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Prospective sur l'aspect sécurité via de nouveaux électrolytes

Michel Armand
(Directeur de Recherches honoraire CNRS-LRCS)

- ***Le sodium ?***
- ***Oui monsieur. Mélangé avec du mercure, il forme un amalgame, qui remplace le zinc dans les éléments Bunsen. le ne s'use jamais. Seul le sodium est consommé et le mer me le fournit elle-même. Je vous dirai que les piles au sodium doivent être considérées comme les plus énergétiques et que leur force électromotrice est double de celle des piles au zinc.***

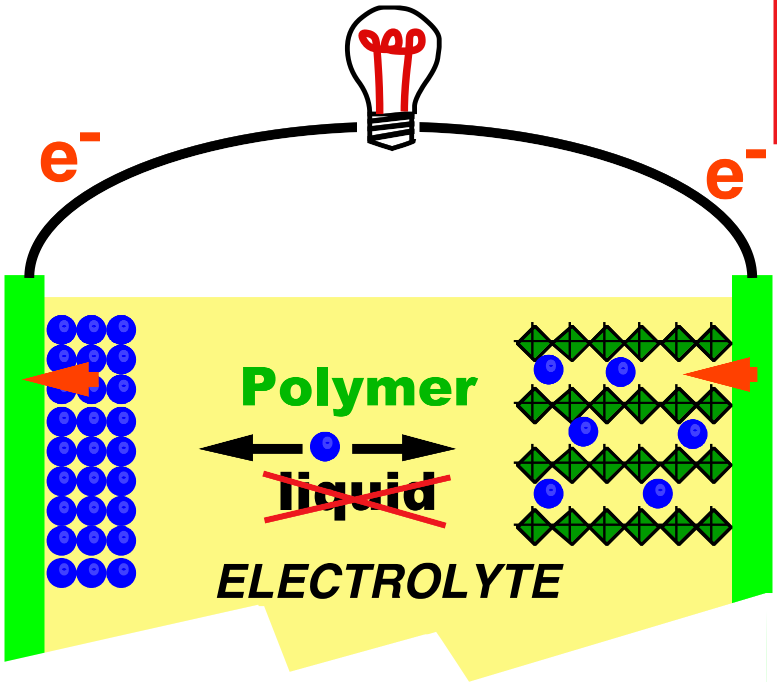
Jules Verne
20 000 Lieues sous les mers
Hetzel ed, Paris 1870

1 Billion Cars in 2010 and ↗

…and 1.3 Millions fatalities on the roads!

> 2 millions deaths from air-borne particles in big cities

L’électrolytes au cœur des batteries…



Li° Solid-state batteries
T > 50°C

Only Al current collectors

All $LiPF_6$

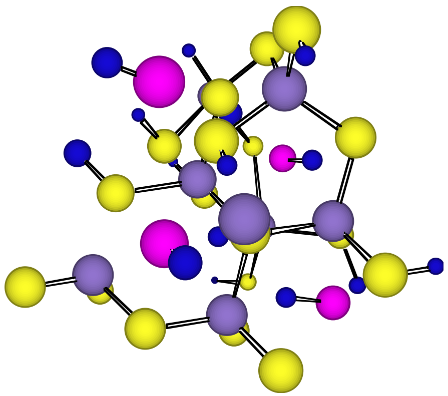
Only Cu

-20 < T < 55°C

Higher energy density
But which electrolyte ??

