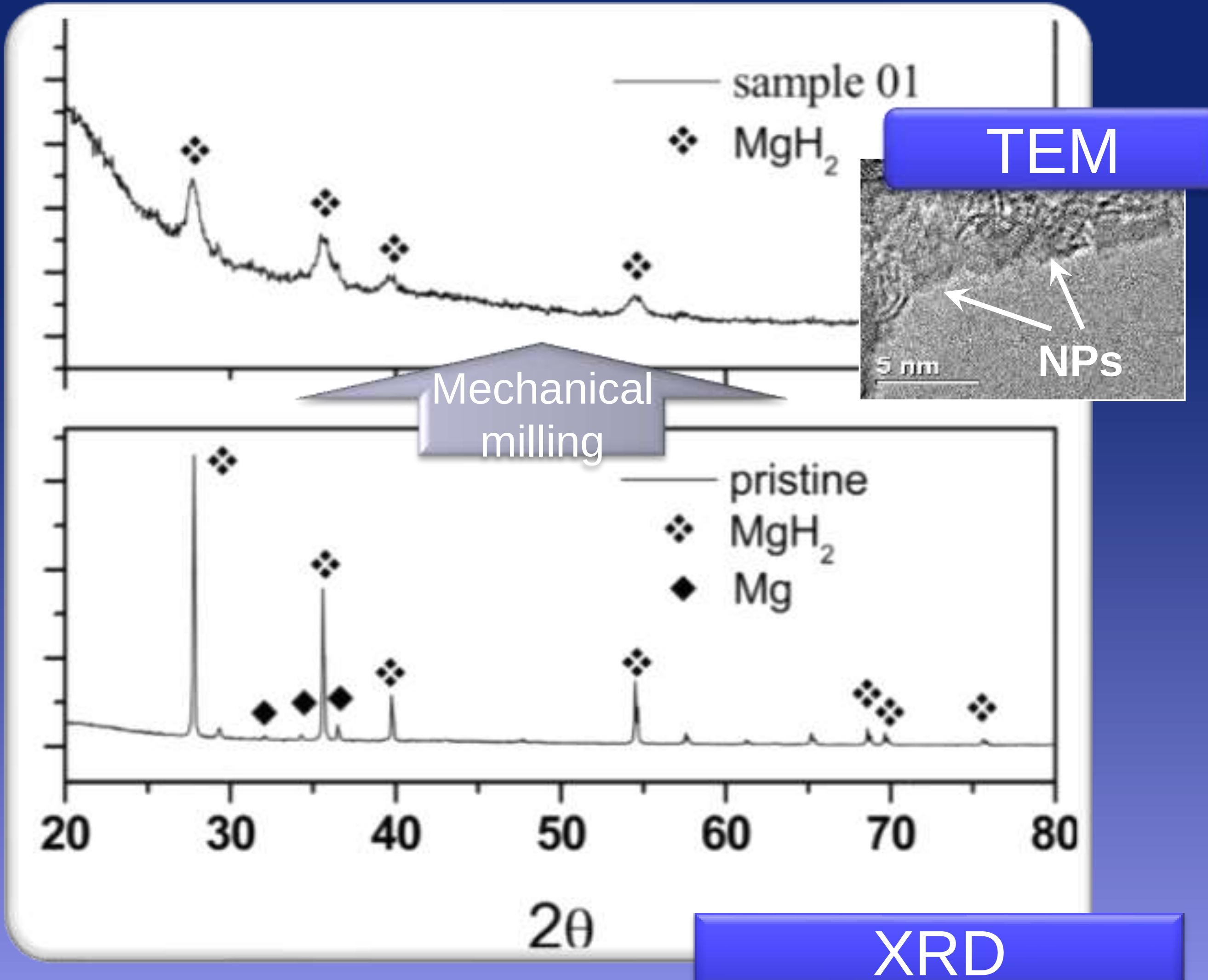


1. The SEI is an interphase layered over the surface of graphite;
2. SEI forms spontaneously upon discharge in Li-cells;
3. SEI has a complex inorganic/organic nature;
4. SEI allows lithium transport;
5. After formation the SEI inhibit charge-transfer to the electrolyte.

Negative electrodes: MgH_2

Mg hydride
tP6 SG 136





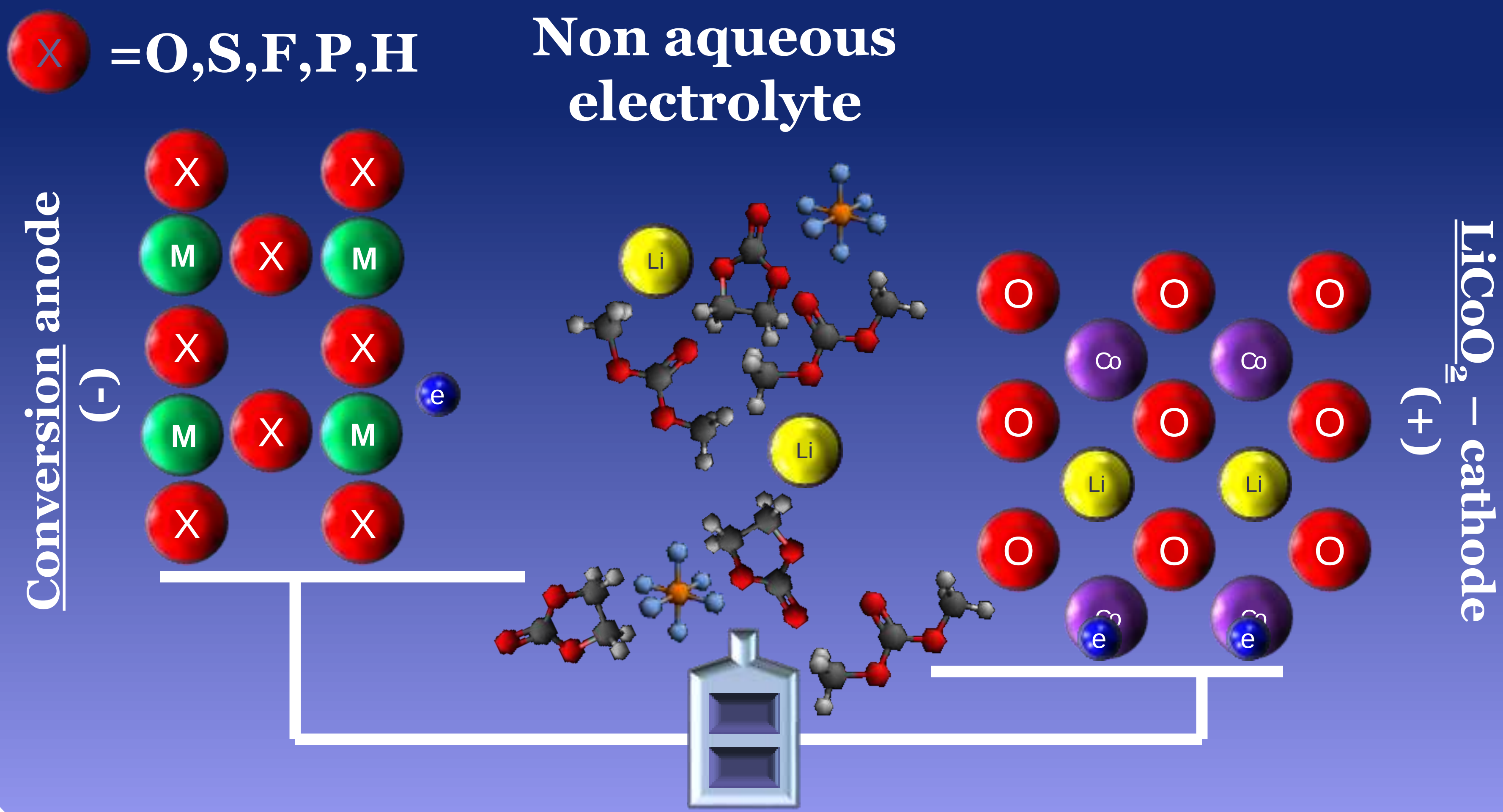
Collector: **Cu**

Theoretical capacity:
2048 mAh/g

Nominal voltage:
0.5 V vs. Li

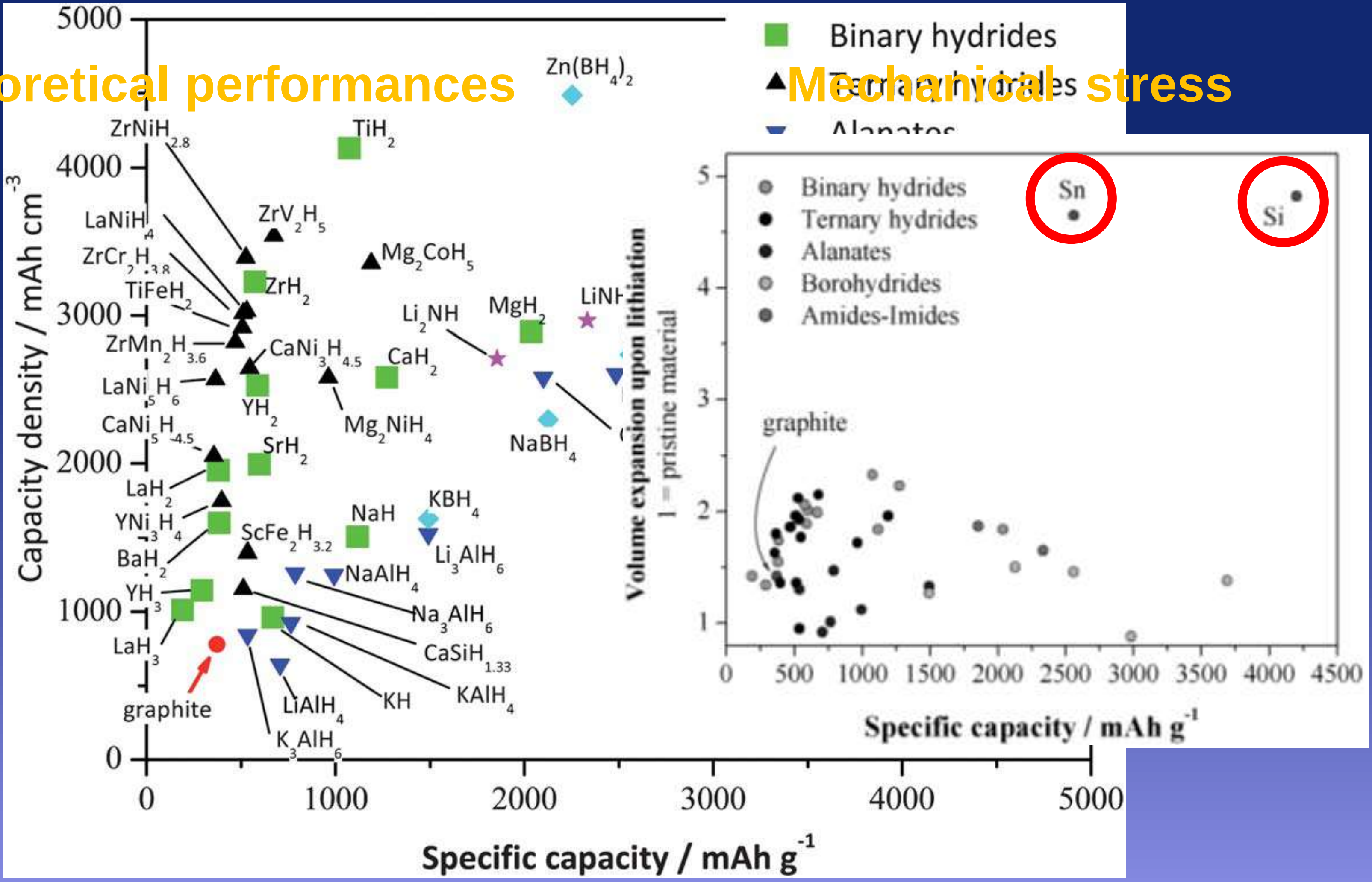
Li-ion N-E materials: Conversion reactions

$$MX_y + y\ e^- + y\ Li^+ \rightarrow M + y\ LiX$$



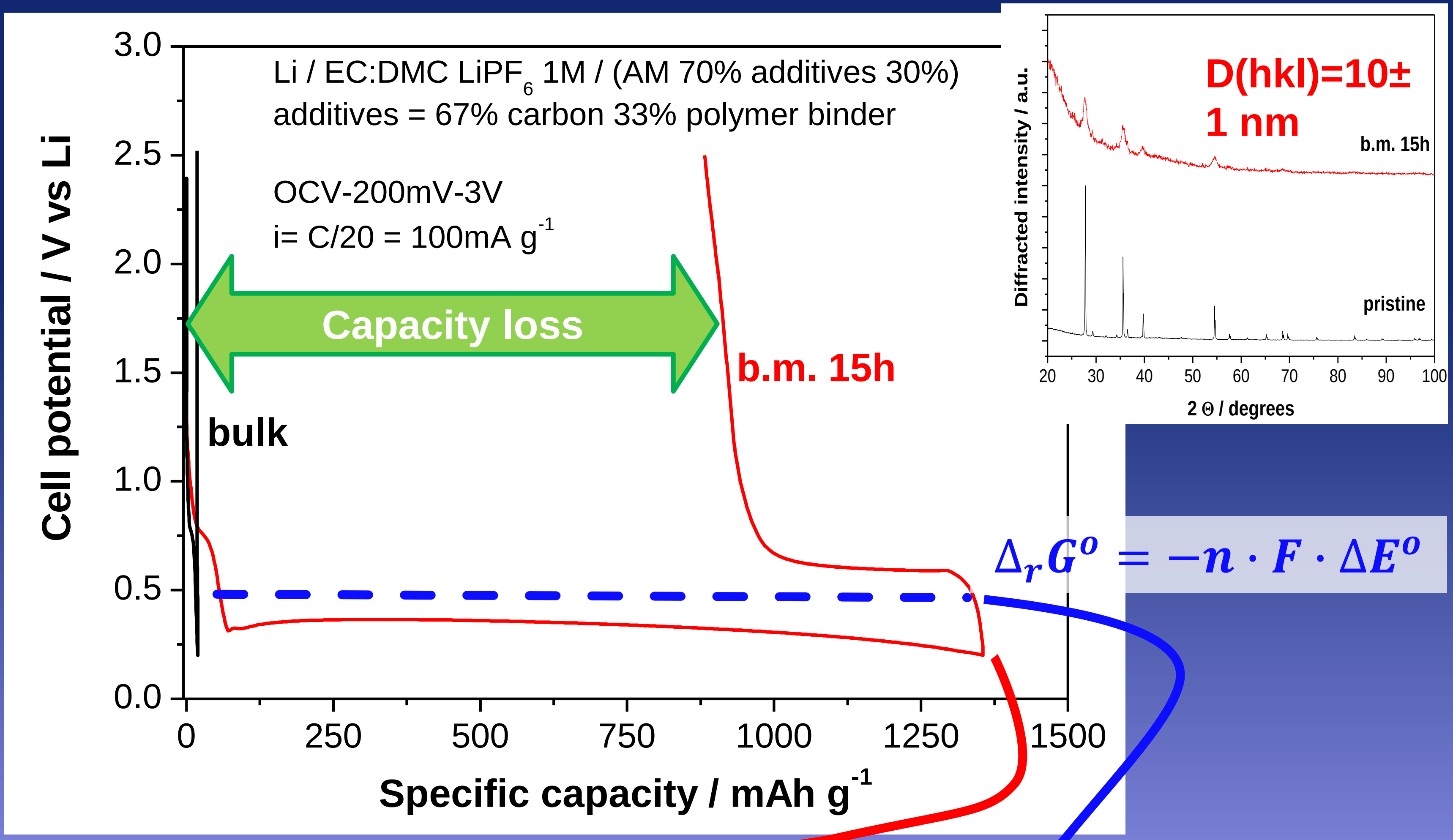
Hydrides conversion reactions: advantages

Theoretical performances **Mechanical stress**



$$MH_x + xLi^+ + xe^- = M + xLiH$$

(+)MgH_2/ electrolyte / Lithium (-)