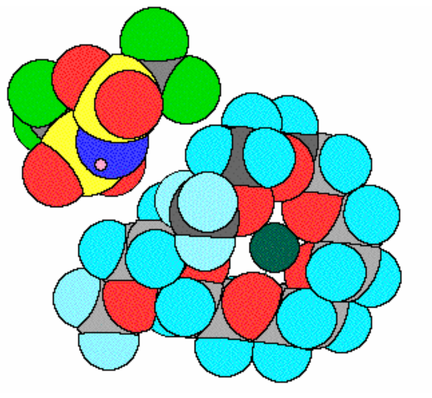
3 Familles d'électrolytes

Glasses: $SiS_2/Li_2S/LiI$



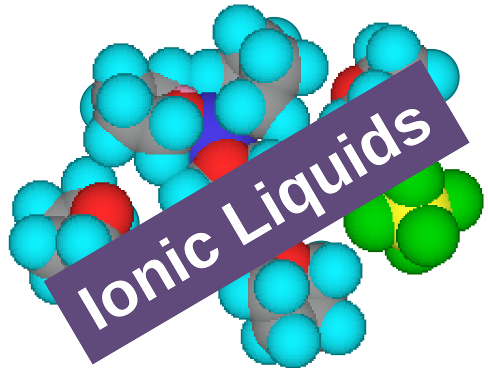
$T_g \approx 270°C$; $t_{Li+} = 1$

PEO / $[(LiCF_3SO_2)_2N]$

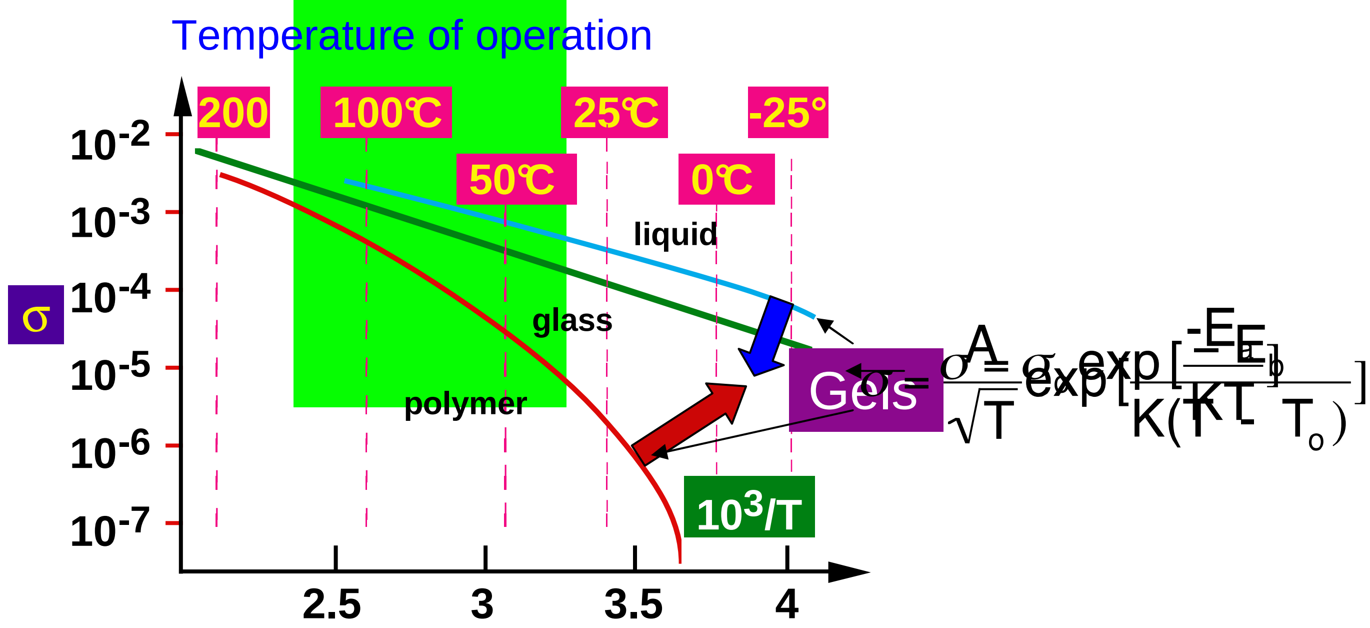


$T_g \approx -40°C$; $\mathbf{t_{Li+} = 0.3}$

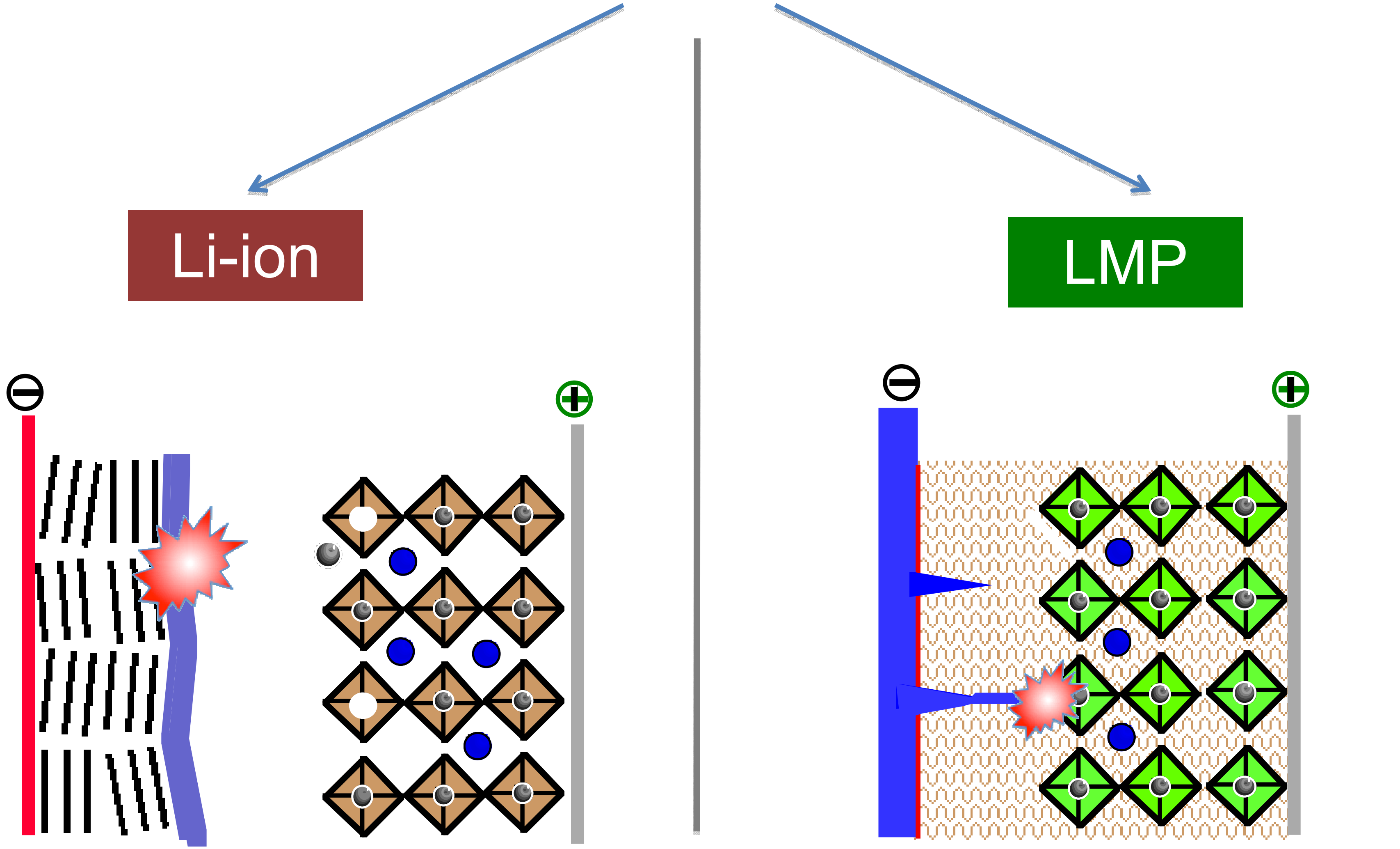
Liquids: $LiPF_6$ in THF



$T_g \approx -100°C$; $\mathbf{t_{Li+} = 0.3}$



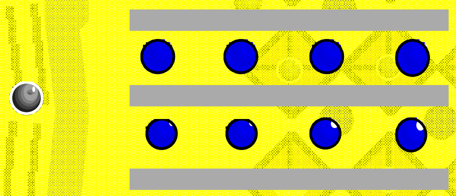