$$\Delta_r G^o = -n \cdot F \cdot \Delta E^o$$

Theoretical capacity
2048 mAhg^{-1}

Thermodynamic E°
0.52 V vs Li

Post-mortem XRD sample preparation procedure

The preparation of the samples analysed by TEM requires a multistep procedure

Electrodes recuperated from cells in glove box

Washed with DME/THF and dried in vacuum

Post mortem electrode materials

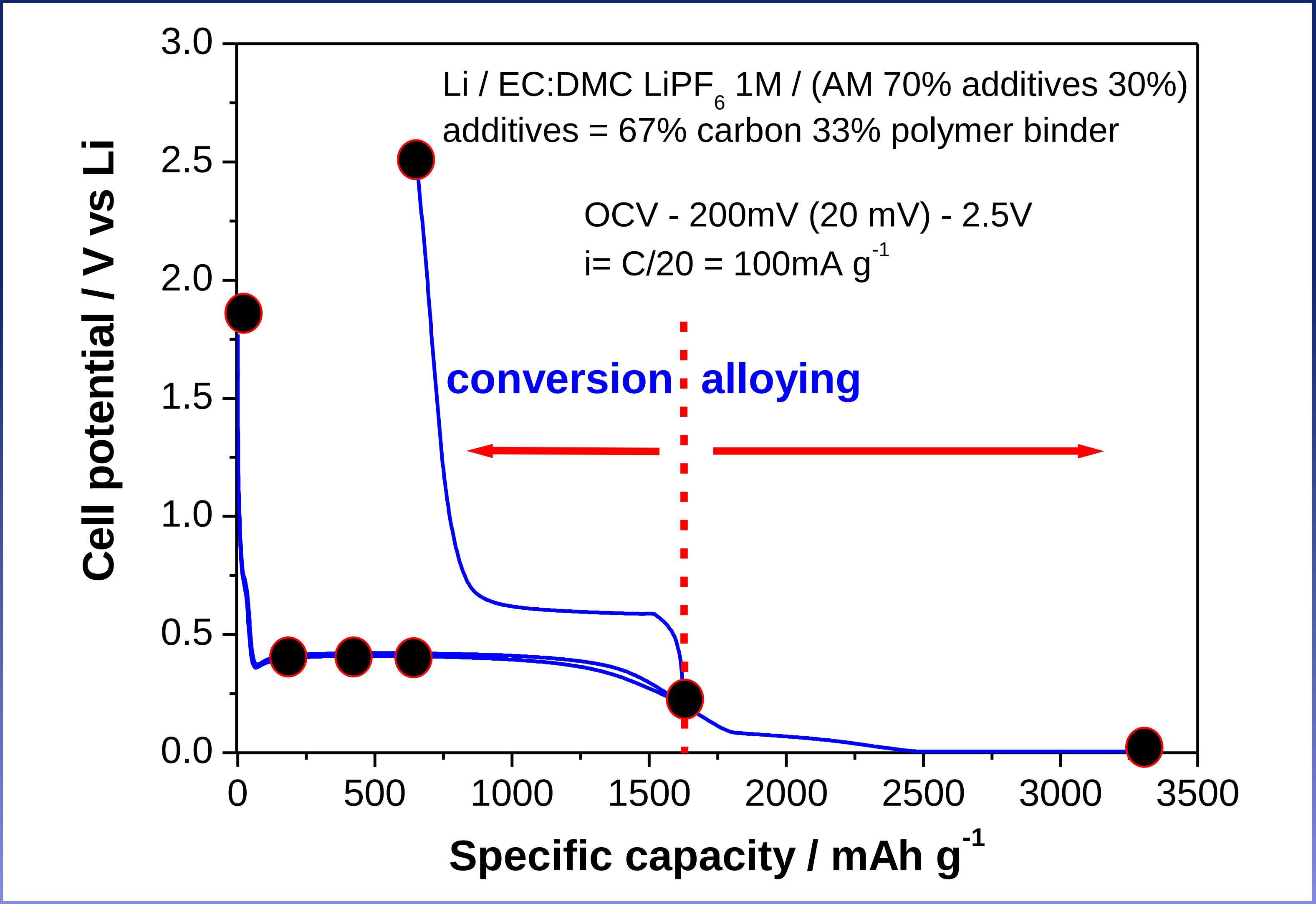
Sealed in capillaries in box and stored

Glove box

Structure after cycling

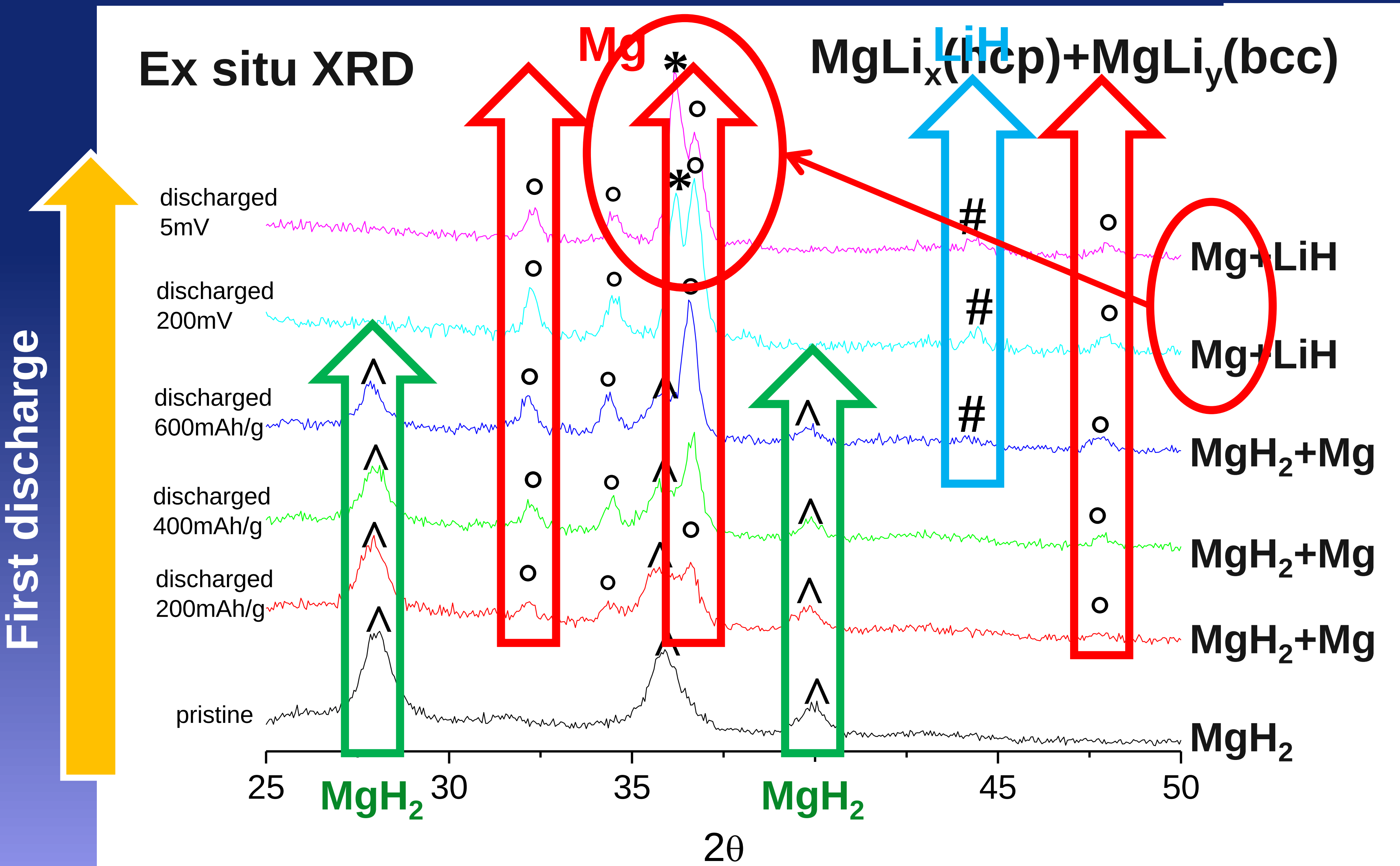
Transferred to ELETTRA and studied at the MCX beamline by synchrotron **XRD**

MgH_2: ex situ reaction mechanism



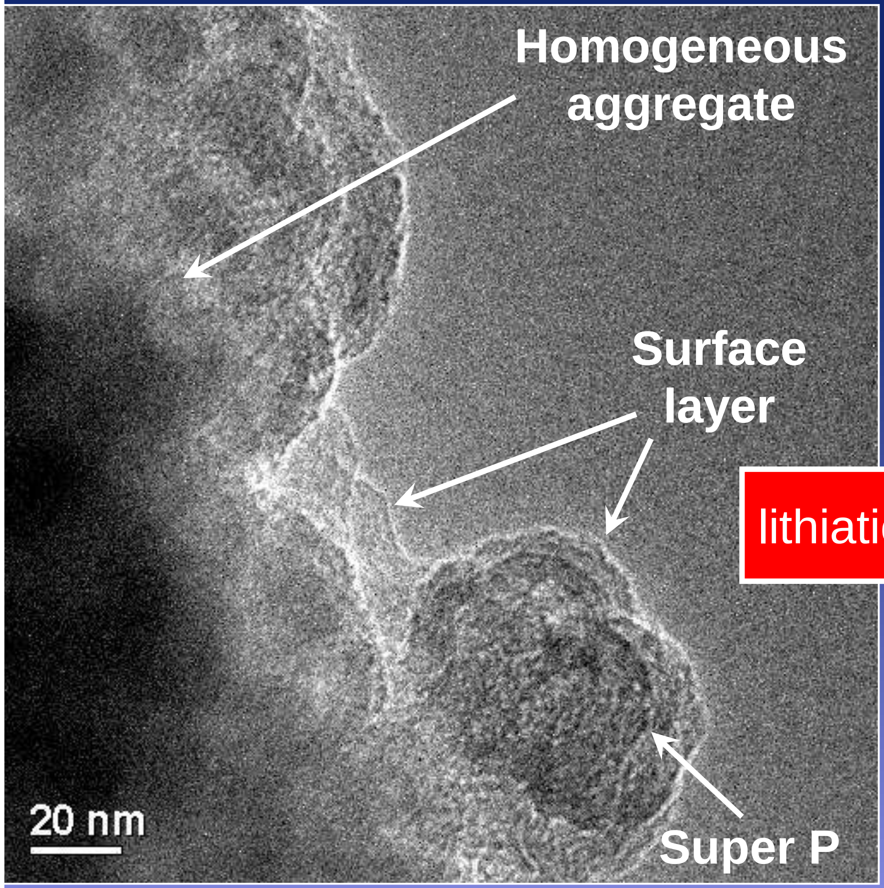
(+)MgH_2/ electrolyte / Lithium (-)

MgH_2: XRD study

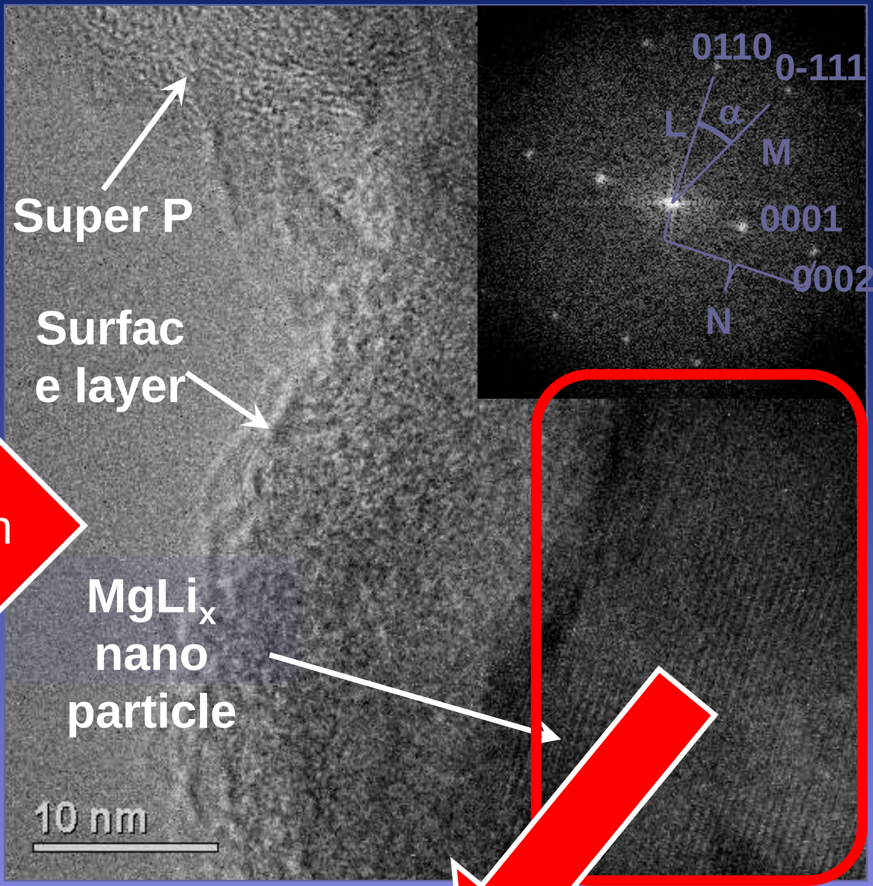


MgH$_2$: TEM study

MgH$_2$ fully discharged at 200 mV in a lithium cell



lithiation

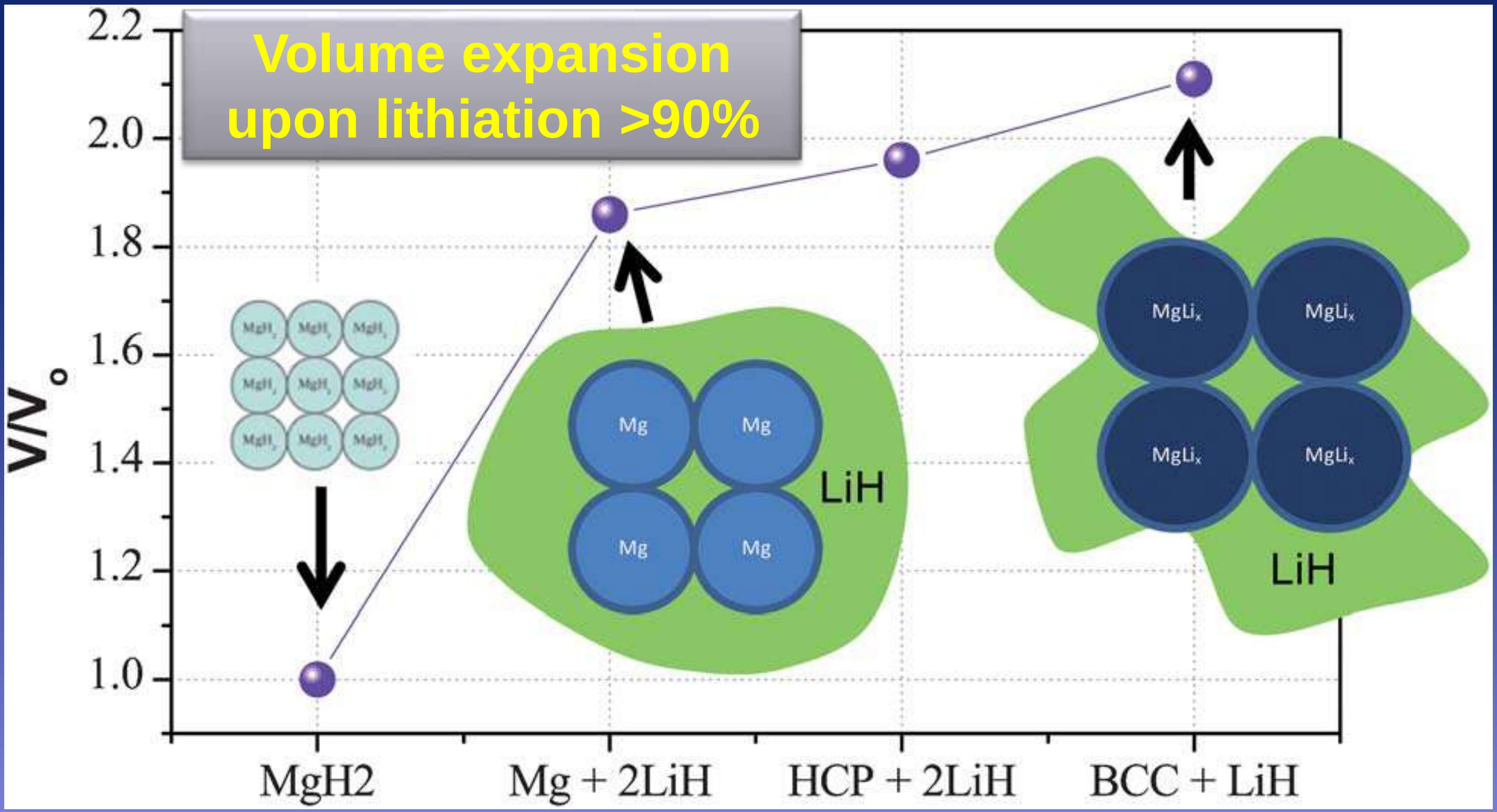


NANO-PARTICLES SINTERING UPON DISCHARGE

MgH_2 conversion in Li-ion cell

Nature of the capacity losses

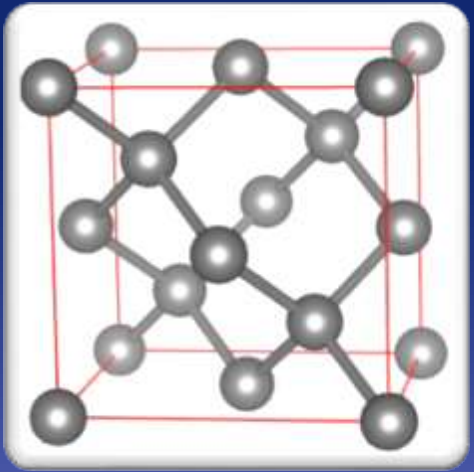
Volume expansion upon lithiation >90%



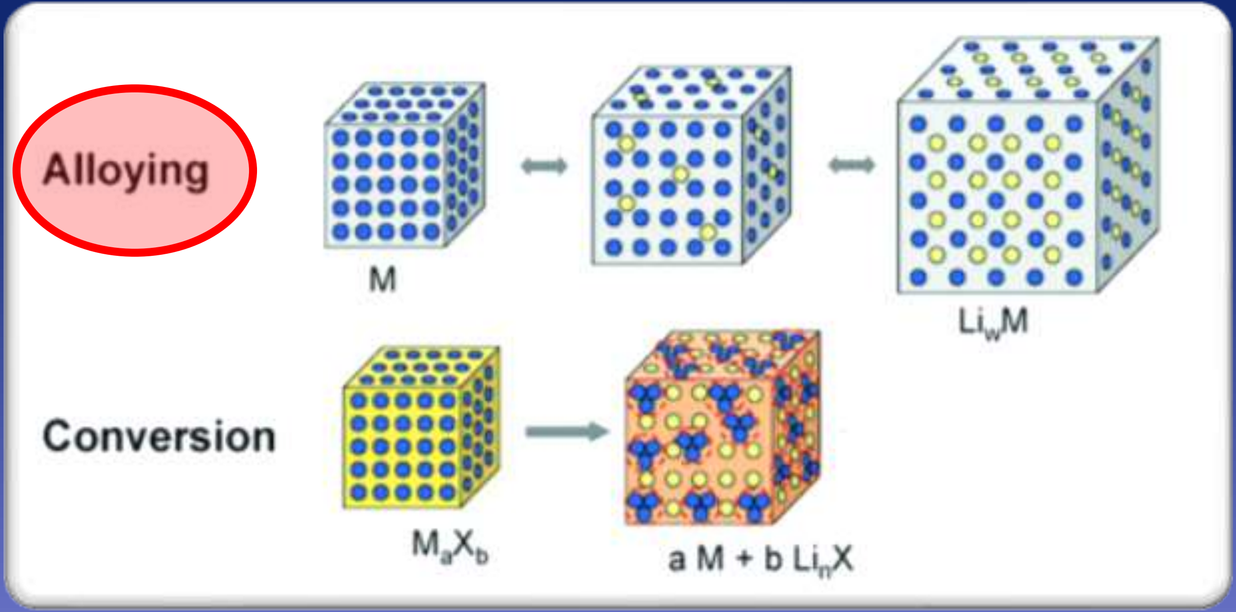
Electrode pulverization
Loss of electron conductivity

Alloying reactions and volume changes

Silicon
cF8 SG 227



$$Si + \frac{15}{4}Li^{+} + \frac{15}{4}e^{-} \rightarrow \frac{1}{4}Li_{15}Si_{4}$$



Collector: **Cu**

Theoretical capacity:
3579 mAh/g

Nominal voltage:
0.2-0.5 V vs. Li

Si volume expansion upon lithiation +320%

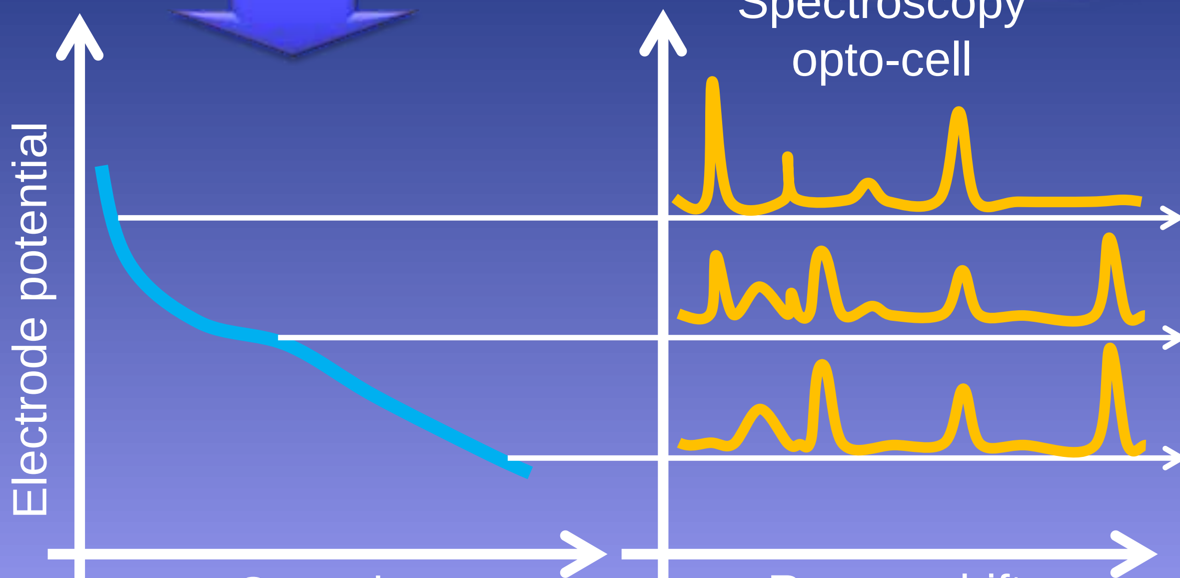
In operando Raman experiments

The in operando analysis implies the simultaneous electrochemical cell discharge/charge and Raman tests