Aging / Failure modes



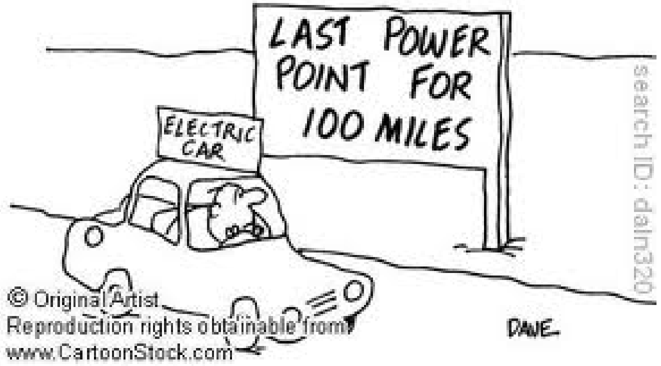
Aging / Failure modes

Li-ion

Simplistic remedy:
Add a Mn^{++} trap
N(i)C(o)A(l), ⅓,⅓,⅓

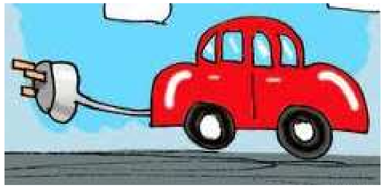


- **15 - 25% unsustainable (Co), toxic (Ni)!**
- **Less safe than $LiMn_2O_4$**

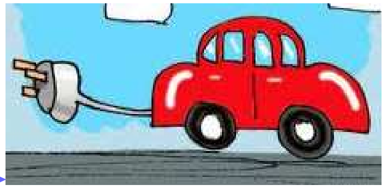


Autonomie

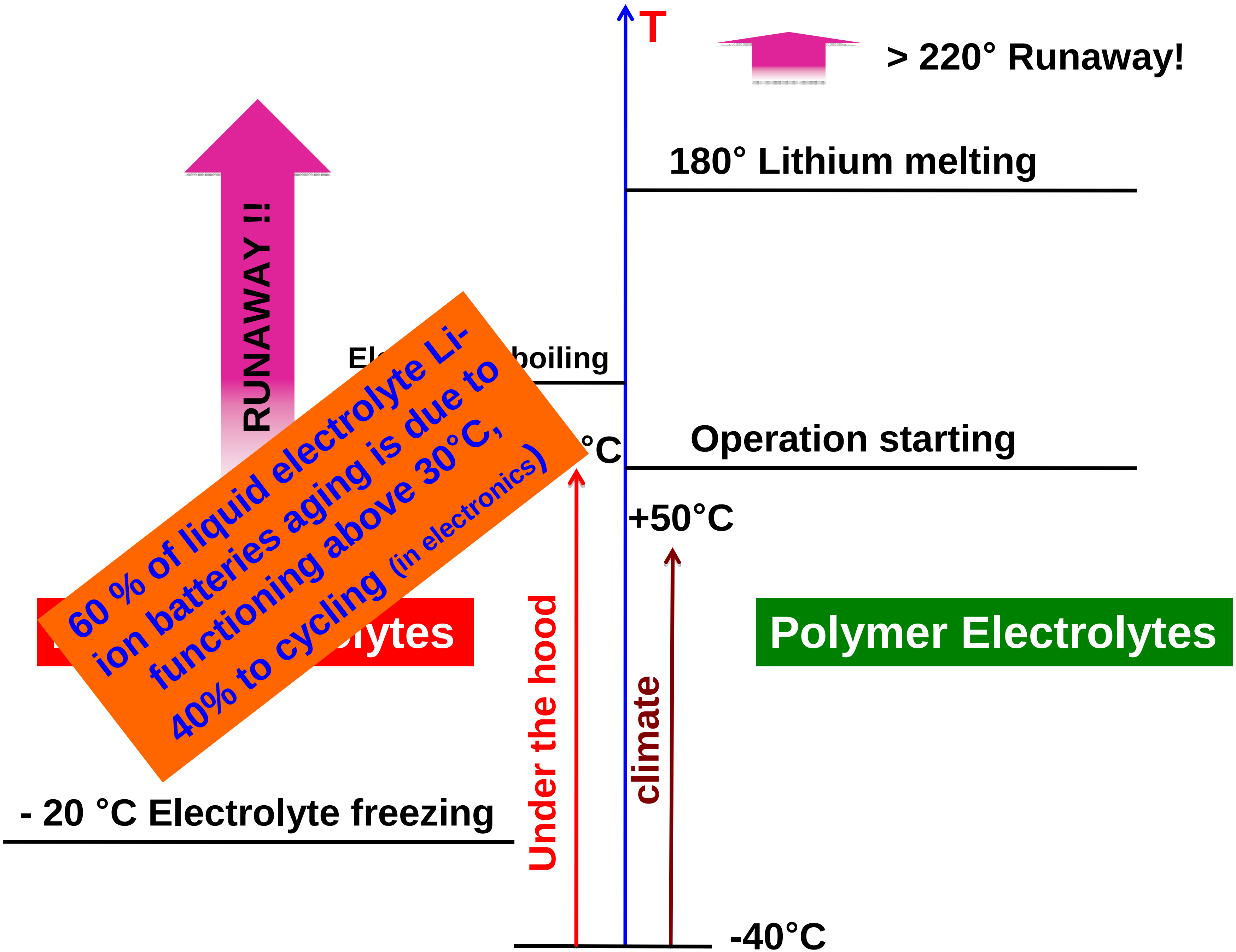
Li-ion = 150 km



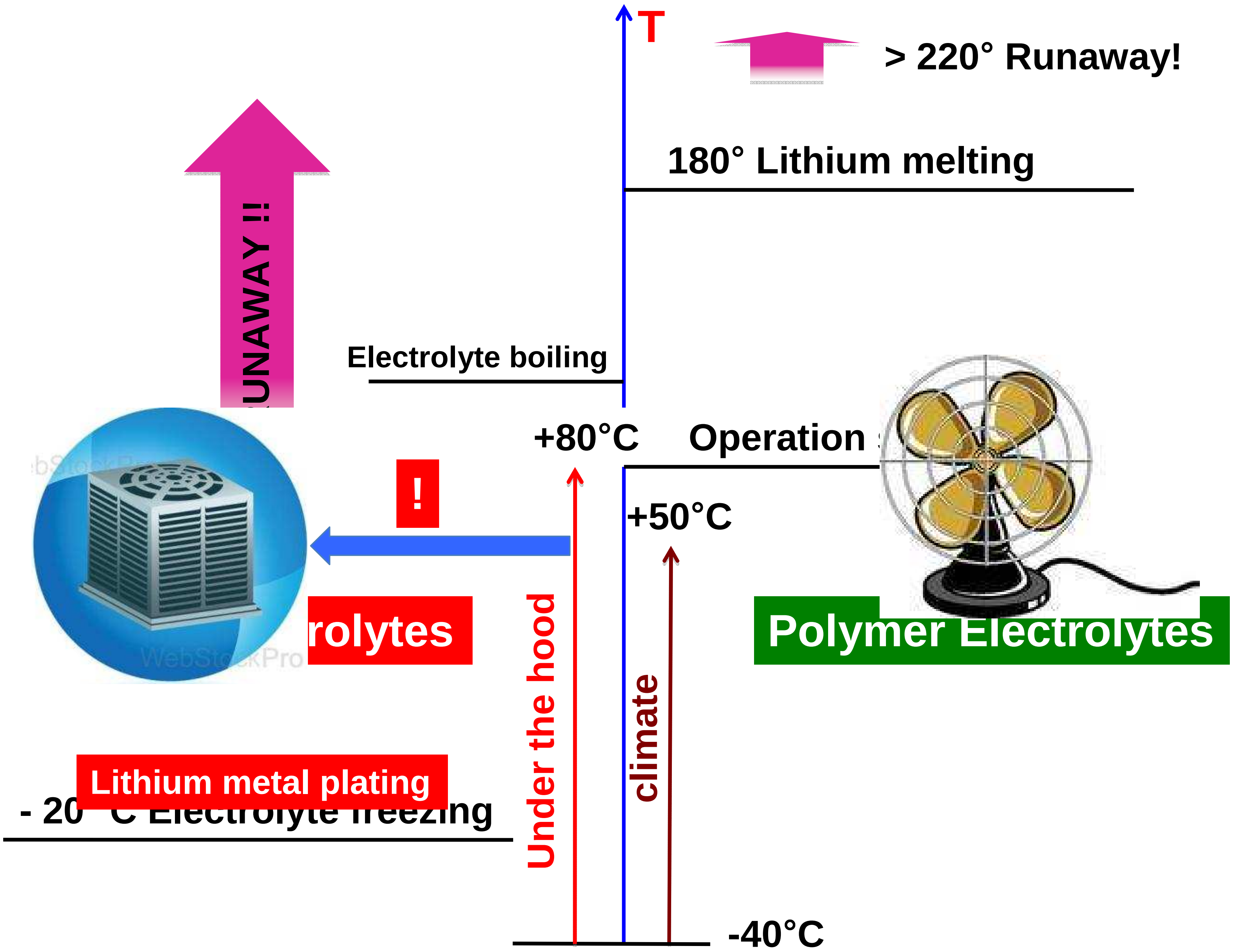
Lithium metal / polymer = 250 km