Galvanostat

Spectroscopy opto-cell

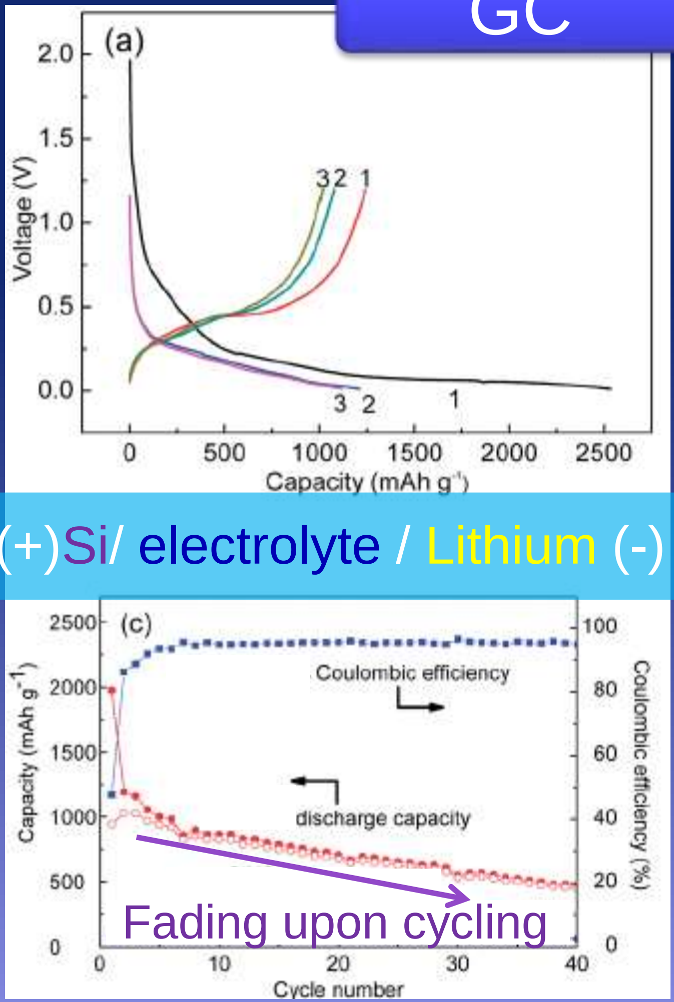
Alligned in the micro Raman spectrophotometer



Vibrational fingerprint upon cycling

Lithium loading into the silicon lattice

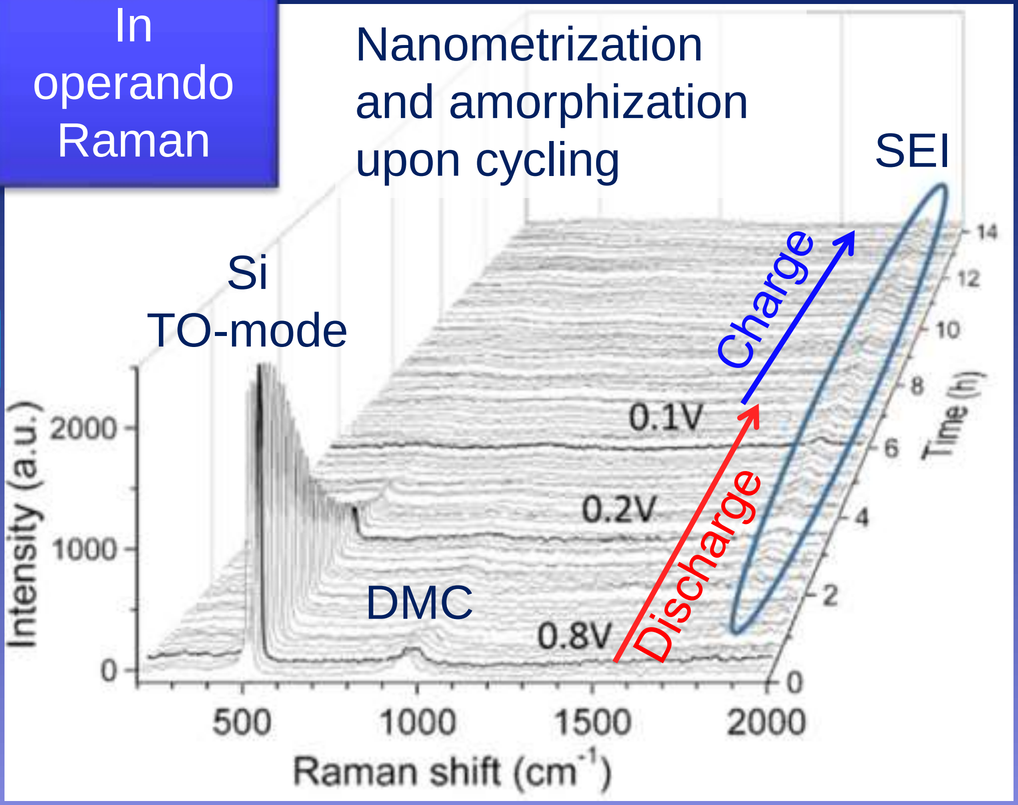
GC



(+)Si/ electrolyte / Lithium (-)

$$Si + \frac{15}{4}Li^{+} + \frac{15}{4}e^{-} \rightarrow \frac{1}{4}Li_{15}Si_{4}$$

In operando Raman

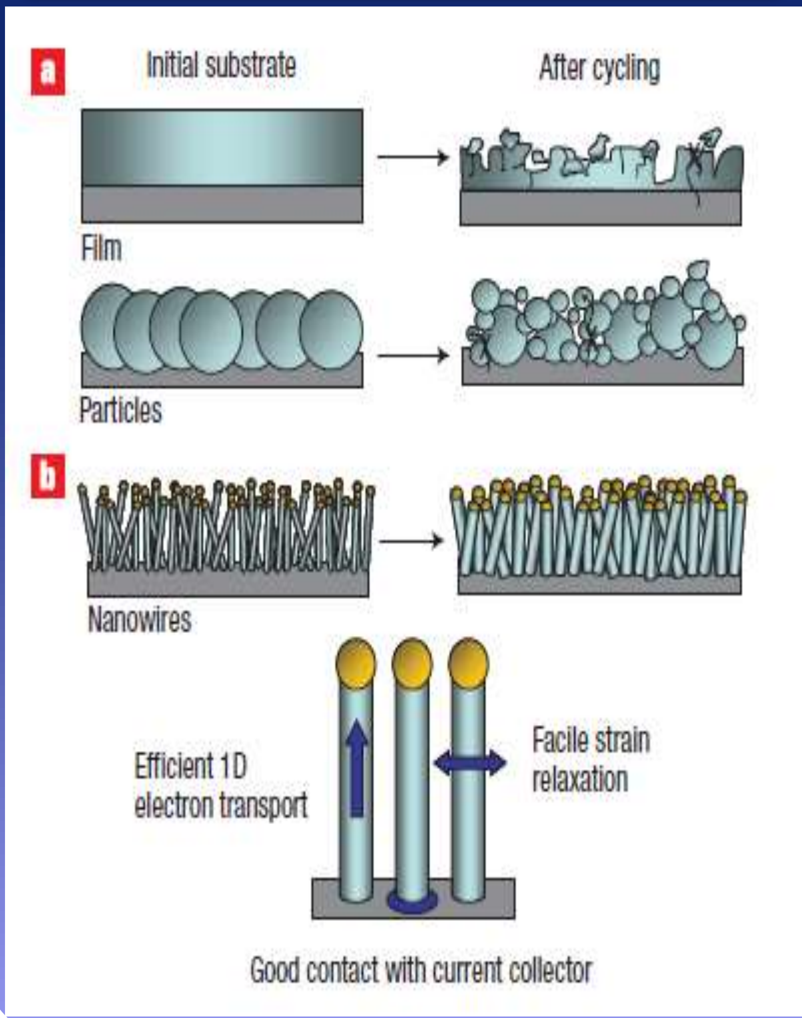


How to handle the volume expansion?

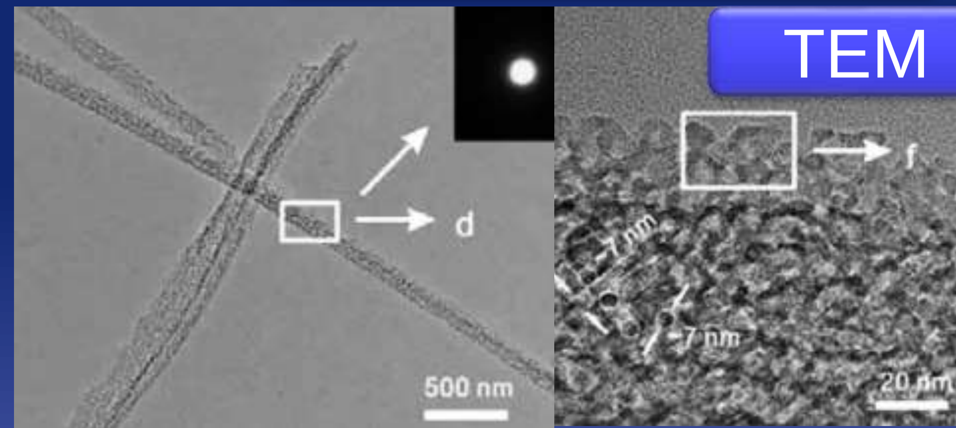
Buffering the volume by going nano

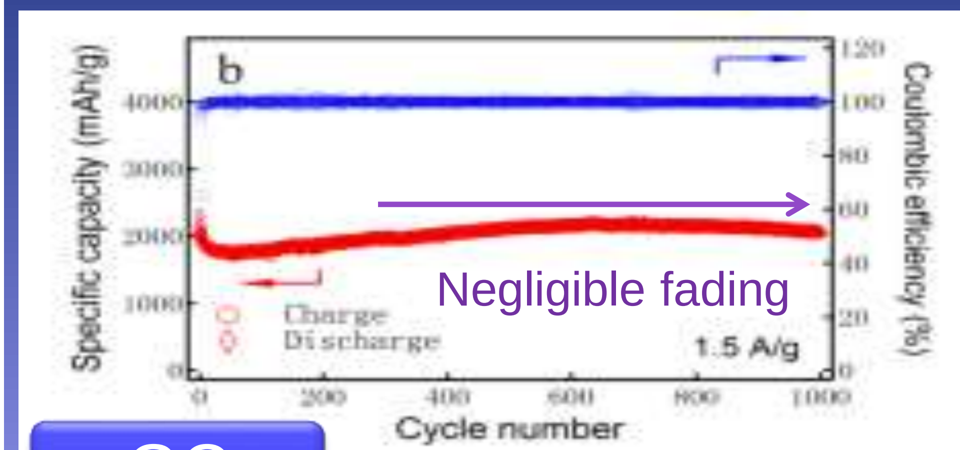
Morphological changes of Si upon lithiation

Hierarchical materials can expand and shrink buffering the stress/strain



TEM

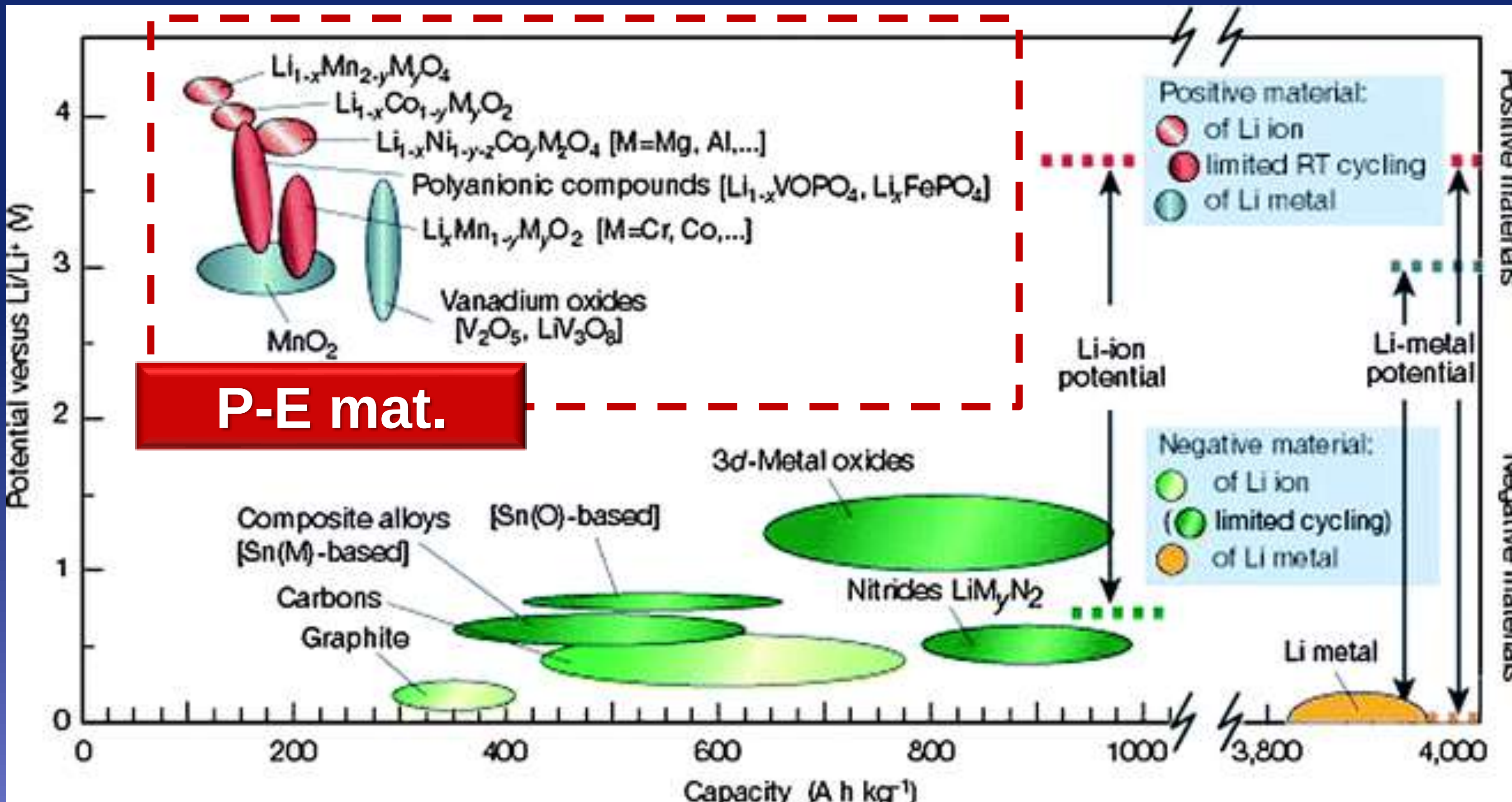




GC

(+)Si/ electrolyte / Lithium (-)

Li-ion battery: positive electrodes



High potential: E° close but below the anodic stability of the electrolyte

Invariant lattice: stable structure upon lithiation

High reversibility: electrochemical reaction in ch/dsch

Li-ion battery: positive electrodes families

Intercalation chemistry

Layered phases

$Li_{½}CoO_2 + ½Li^+ + ½e^- \rightarrow LiCoO_2$

Spinel phases

$Ni_{½}Mn_{3/2}O_4 + Li^+ + e^- \rightarrow LiNi_{½}Mn_{3/2}O_4$

Olivine phases

$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4$

Conversion chemistry

Fluorides

$FeF_3 + Li^+ + e^- \rightarrow LiF + FeF_2$

Anionic redox chemistry

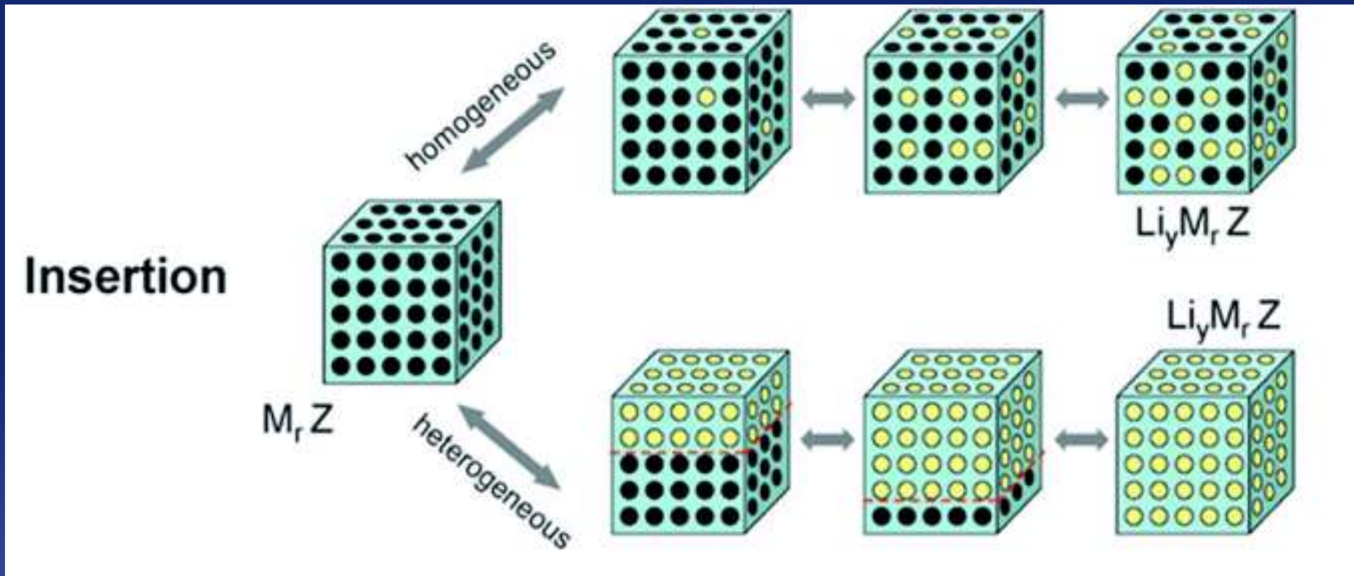
Oxygen

$O_2 + 2\ Li^+ + 2\ e^- \rightarrow Li_2O_2$

Sulphur

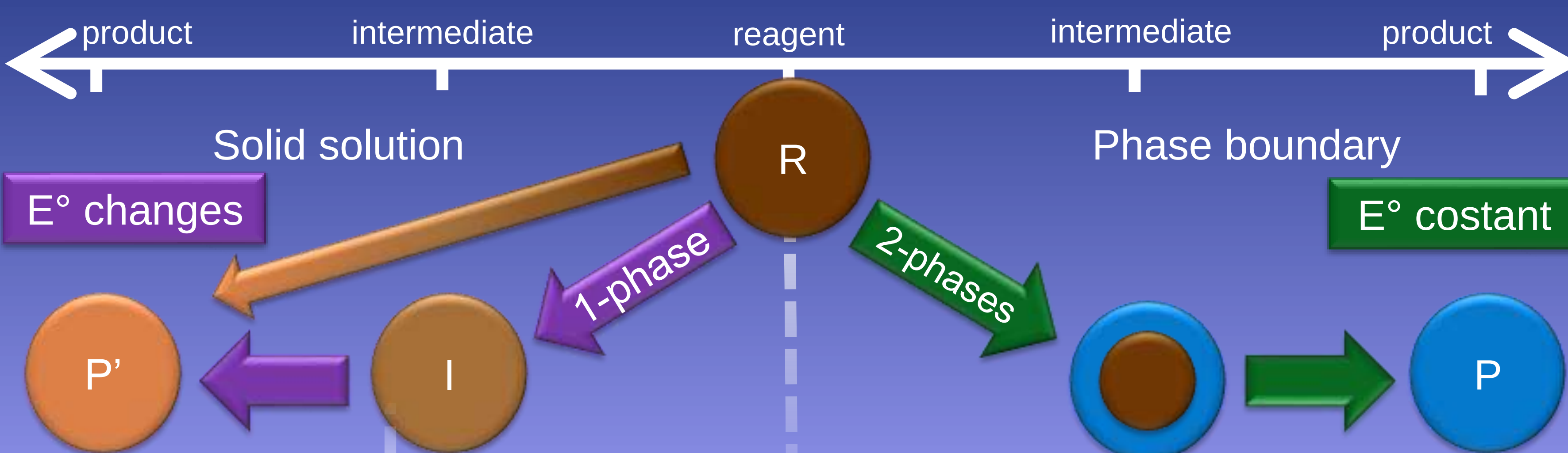
$S + 2\ Li^+ + 2\ e^- \rightarrow Li_2S$

Intercalation chemistry at the P-E



Single phase process

Two phases process



E° changes

E° costant

$$\Delta_r G^{o\,\prime\prime} = \Delta_f G^o(P') + -\Delta_f G^o(I)$$

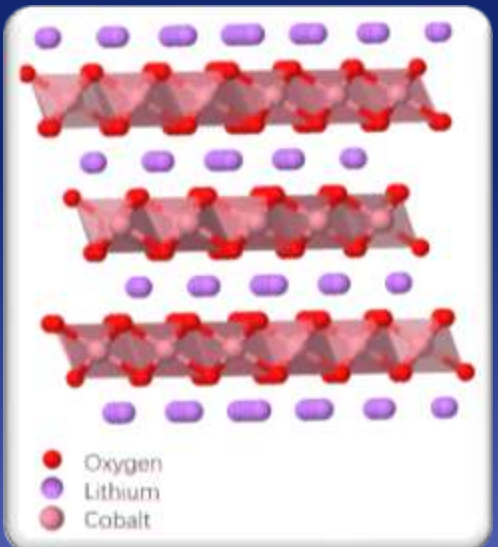
$$\Delta_r G^{o\,\prime} = \Delta_f G^o(I) + -\Delta_f G^o(R)$$

$$\Delta_r G^o = \Delta_f G^o(P) - \Delta_f G^o(R)$$

Layered positive electrodes: $LiCoO_2$

$LiCoO_2$ / LCO
cI2 SG 229

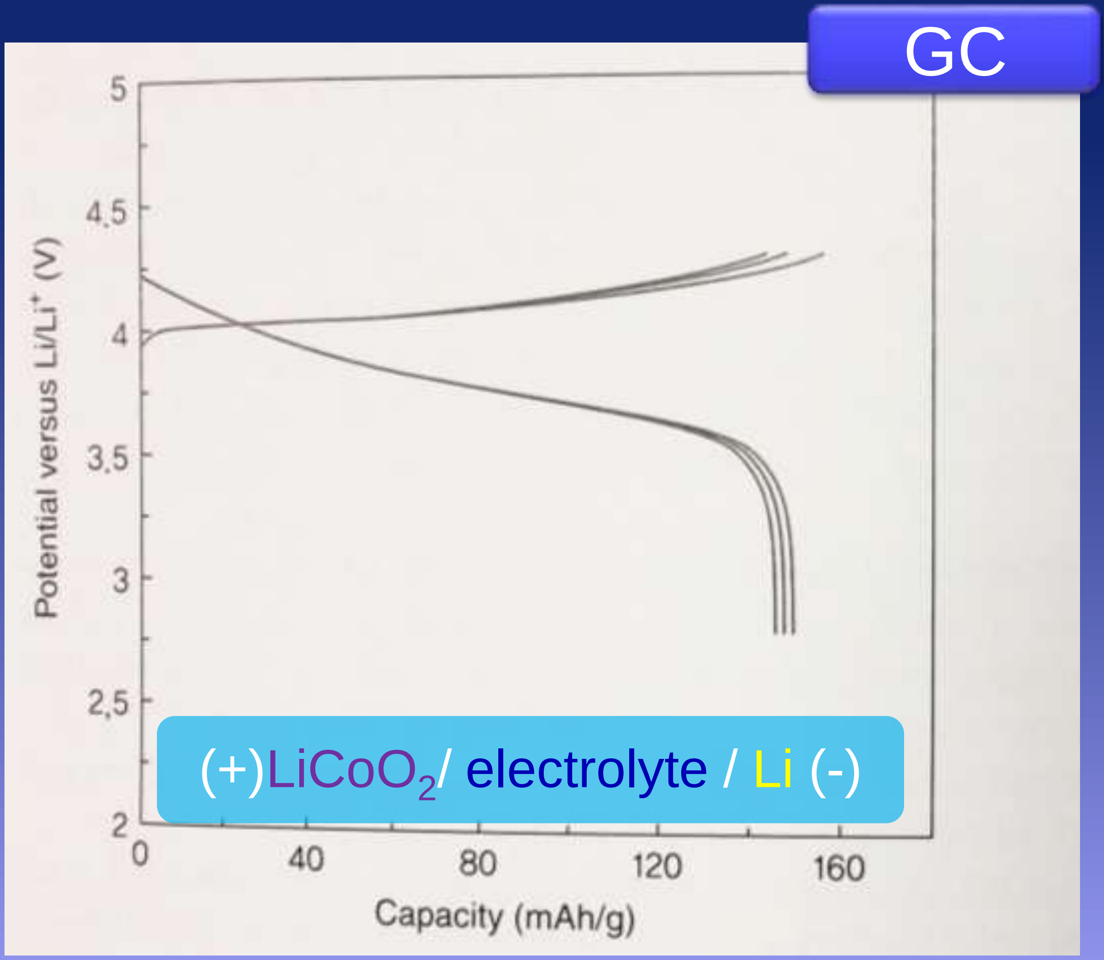
$$Li_{\frac{1}{2}}CoO_2(O3) + xLi^+ + xe^- \rightarrow Li_{\frac{1}{2}+x}CoO_2(O3)$$



Collector: **Al**

Theoretical capacity:
137 mAh/g (0.5 Li_{eq})

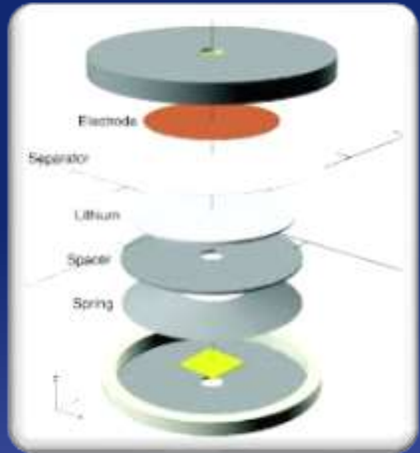
Nominal voltage:
3.3-4.3 V vs. Li



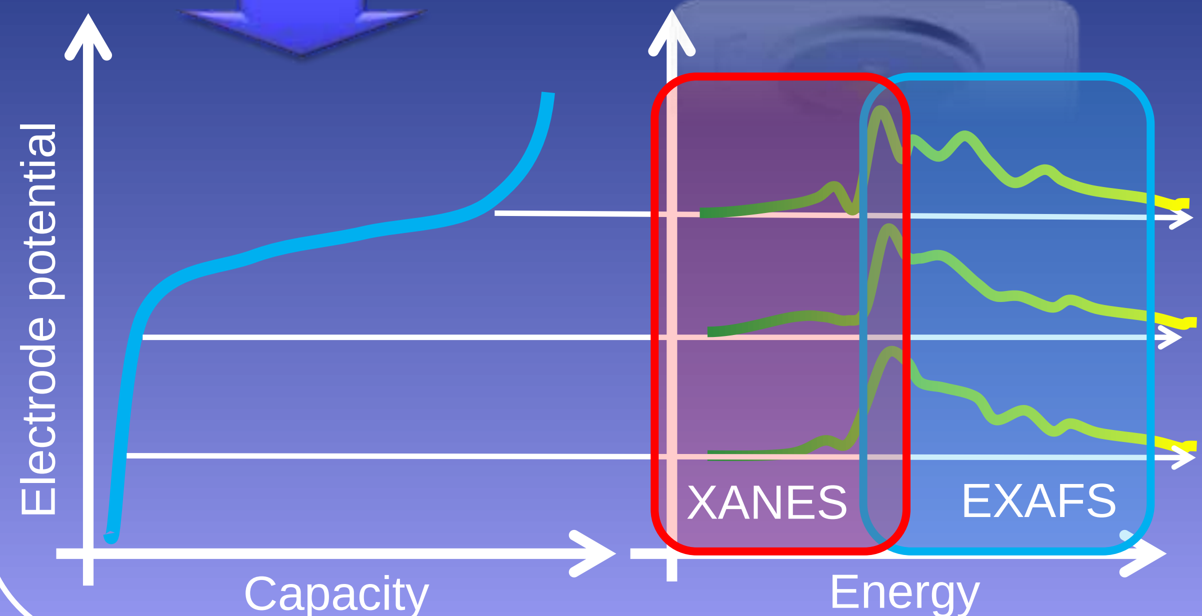
In operando XAS experiments

The in operando analysis implies the simultaneous electrochemical cell discharge/charge and XAS tests at synchrotrons

Galvanostat



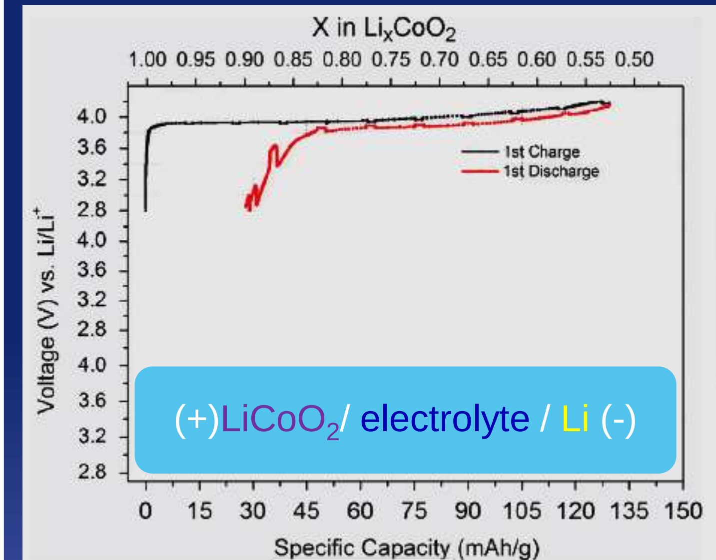
Alligned in the synchrotron beamline



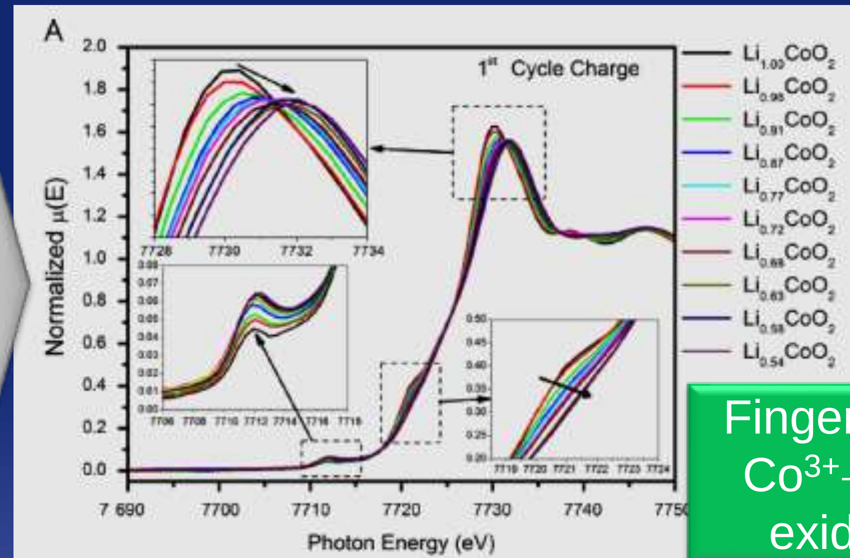
Electronic configuration upon cyling

Local coordination upon cyling

Homogeneous/heterogeneous intercalation: $LiCoO_2$



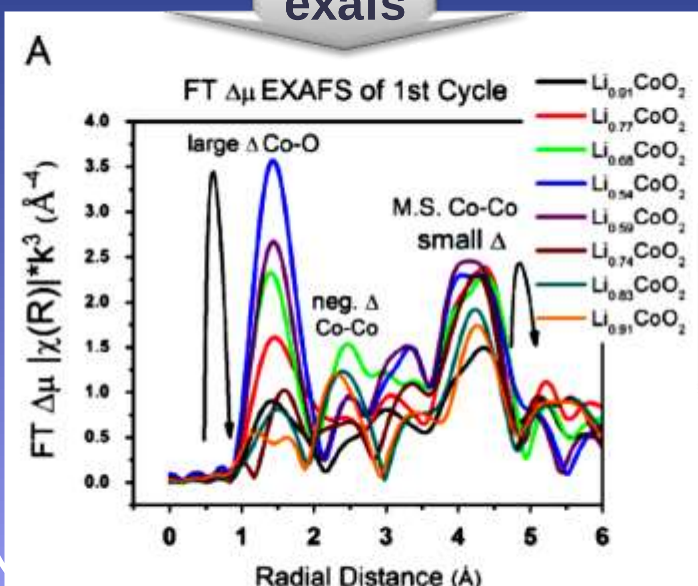
xanes



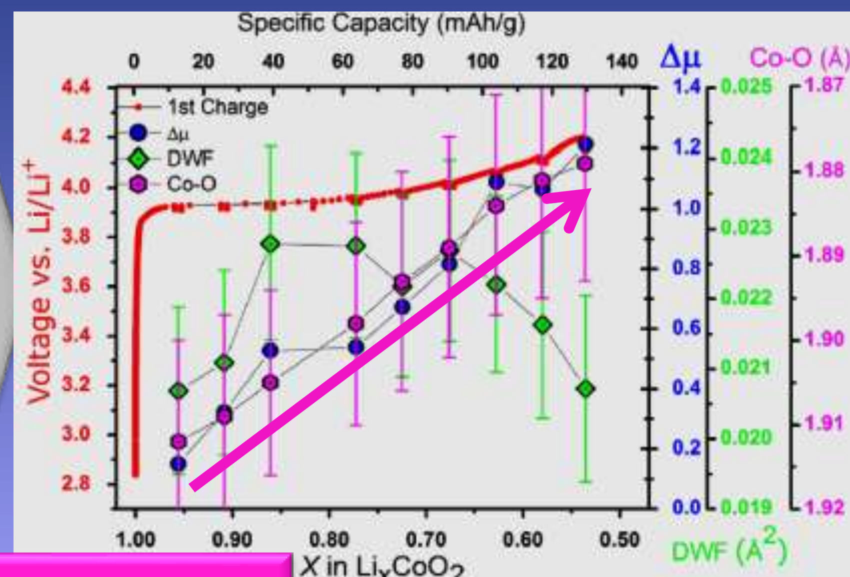
In operando XAS

Fingerprint of $Co^{3+} \rightarrow Co^{4+}$ exidation

exafs



trends

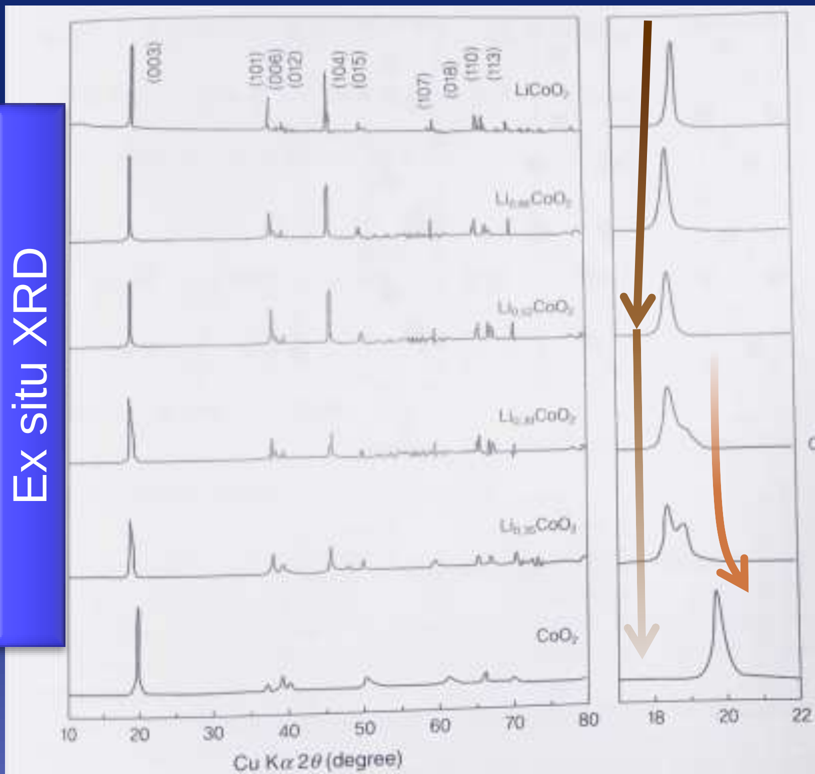


In operando XAS

Co-O bond

Homogeneous/heterogeneous intercalation: $LiCoO_2$

Ex situ XRD



X(Li): 1.00, 0.66, 0.52, 0.39, 0.35, 0

Peak shifts

O3 fades
P3 increases

$LiCoO_2$ (O3)

$Li_{1/2+x}CoO_2$ (O3)