Taxi on average ∀ country ≈ 200 Km/day

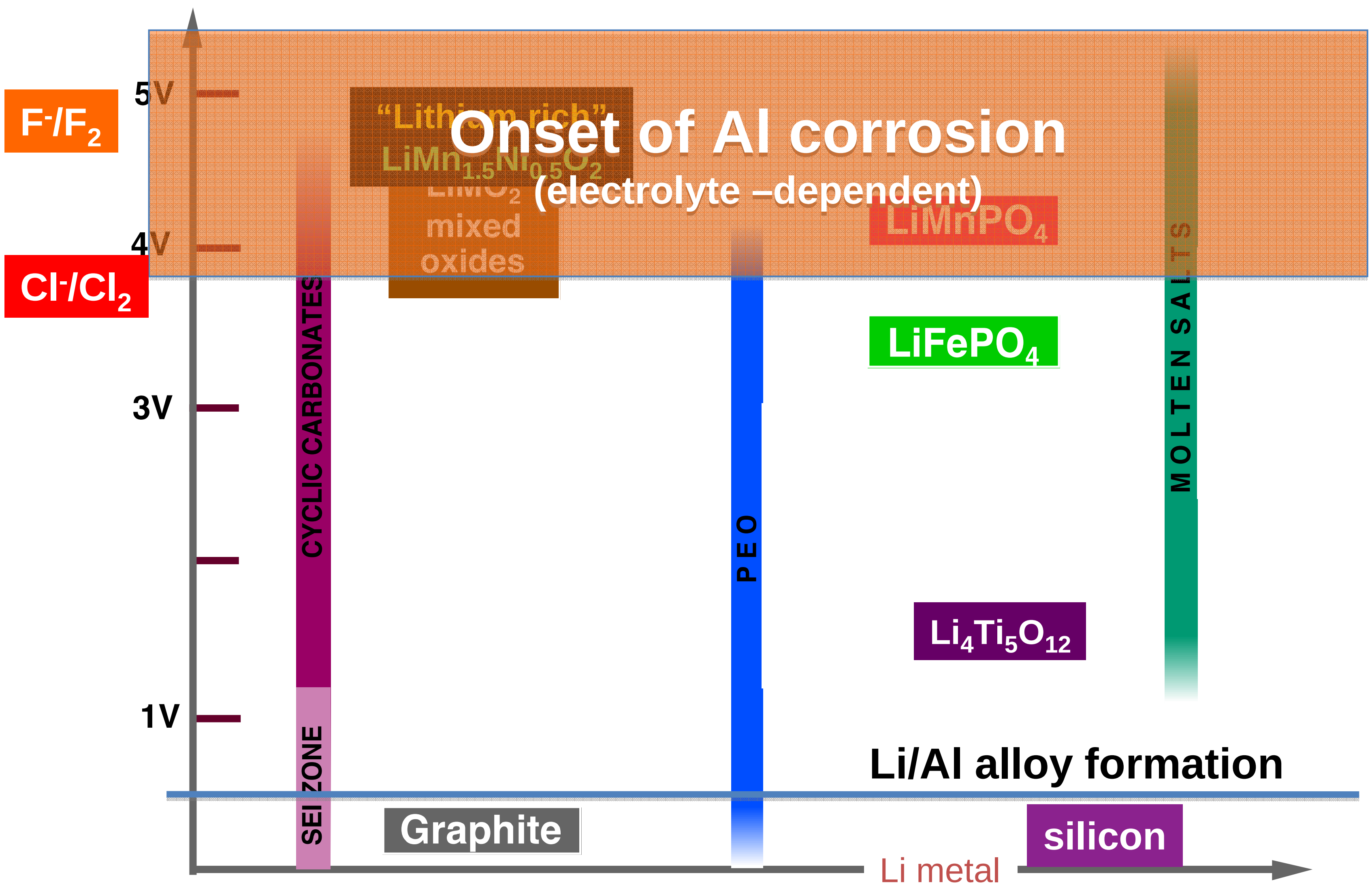


T
> 220° Runaway!
180° Lithium melting
RUNAWAY !!
boiling
°C
Operation starting
+50°C
60 % of liquid electrolyte Li-ion batteries aging is due to functioning above 30°C, 40% to cycling (in electronics)
lytes
Polymer Electrolytes
Under the hood
climate
- 20 °C Electrolyte freezing
-40°C

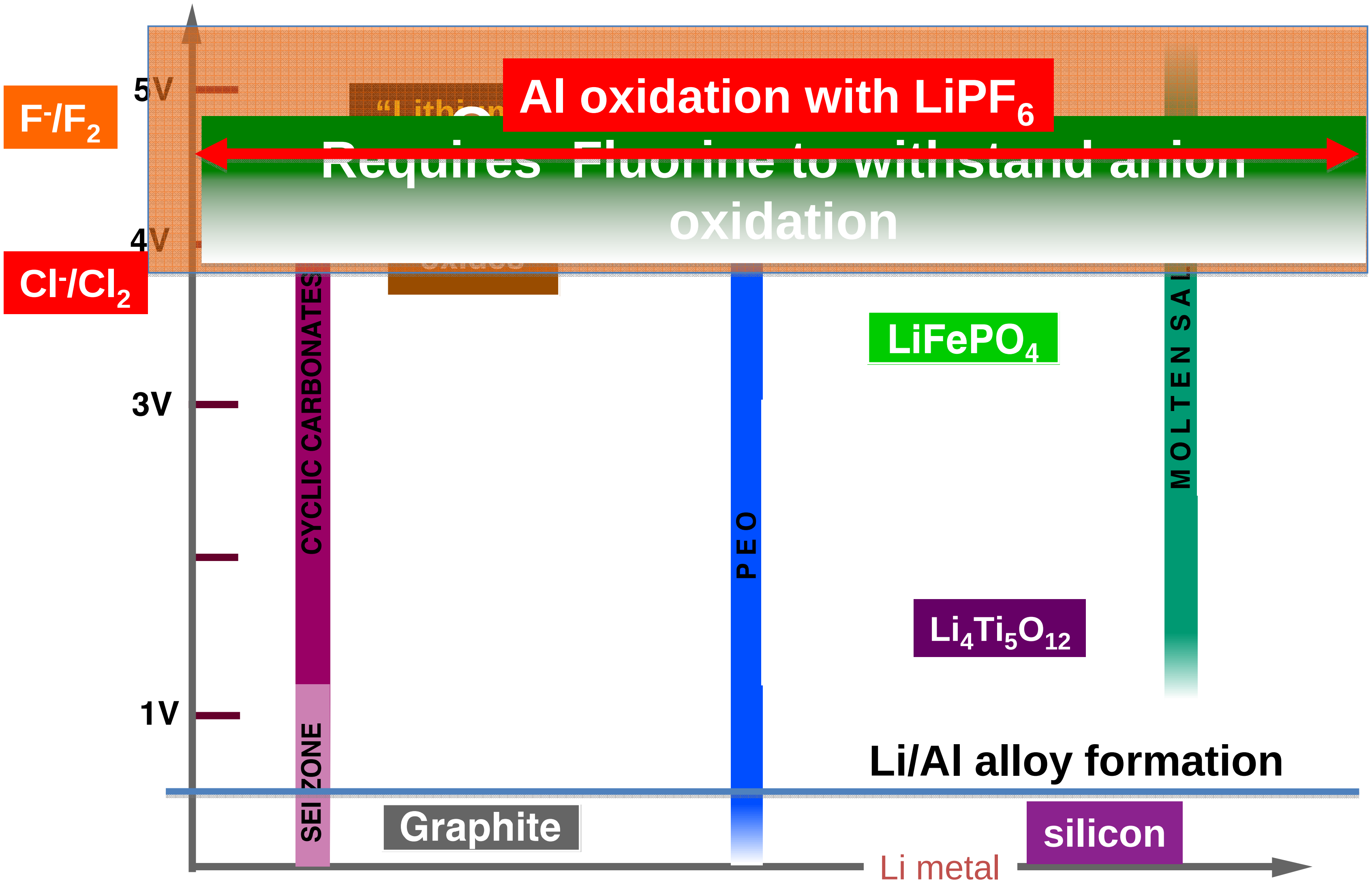


T
> 220° Runaway!
180° Lithium melting
UNAWAY !!
Electrolyte boiling
+80°C
Operation
!
+50°C
rolytes
Polymer Electrolytes
Under the hood
climate
Lithium metal plating
- 20
-40°C

Stability Domains



Stability Domains

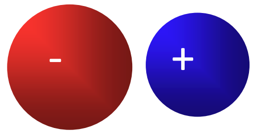


Sécurité active / Passive

Technologie

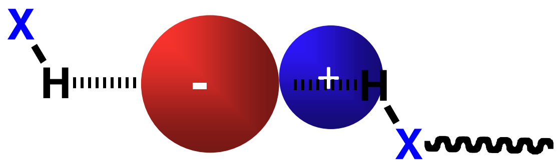
$LiMn_2O_4$		$LiFePO_4$
	Court circuit	
	comburant de l'élect	
	durée de vie	
	capacité spécifique (	
	simplicité du « BM	
	Toxicité en cas de feu	