CoO_2 (P3)

$$CoO_2(P3) + \frac{1}{2}Li^+ + \frac{1}{2}e^- \rightarrow Li_{\frac{1}{2}}CoO_2(O3)$$

$$\Delta_r G^o = \Delta_f G^o(O3) - \Delta_f G^o(P3)$$

heterogeneous

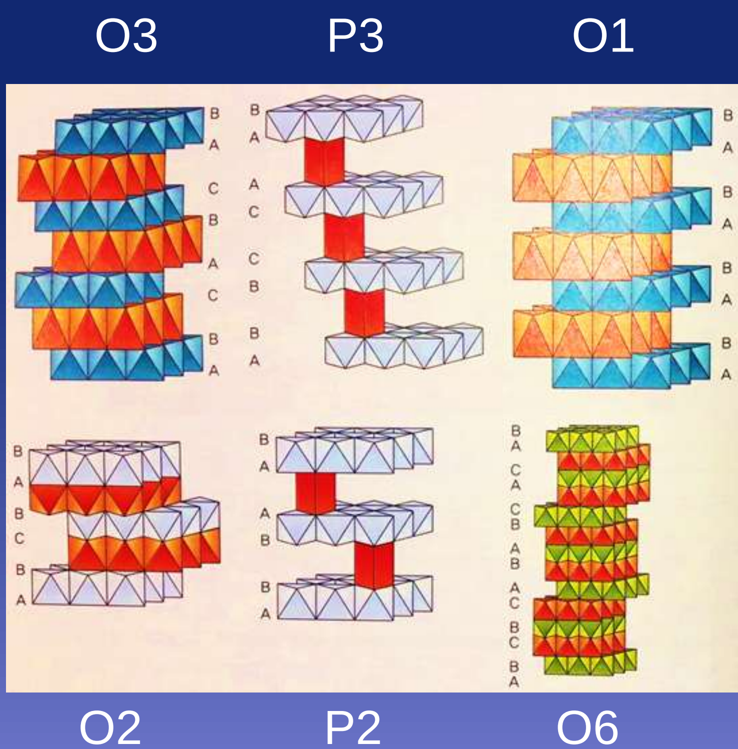
$$Li_{\frac{1}{2}}CoO_2(O3) + xLi^+ + xe^- \rightarrow Li_{\frac{1}{2}+x}CoO_2(O3)$$

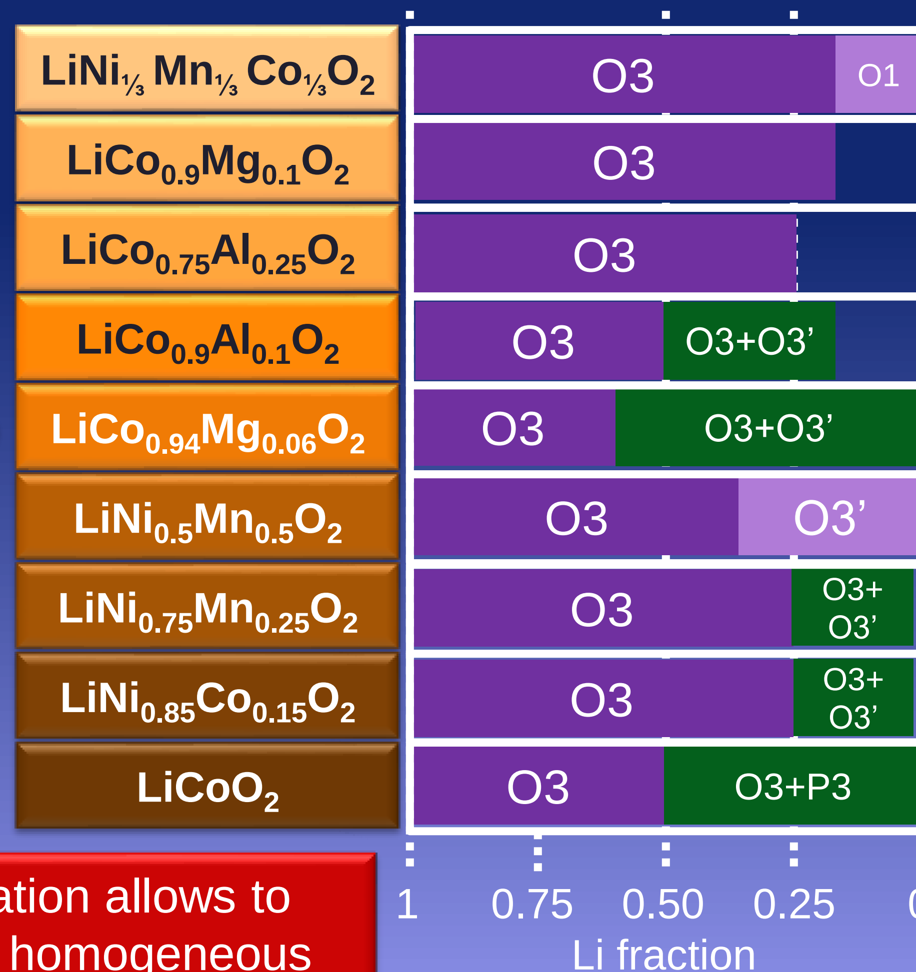
$$\Delta_r G^o = \Delta_f G^o(O3_{Li=1/2+x}) + - \Delta_f G^o(O3_{Li=1/2})$$

homogeneous

Layered positive electrode materials

Stoichiometry of the $LiMO_2$-layered phases drives the stacking disorder and the electrochemical lithium de-intercalation/intercalation.



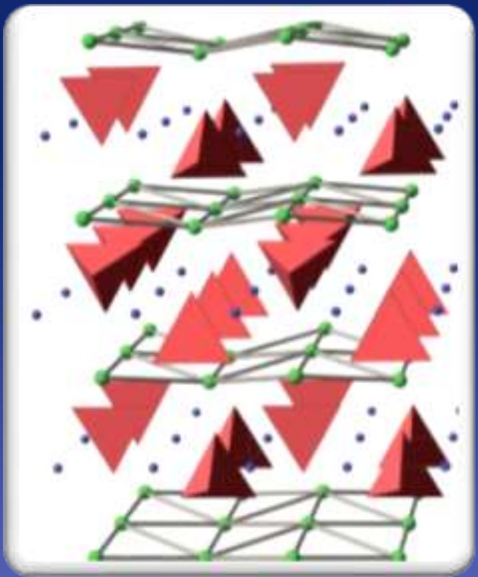


Overlithiation allows to increases homogeneous reversibility (Li-rich layered)

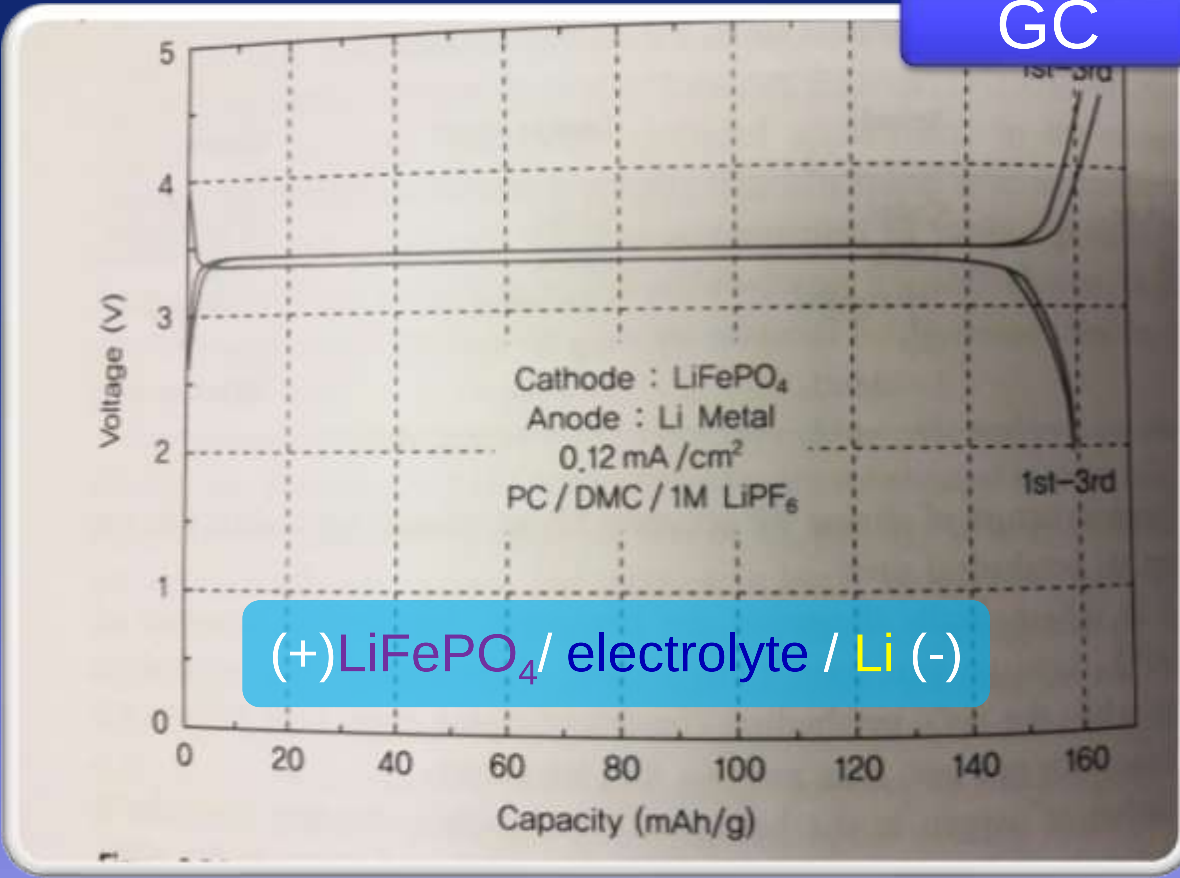
Olivine lattice: diffusion in 1D channels

$LiFePO_4$ / LFP
oP28 SG 62

$$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4$$



GC



(+)$LiFePO_4$/ electrolyte / Li (-)

Collector: **Al**

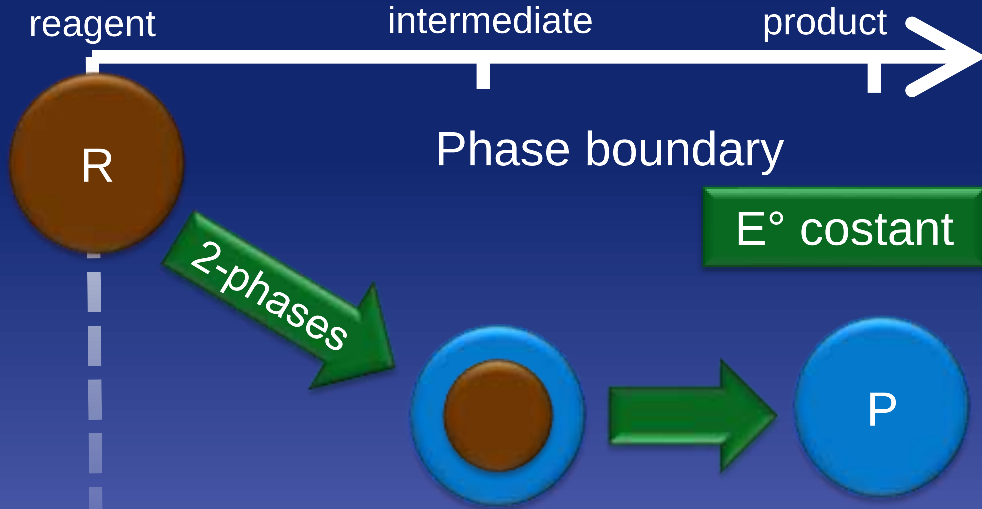
Theoretical capacity:
170 mAh/g (1 Li_{eq})

Nominal voltage:
3.45 V vs. Li

Olivine intercalation mechanism

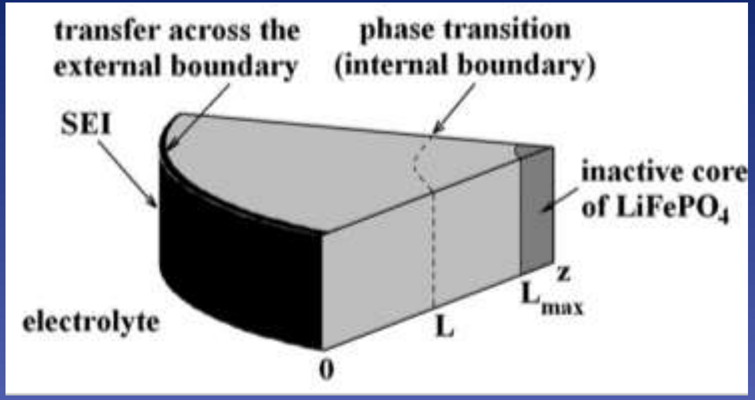
$$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4$$

Two phases process



$$\Delta_r G^o = \Delta_f G^o(P) - \Delta_f G^o(R)$$

Solid state **diffusion** od lithium ions through the particle limits the redox reactivity



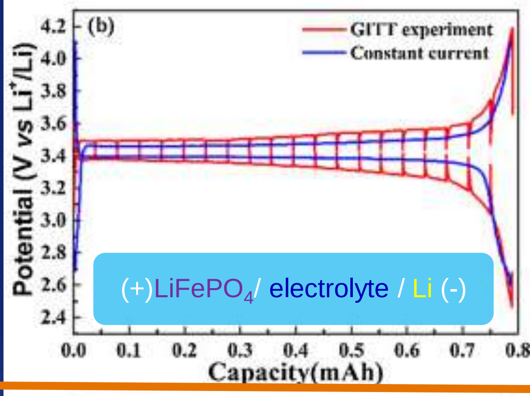
Electrochemical methods (CV, PITT, GITT)

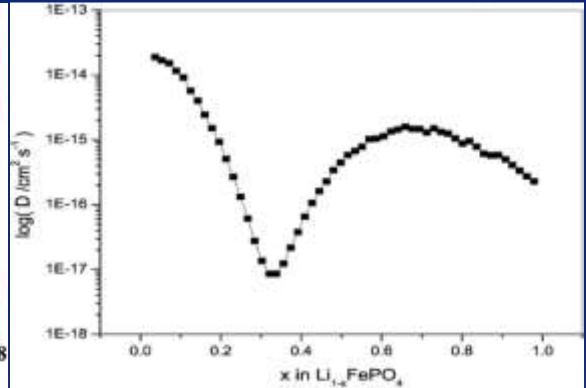
Impedance spectroscopy (EIS)

Li-NMR (chemical diffusion)

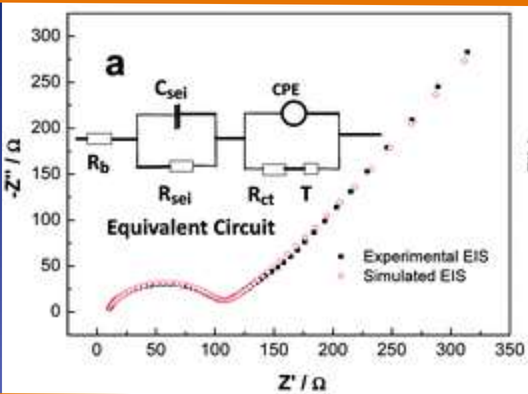
$LiFePO_4$ diffusion coefficients

GITT



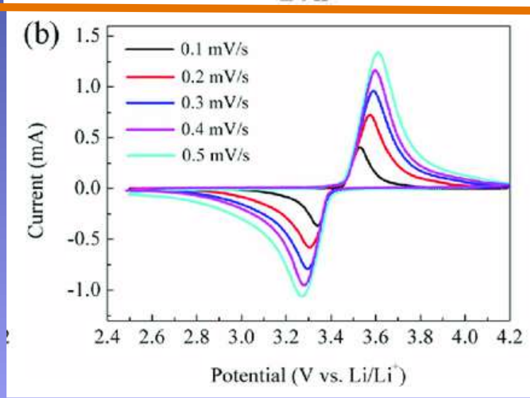


EIS



X in Li_xFePO_4 ($cm^2\ s^{-1}$)	$LiFePO_4$
0.1	4.85×10^{-16}
0.2	5.91×10^{-16}
0.3	3.33×10^{-16}
0.4	4.14×10^{-16}
0.5	
0.6	
0.7	
0.8	

CV



Cathode materials	$LiFePO_4$
Anodic D ($cm^2\ s^{-1}$)	6.91×10^{-16}
Cathodic D ($cm^2\ s^{-1}$)	6.56×10^{-16}

How to improve transport?

Particle size to shorten diffusion paths

Particle morphology to enhance (001) diffusion

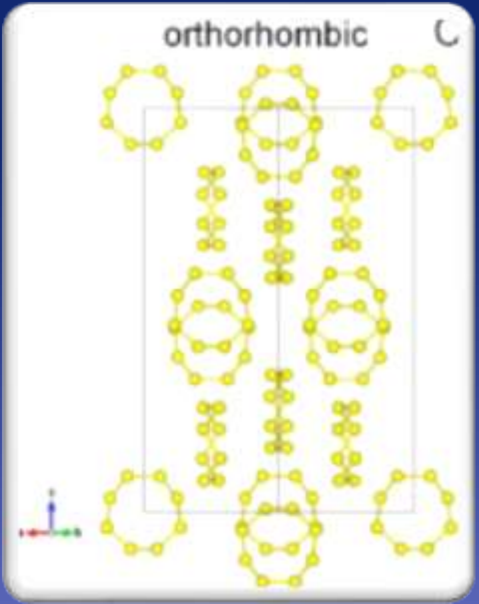
Ipervalent cation doping to induce Li^+ voids

Redox inactive doping to stabilize the lattice

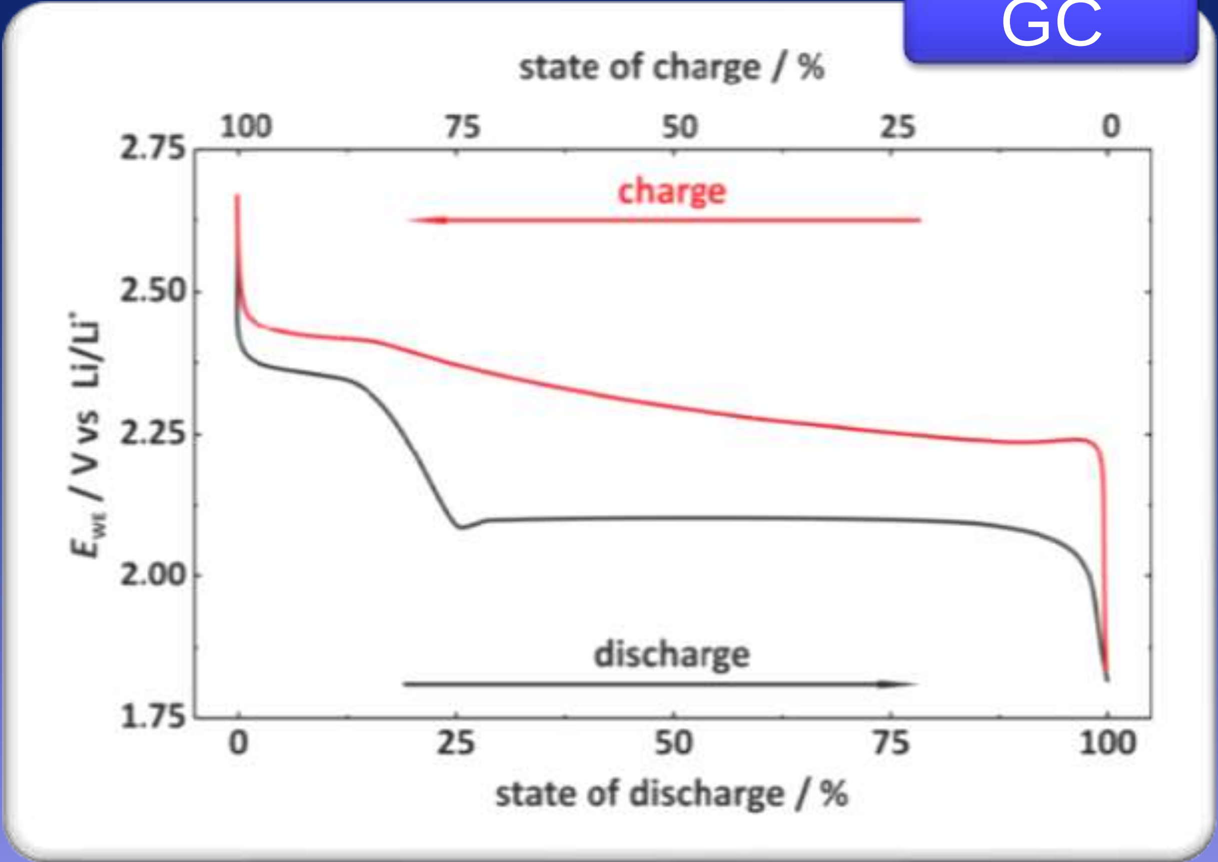
Sulphur – anionic redox chemistry at the positive electrode

S_8
tF64 SG 70

$$S + 2Li^{+} + 2e^{-} \rightarrow Li_2S$$



GC



Collector: Al
Theoretical capacity:
1675 mAh/g (2 Li_{eq})

Nominal voltage:
2.3-2.1 V vs. Li

(+)S/ electrolyte / Li (-)

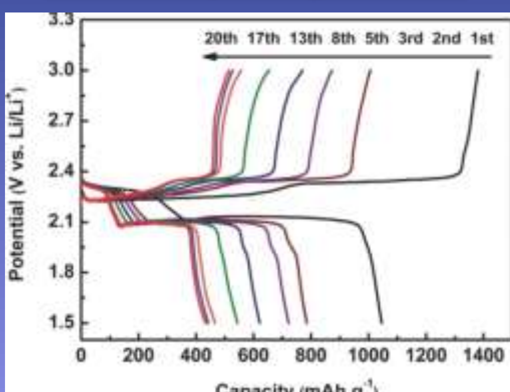
Sulphur – long chain polysulphide and solubility

GC

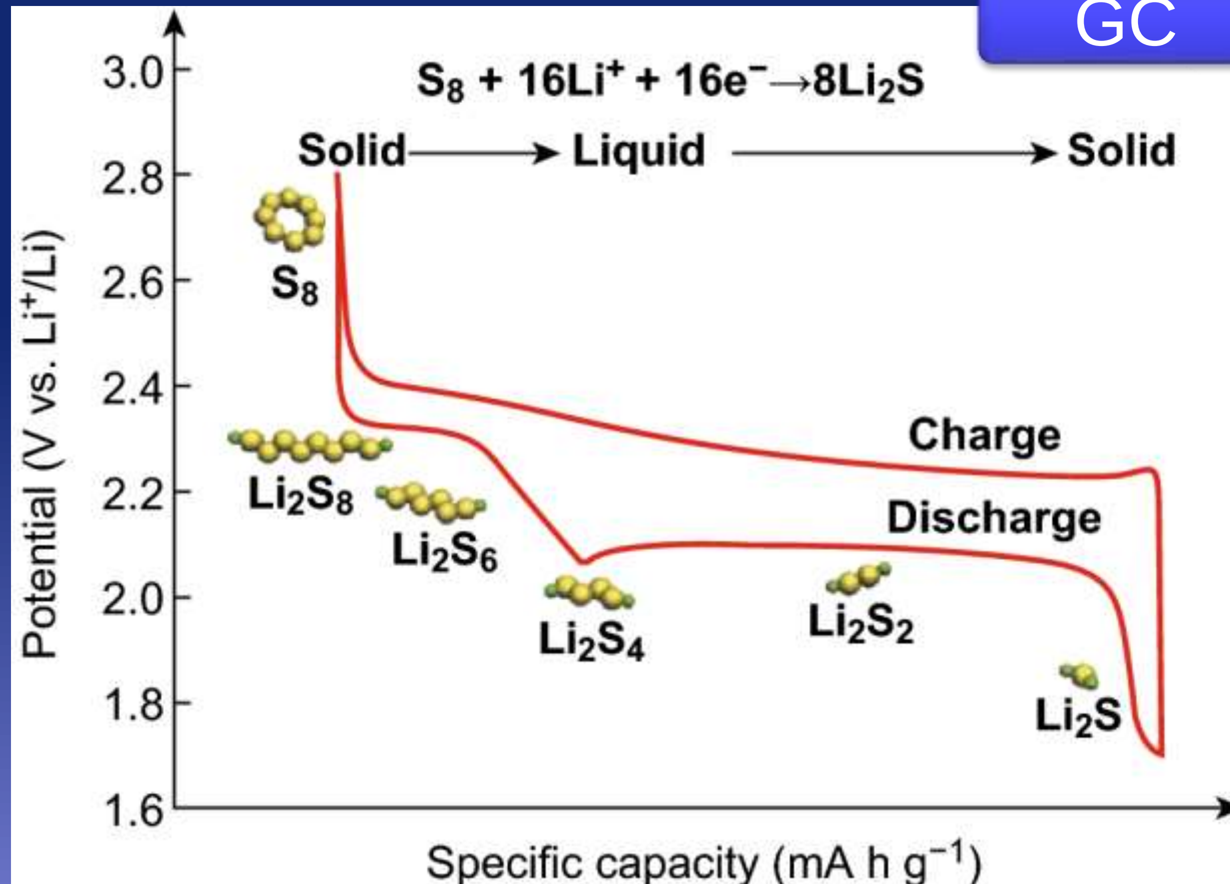
$$2Li^{+} + S_8^{2-} \Leftrightarrow Li_2S_8$$
$$2Li^{+} + S_4^{2-} \Leftrightarrow Li_2S_4$$
$$2Li^{+} + S_2^{2-} \Leftrightarrow Li_2S_2$$
$$2Li^{+} + S^{2-} \Leftrightarrow Li_2S$$

$$2Li^{+} + S + 2e^{-} \Leftrightarrow 2Li_2S$$

S loss upon cycling



Capacity fading

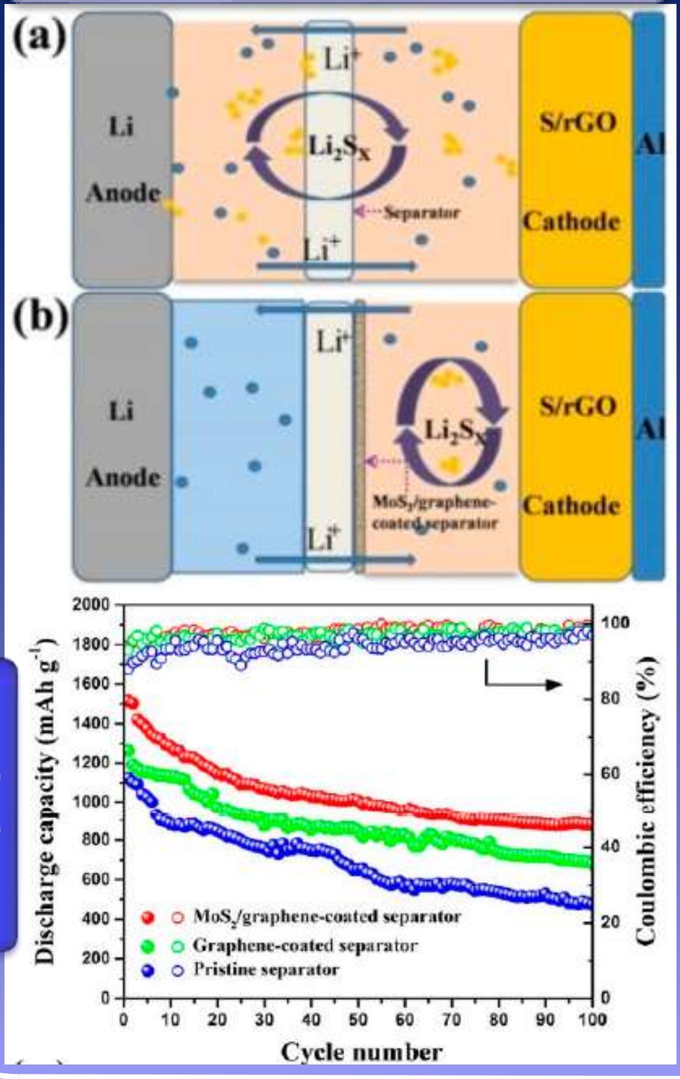


How to fix?

Mitigation strategies

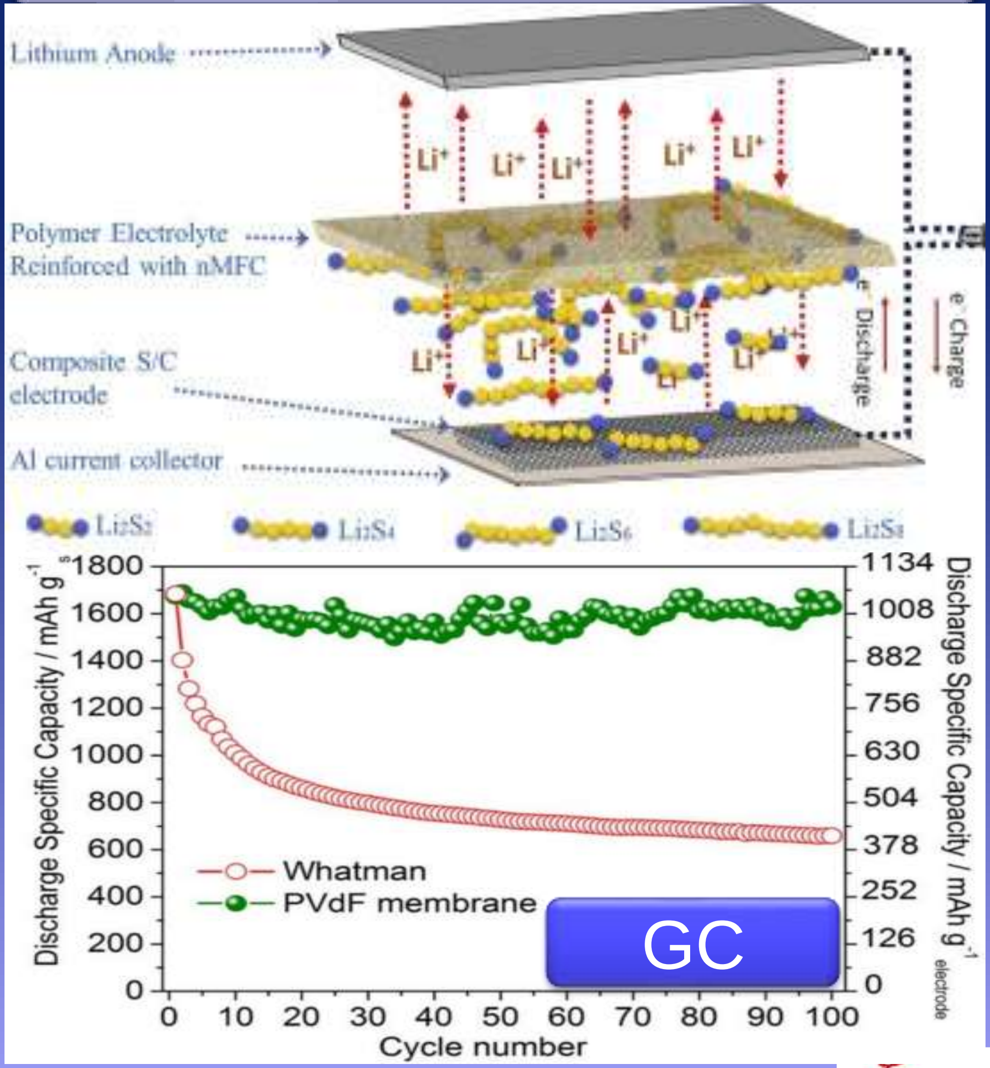
Sulphur – mitigation strategies

Polysulphide absorption on the separator



GC

Polymeric electrolytes to limit diffusion



GC

Electrolytes for Li-ion batteries requirements

Electrolyte: medium for the movement of ions

- High ionic conductivity >1 mS/cm @ RT
- High chemical & electroichemical stability on electrodes
- Stable & functionally active in a wide T range (-20°C and 60°C)
- High safety and low hazard (low toxicity, high flesh points)
- Low cost (simple and cost effective synthetic routes)

Liquid solution (Li^+ salt and solvent)

Gel electrolyte (Li^+ salt, solvent and polymer)

Polymer electrolyte (Li^+ salt and polymer)

Solid electrolyte (crystalline Li^+ ionic conductor)

Liquid electrolytes

Electrolyte: medium for the movement of ions → **Liquid** solution (Li^+ salt and solvent)

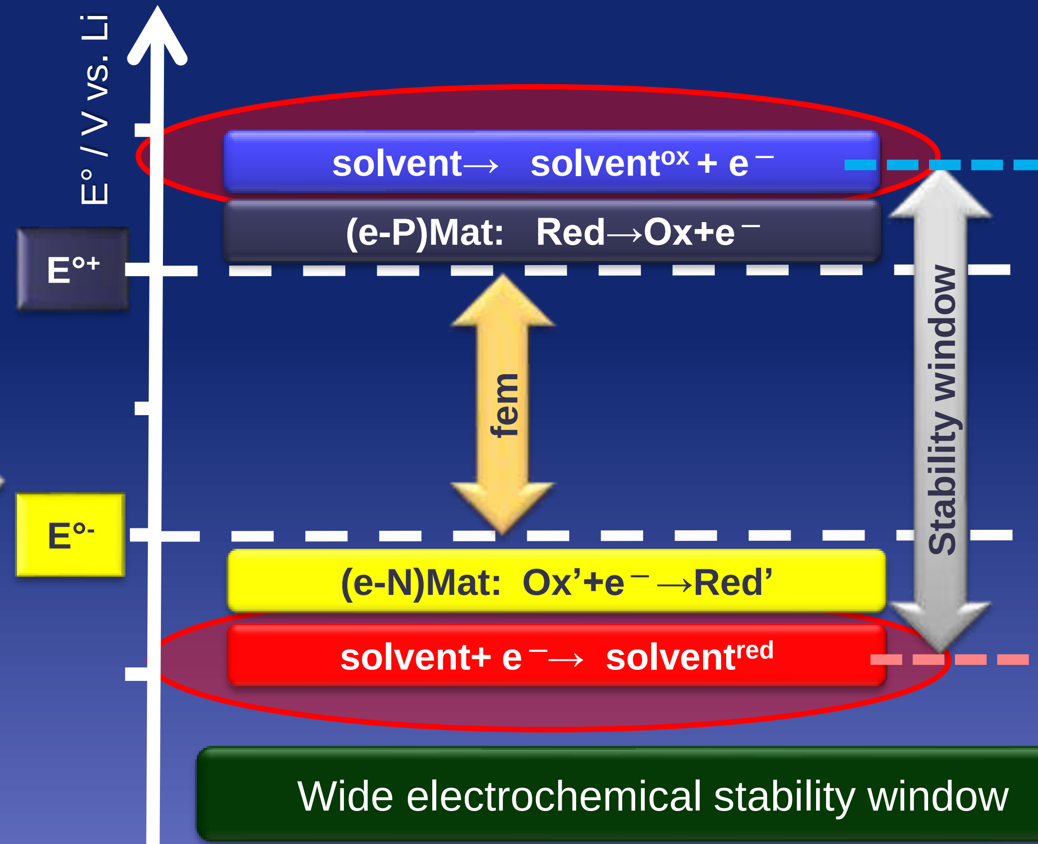
- **Solvent**: Organic liquid substances inert and supporting conductivity
  - ~~water~~
- **Li-salt**: Ionic lithium substance easily dissociated and inert
  - ~~Small anions~~
- **Additives**: Substances to tune the electrolyte functional properties

Solvents: requirements

Electrolyte: medium for the movement of ions

Solvent

- Aprotic (avoid reaction with Li metal)
- High dielectric constant (ε>20, to dissolve Li salts)
- Low viscosity (<1cP)
- High DN to facilitate Li salts dissociation
- Low volatility @RT and high boiling points