The role of solvation

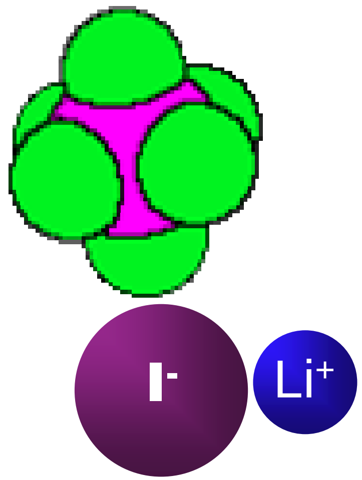


$$E \approx \varepsilon \frac{q_{M^+} \cdot q_{x^-}}{r_{M^+} + r_{x^-}}$$

Protic solvents (water)

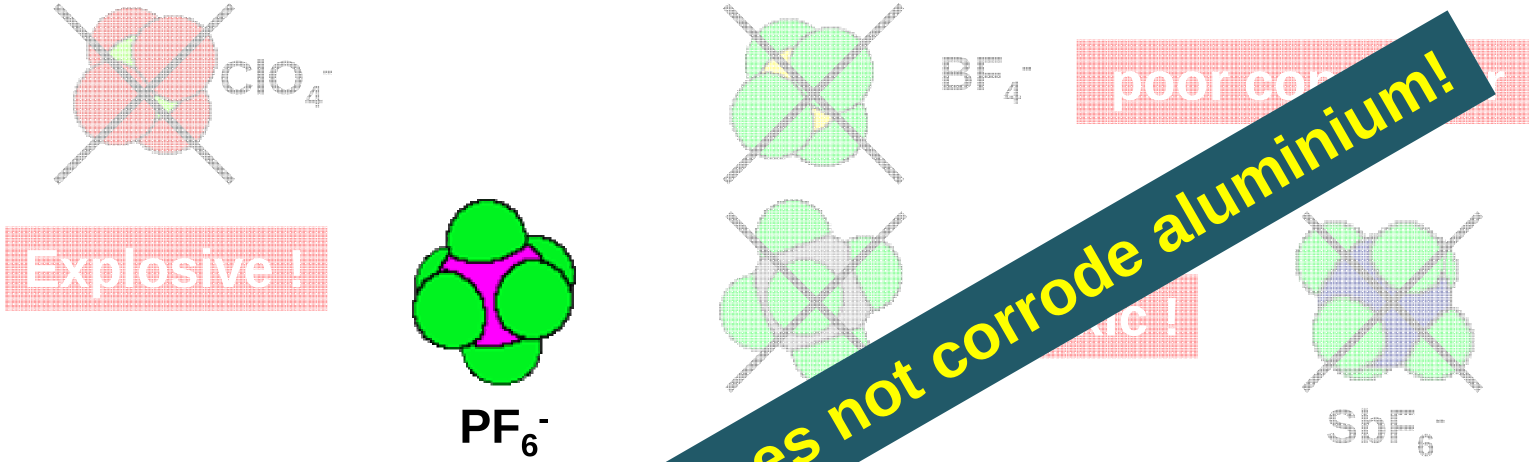


Non-protogenic solvents



⇒ design of polyatomic anions
⇒ Chemical fragility

Les Classiques…



Only justification: does not corrode aluminium!

Tendency … ompose according to equilibrium:

$LiPF_6 \Rightarrow PF_5 + <LiF>$

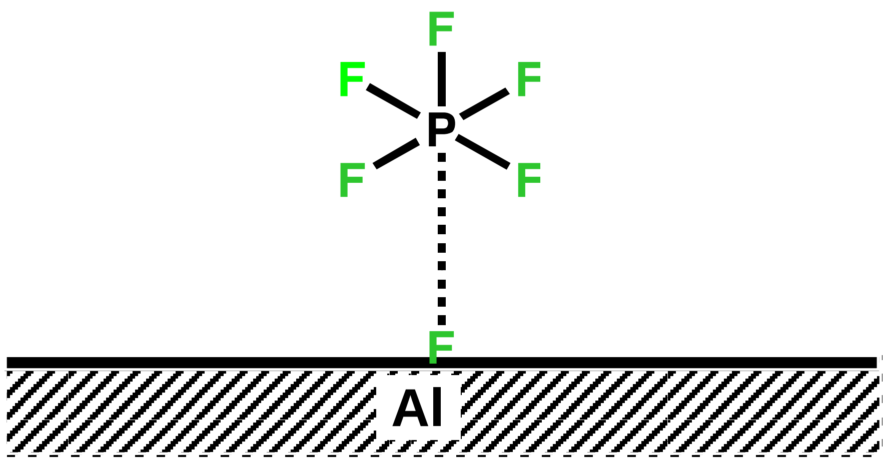
$PF_5 + H_2O \Rightarrow HF$

…truction of electrolyte and interfaces (dissolution of Mn, Fe …)