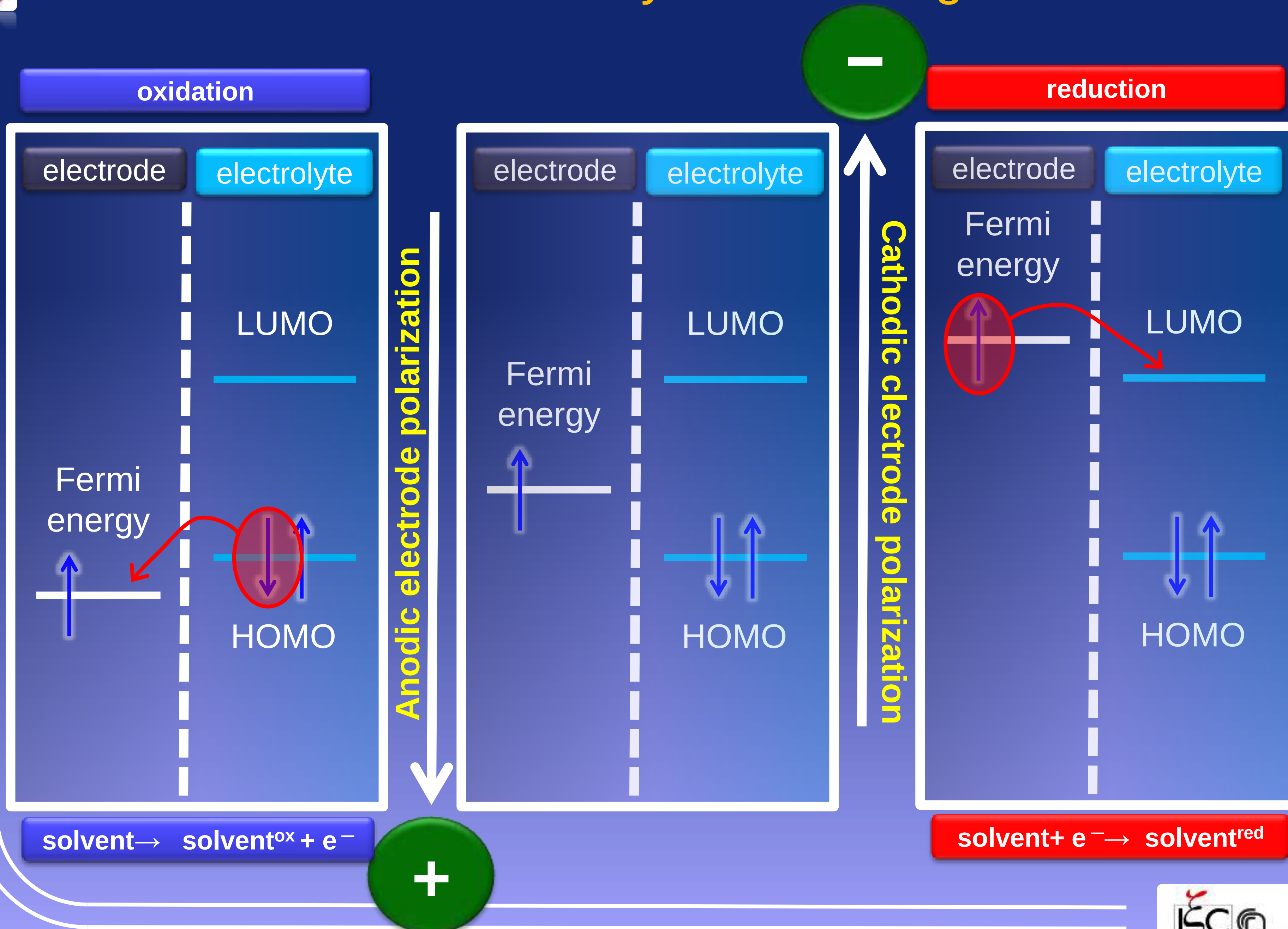


Wide electrochemical stability window

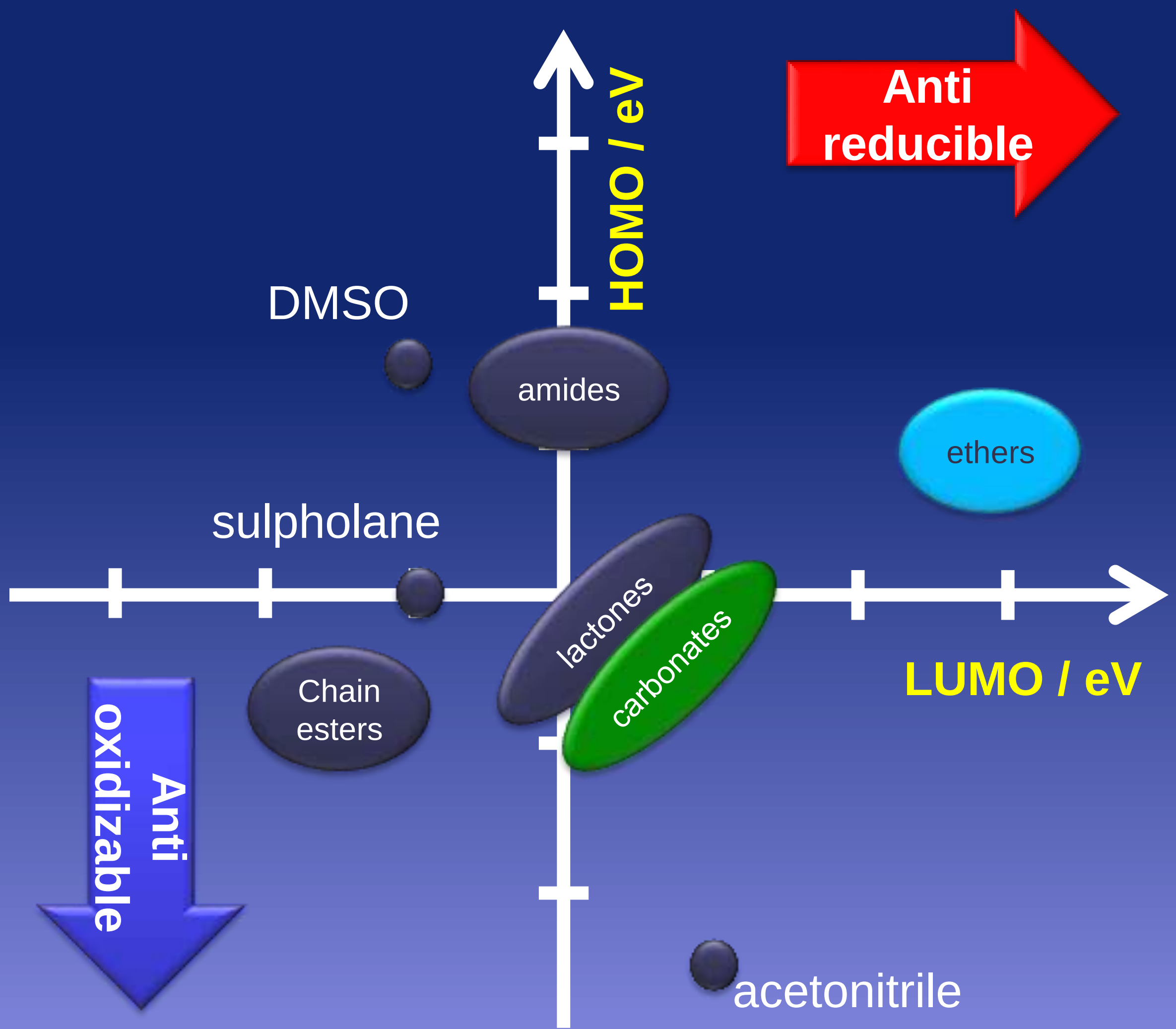
Low viscosity goes together with low dielectric constants and high volatility.

Solvent blends (e.g. EC:DMC)

Solvents: thermodynamic background



Solvents: HOMO-LUMO energy levels



Wide electrochemical stability window

Liquid electrolytes: solvents

Electrolyte: medium for the movement of ions

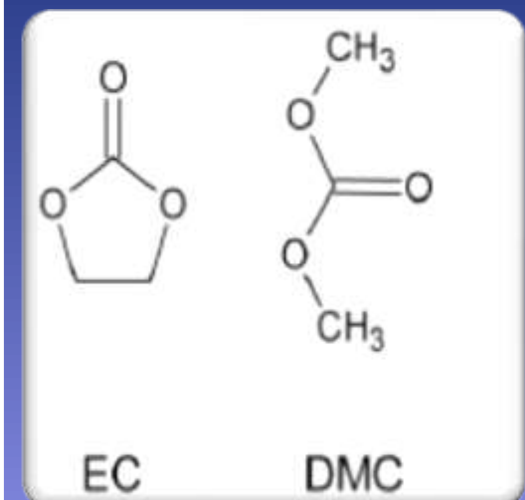
Liquid solution (Li^+ salt and solvent)

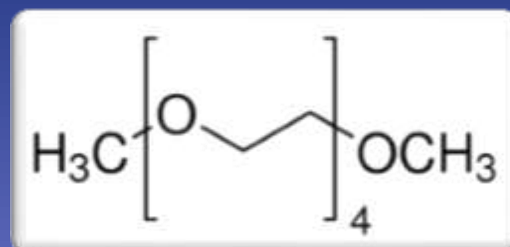
Others: sulphones; for high voltage Li-ion

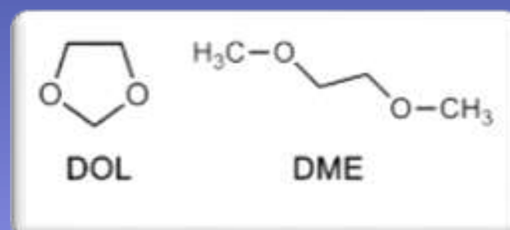
Solvents: organic carbonates (cyclic/linear)

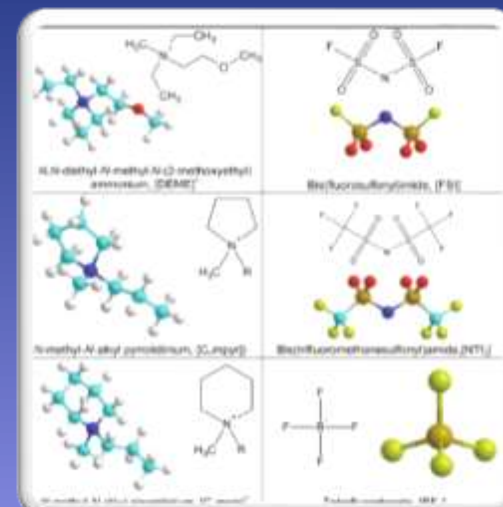
Solvents: ethers (cyclic/linear)

Solvents: Ionic liquids









Li-ion

Li-S & Li-O_2

Li-ion & Li-S & Li-O_2

Salts: requirements

Electrolyte: medium for the movement of ions → Salts

- High solubility
- High ionic conductivity
- Poor coordination at low temperature
- Thermal stability
- Electrochemical and chemical stability towards Al/Cu

Large anions (larger dissociations and smaller transport number)

$$(\sigma/Sm^{-1}) = (\Lambda_m/Sm^2mol^{-1}) \cdot (c/mol \cdot m^{-3})$$

$$\Lambda_m = \Lambda^+ + \Lambda^-$$

And the Stokes-Einstein law:

$$\Lambda^i \propto \frac{Z}{(\eta/cP) \cdot (r/\text{Å})}$$

Transport number

$$\Lambda_{Li^+} = \frac{\Lambda_{Li^+}}{\Lambda_{Li^+} + \Lambda^-}$$

Dissociation costant

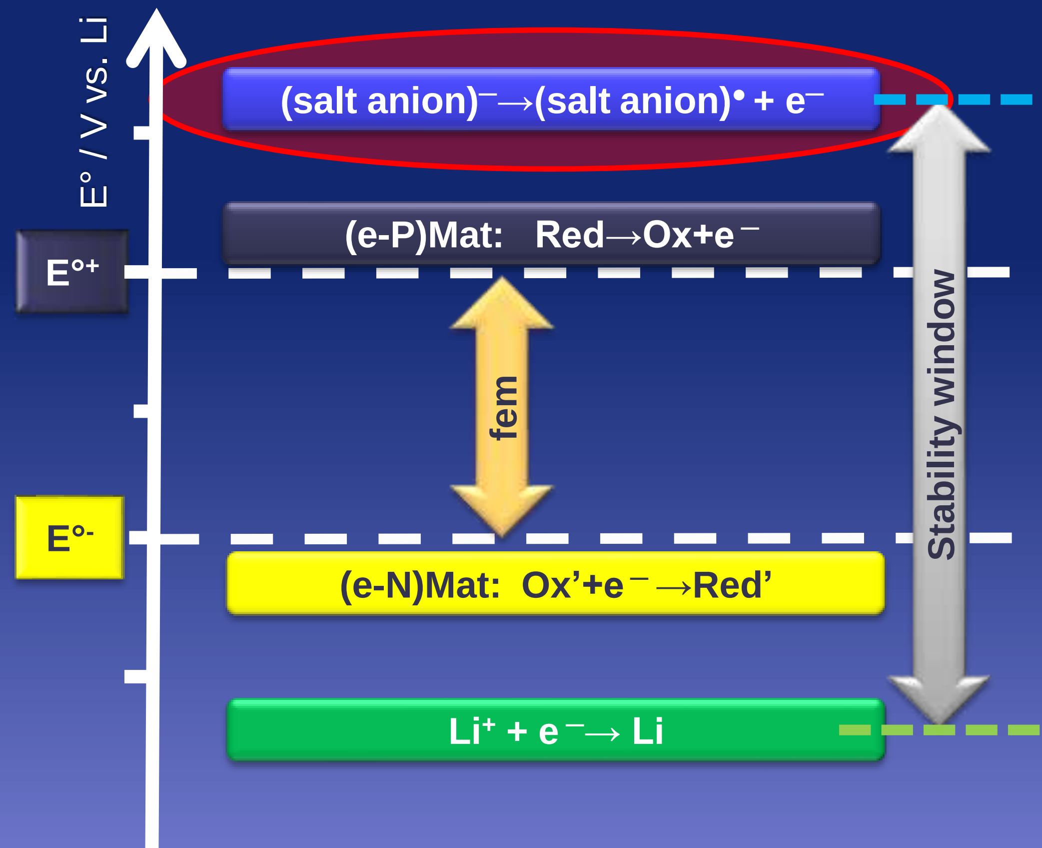
$$LiA(solv) \rightleftarrows Li^+(solv) + A^-(solv)$$

$$K_{eq} = \frac{a_{Li^+} \cdot a_{A^-}}{a_{LiA}} = e^{-(\Delta_{diss}G^o/RT)}$$

Salts: thermodynamic requirements

Electrolyte: medium for the movement of ions

Salts



Wide electrochemical stability window

Lithium salts for electrolytes

Electrolyte: **medium for the movement of ions**

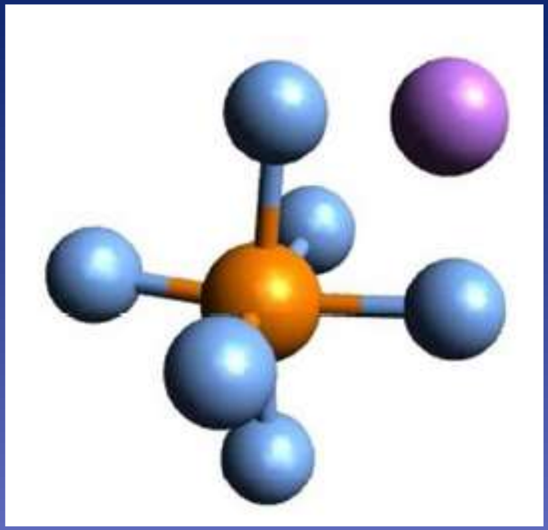
Salts

- **$LiClO_4$** explosive
- **$LiAsF_6$** highly toxic
- **$LiBF_4$** poor anodic SEI
- **$LiSO_3CF_3$** small Li^+ conductivity
- **LiTFSI** poor catodic SEI film & Metal ion scavenger

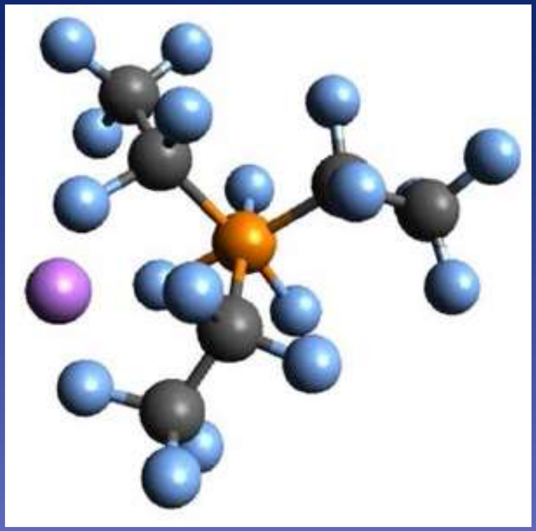
$LiPF_6$ **best compromise**

New salts: Li FAP

In the last decade a quite large number of innovative salts has been proposed: Li bis-(oxalato)borate (LiBOB), Li bis(malonato)borate (LiBMB), Li (malonato oxalato)borate (LiMOB), Li pentafluoroethyl trifluoroborate ($LiC_2F_5BF_3$), Li tetrafluoro(oxalate)phosphate ($LiPF_4C_2O_4$)



$Li^+ PF_6^-$



$Li^+ (R)_nPF_{3-n}^-$

Li perfluoro-alkyl-fluorophosphates are hybrid organic-inorganic salts

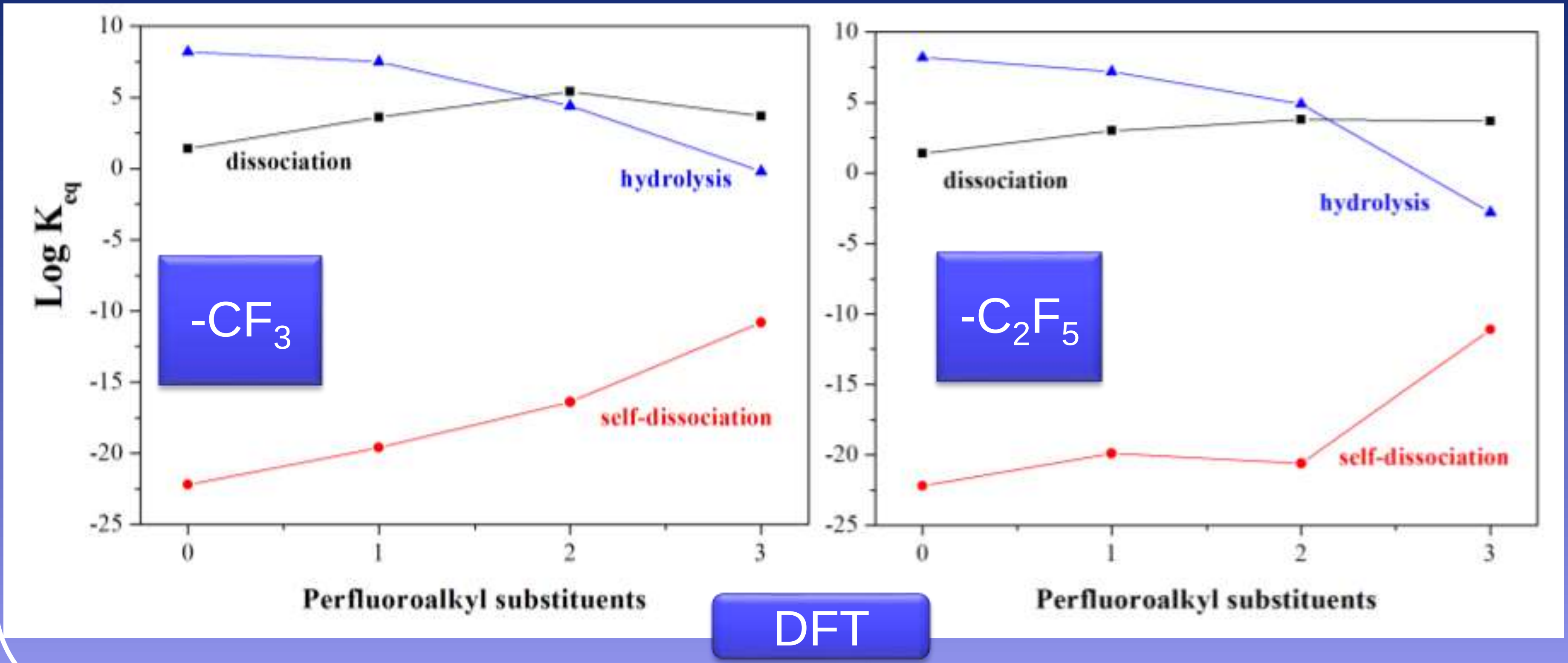
Dissociation, self-dissociation & hydrolysis