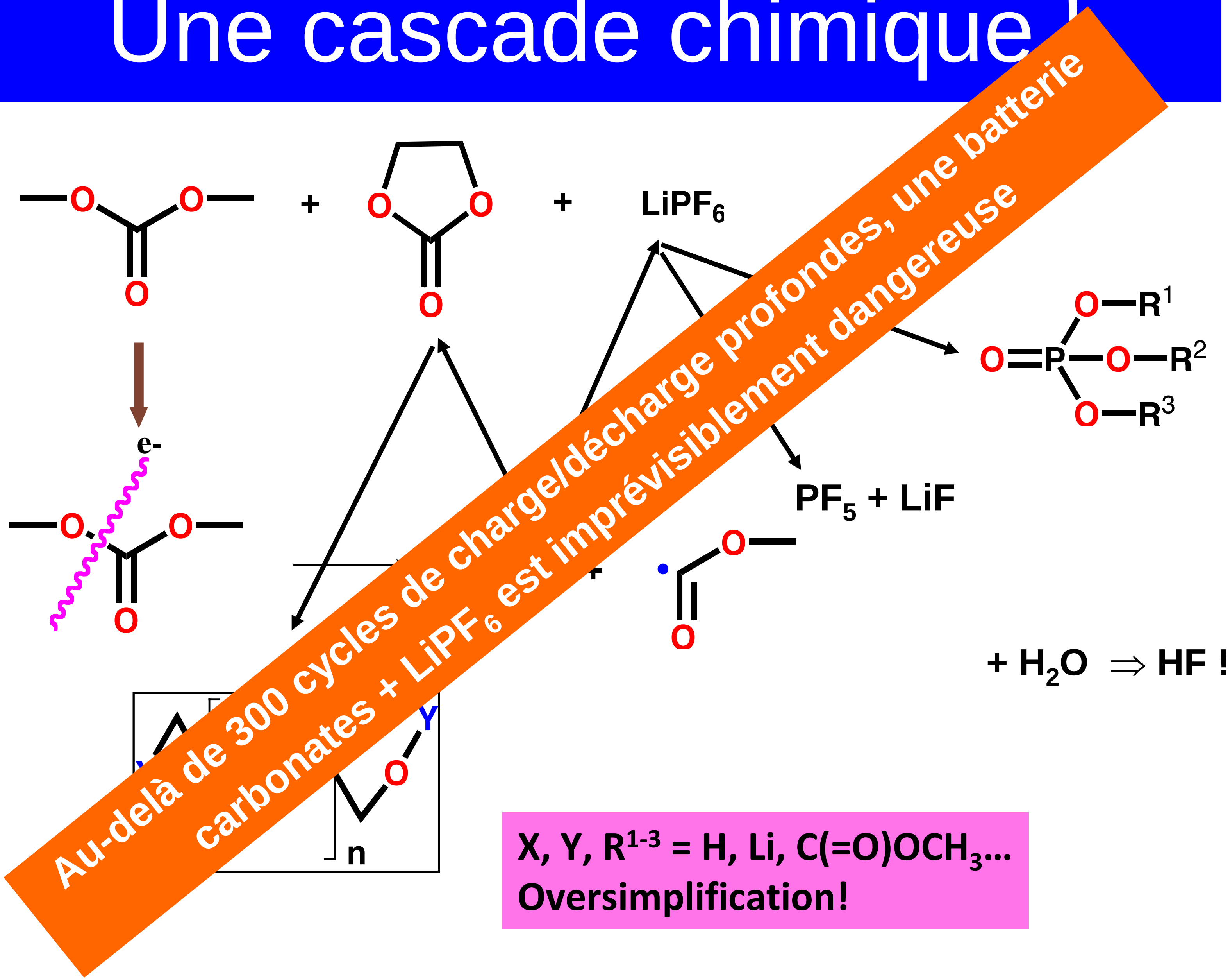
Al: conventional wisdom

Al^{3+}: Al° is 1.3 V positive of lithium ⇒ always in the passive zone for the + electrode. There is no other choice (Ti !)

C W: Some solvolytic instability of the anion is needed to prevent breakdown of the Al_2O_3 / AlF_3 passivating layer ⇒ vicious circle



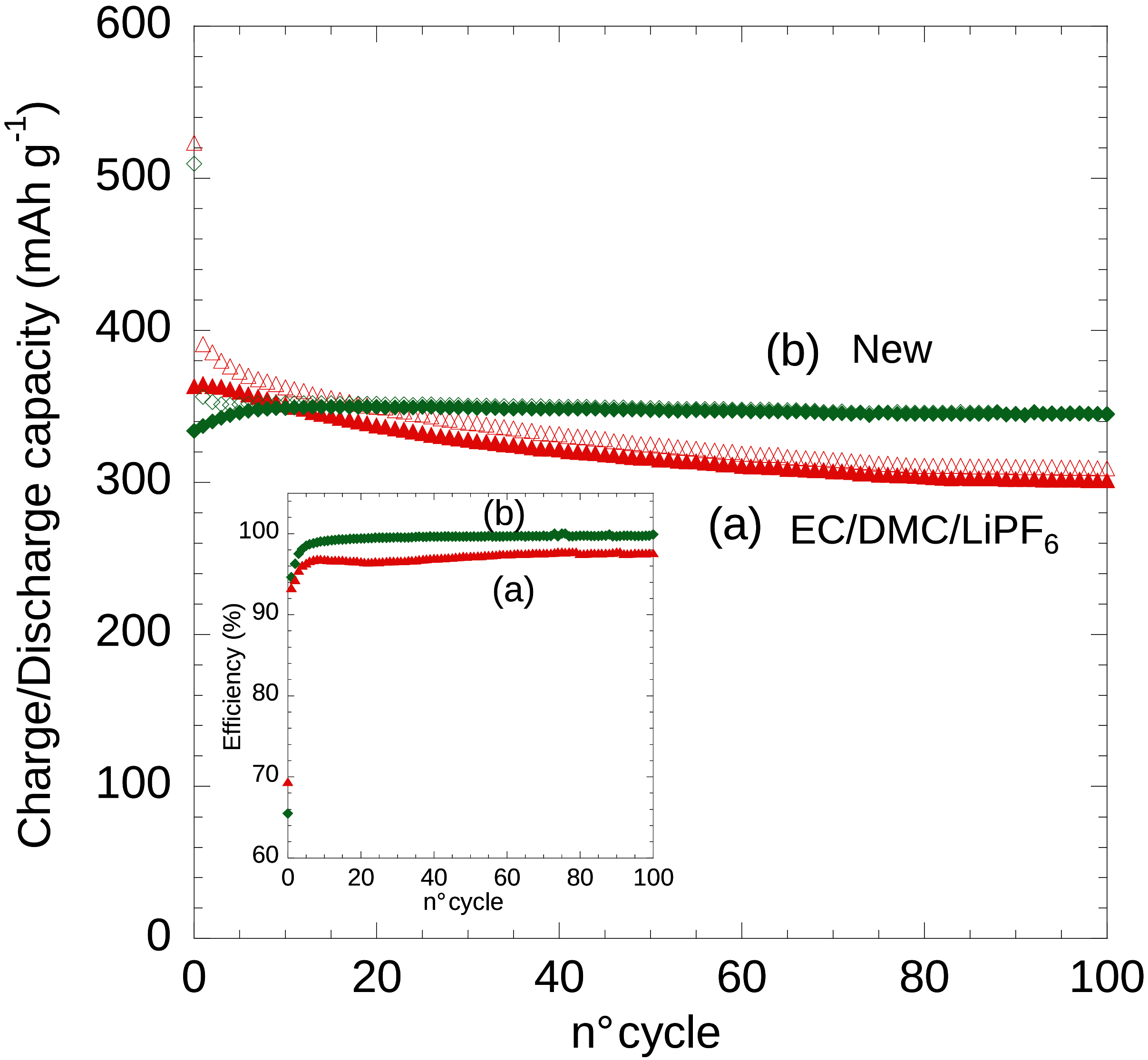
Une cascade chimique !