- dissociation
- Self-dissociation
- hydrolysis

$$LiPF_{6-x}R_x \leftrightarrows Li^+ + PF_{6-x}R_x^- \quad (1)$$

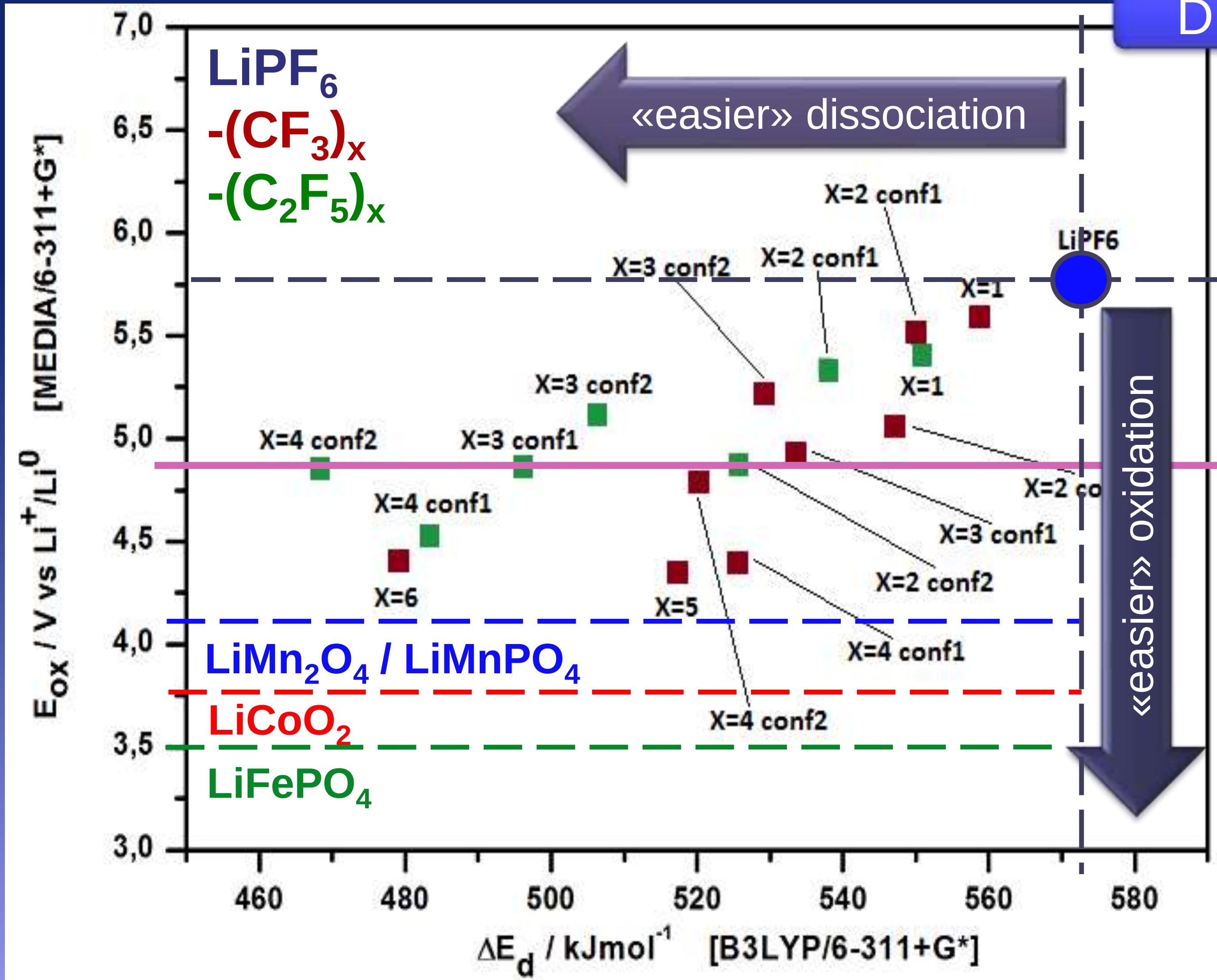
$$LiPF_{6-x}R_x \leftrightarrows LiF + PF_{5-x}R_x \quad (2)$$

$$PF_{5-x}R_x + H_2O \leftrightarrows 2HF + POF_{3-x}R_x \quad (3)$$



Ionization vs. Dissociation

DFT



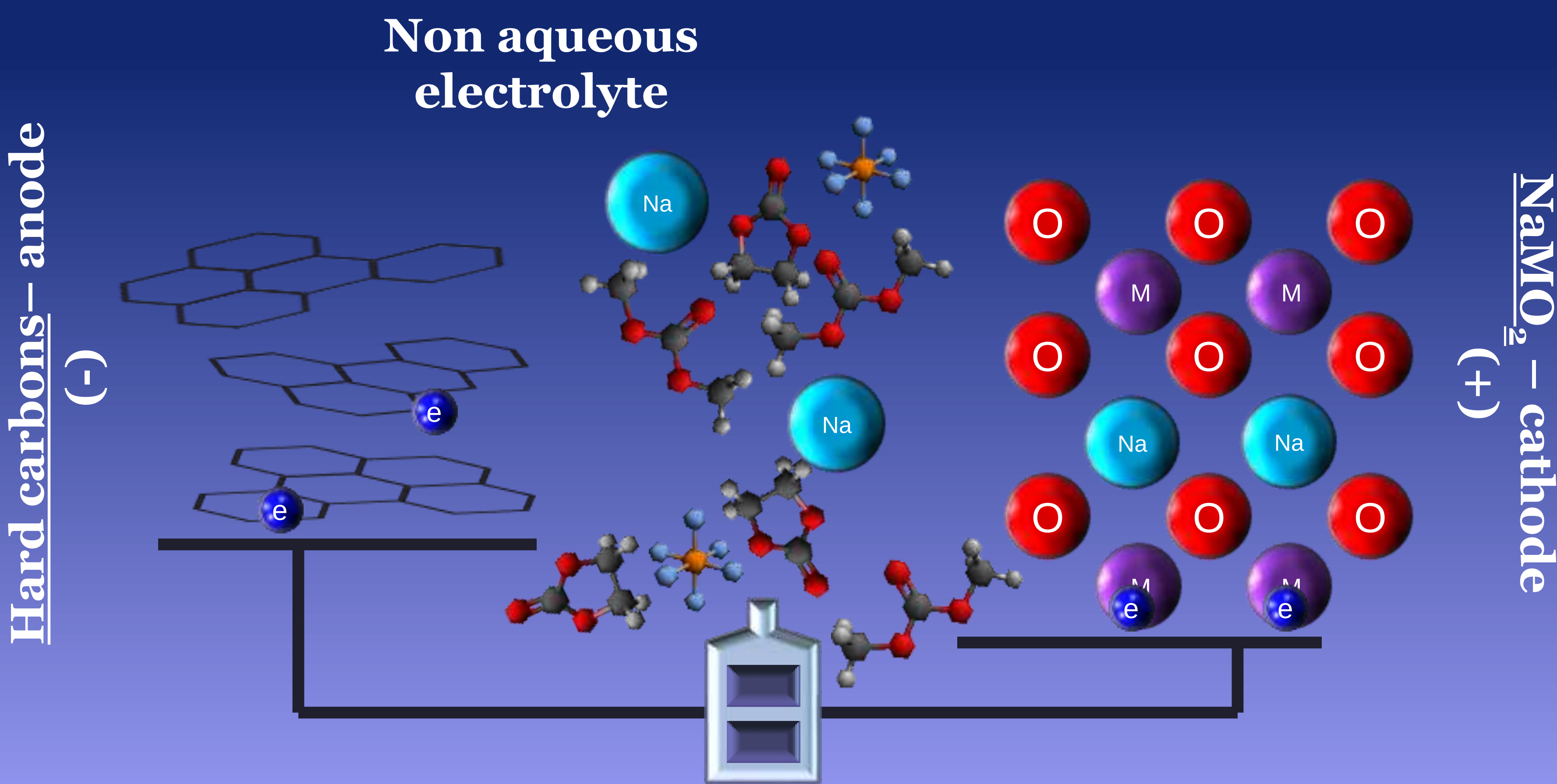
High voltage cathodes

$LiCoPO_4$

$LiMn_{3/2}Ni_{1/2}O_4$

Sodium ion cell

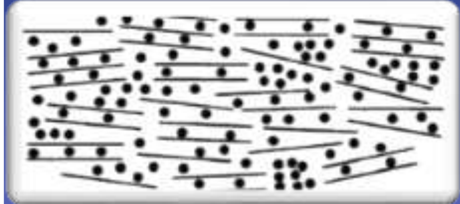
Similar to the lithium analogue Li-ion cell. It exploits the intercalation and de-intercalation of sodium ions into host materials



Na-ion battery: negative electrodes families

Intercalation & absorption chemistry

Hard carbons
$nC + Na^{+} + e^{-} \rightarrow NaC_n$

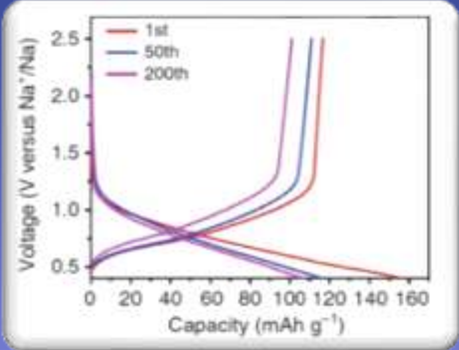


«HOUSE OF CARDS»

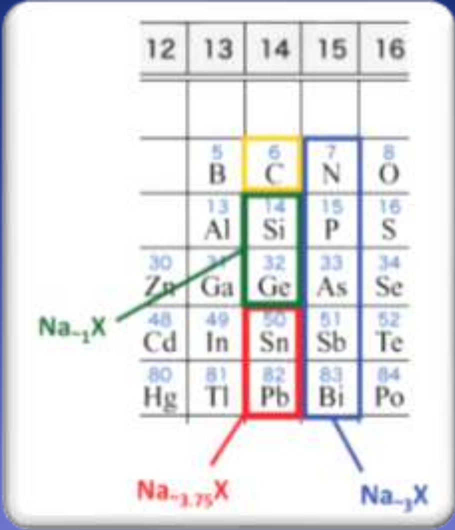
Insertion of Na^{+} : between ≈ parallel graphene sheets & into the pores

Intercalation chemistry

Na - titanate
$Na_2Ti_yO_z + xNa^{+} + xe^{-} \rightarrow Na_{2+x}Ti_yO_z$



Alloying chemistry



Sodium

$Na^{+} + e^{-} \rightarrow Na$

Na-ion battery: positive electrodes families

Layered phases intercalation	Polyanion	Prussian blue	others
Na_xMO_2 **P2** Na_xCoO_2 130-140 $mAhg^{-1}$ **O3** $NaFeO_2$ 50-100 $mAhg^{-1}$ **O3** Na(*Fe/Mn/Co/Ni*)O_2 180 $mAhg^{-1}$	Na exchanged $LiFePO_4$ 110 $mAhg^{-1}$ Na_2FePO_4F 90 $mAhg^{-1}$ $Na_3V_2(PO_4)_3$ 100 $mAhg^{-1}$	$Na_xMFe(CN)_6$ M= Fe, Co, Ni… Na exchanges $KFeFe(CN)_6$ 70 $mAhg^{-1}$ $Na_{1.4}MnFe(CN)_6$ 135 $mAhg^{-1}$ $Na_2MnMn(CN)_6$ 180 $mAhg^{-1}$	Intercalation materials (sulphates and sulphides) & Conversion materials (e.g. fluorides)

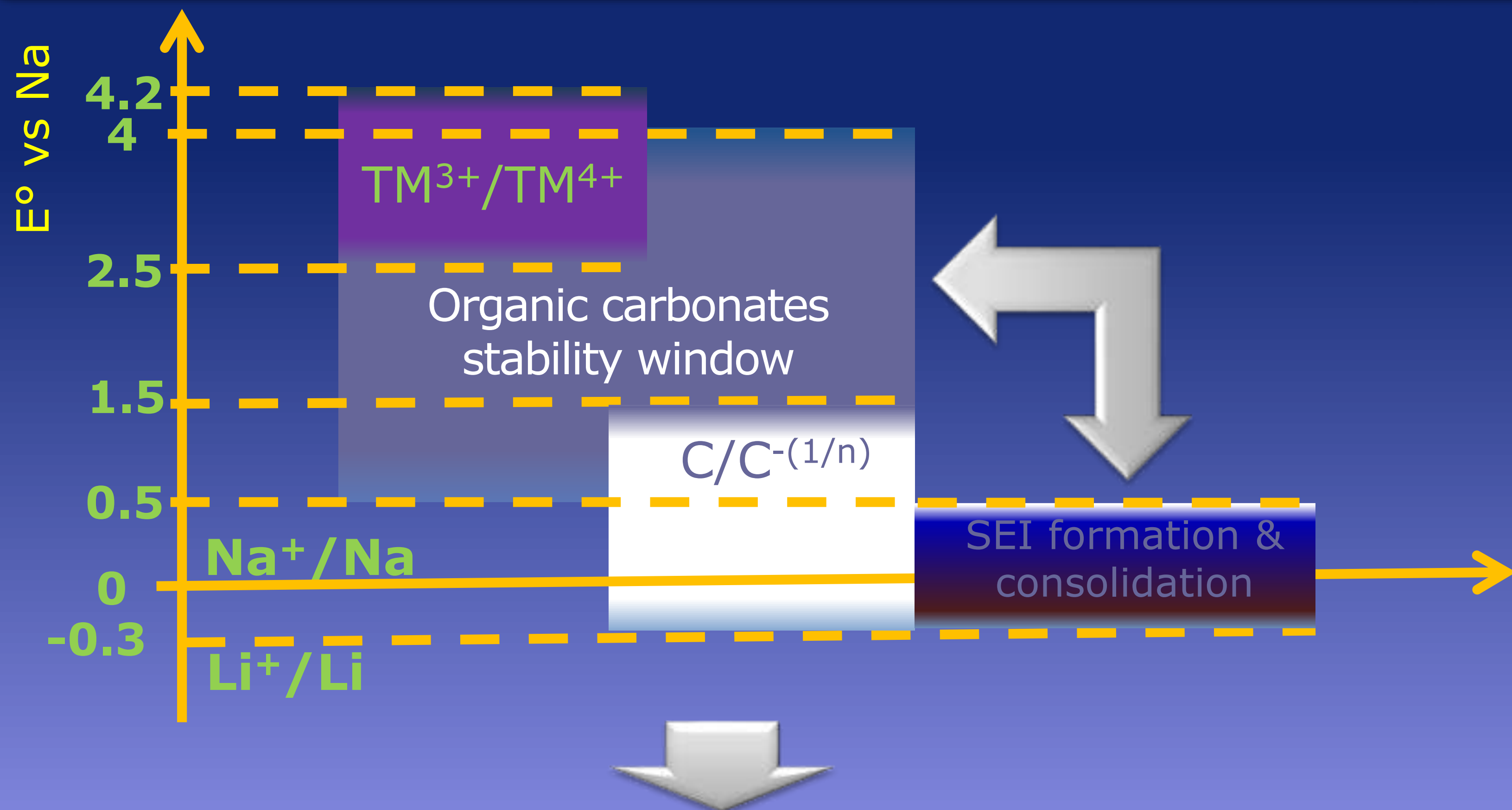
The Na^+ aprotic electrolyte challenge

Similar solvents (organic carbonates) and salts compared to Li-Ion batteries

Dielectric properties	Ionic conductivity	Thermal properties	Electrochemical stability
Organic Carbonates **e.g. ε(PC)=64**	e.g. $NaPF_6$ in PC (1m) **σ= 7 $mScm^{-1}$**	e.g. $NaPF_6$ **T_{dec}>280°C** EC:DMC **T_{dec}>250°C**	e.g. $NaPF_6$/EC:DMC stability window **$0.5<E_{we}<4$ V vs Na**
↓	↓	↓	↓
Na^+ salt dissolution	**Na^+ ions transport**	**Safety upon abuse**	**Interface stability**

The SEI-challenge

Solid electrolyte interphases grown on carbon electrodes show poor stability upon cycling



Modified electrolytes with fluorocarbonates improve stability

Post-mortem XPS sample preparation procedure

The preparation of the samples analysed by XPS requires a multistep procedure

Electrodes recuperated from cells in glove box

Washed with DME/THF and dried in vacuum

Post mortem electrode materials

Glove box

Loaded onto tapes over flat holders and stored in special shuttles

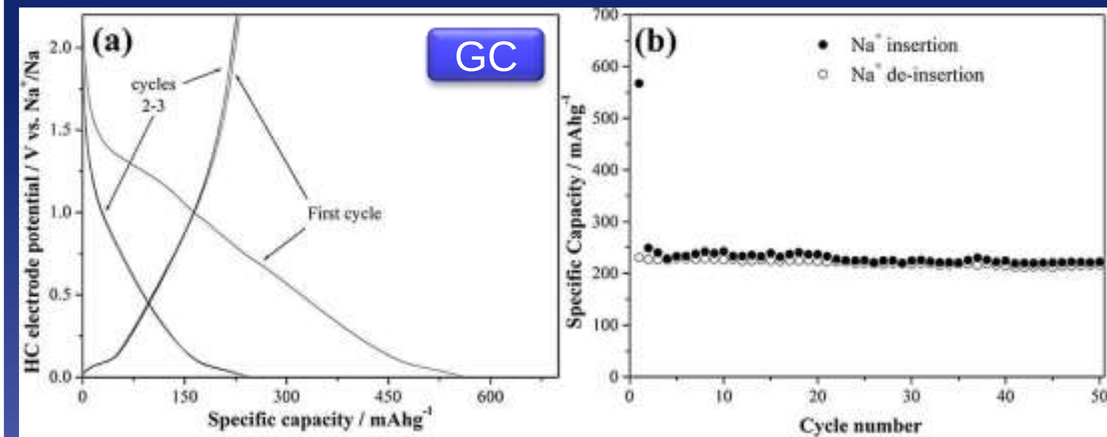
Transferred to XPS chamber using interlocks

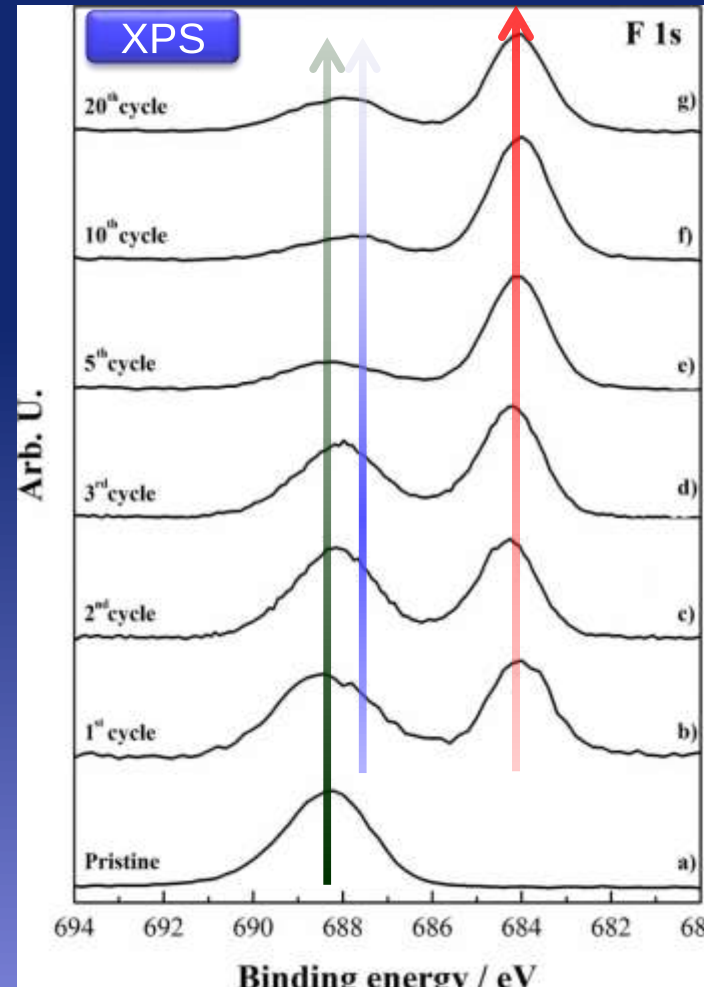
Composition after cycling

Hard carbon surfaces upon cycling

HCs are obtained by pyrolysis of organic matrix above 850°C in reducing environment.

(+)HC/ EC:PC:FEC NaTFSI/ Na (-)





The consolidation of the SEI layer over HC in Na-batteries lasts for many cycles before a full stabilization of the interface.

C-F pvdf

F^- LiF

P-F fluorphosphates

Research in non-aqueous Na/Li batteries is a multi-disciplinary challenge and requires talented people working together