X, Y, R^{1-3} = H, Li, C(=O)OCH_3…
Oversimplification!

S Laruelle, S Grugeon et al.. *J. Power Sources* 178-1, 409-421, (2008)

Électrode de Graphite sans carbonates alicycliques, < 4V



Conception de nouveaux solutés

- plus covalents
- pas / moins de fluor
- pas de corrosion de Al

"O" n'est pas une « brique » très favorable :

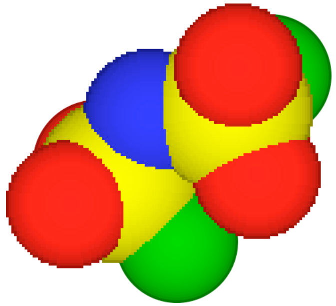
interactions Li—O fortes ⇒ paires d'ions, ≠ ClO_4^-

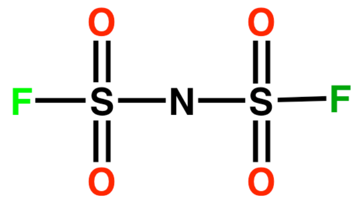
si O présent, F or C_nF_{2n+1} est requis

"N, C" sont favorables :

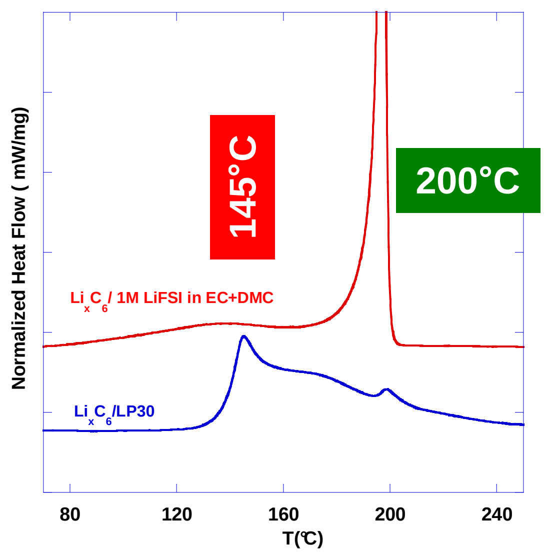
Interactions faibles Li—N / C mais oxydation facile 

FSI

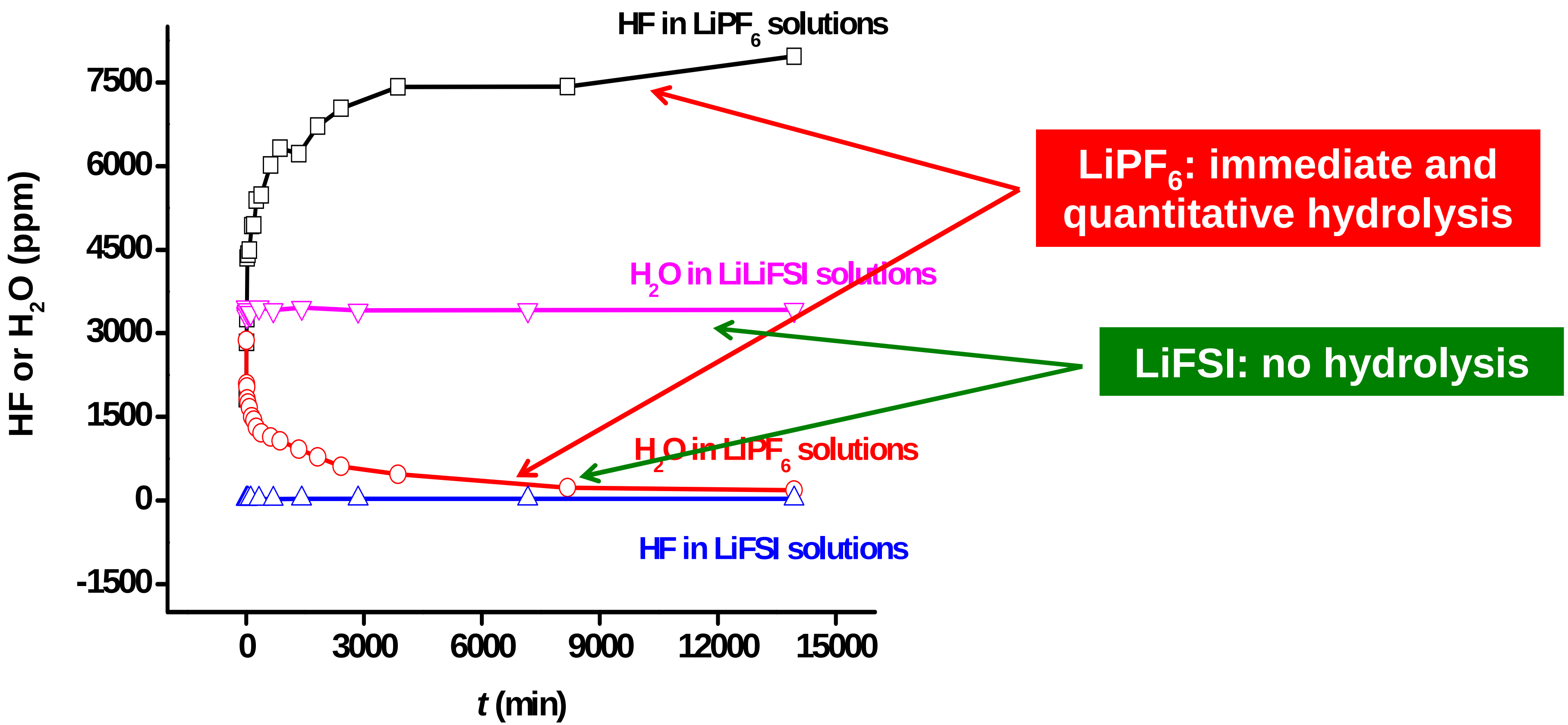




- more conductive than $LiPF_6$
- larger t_+
- 1/3 fluorine, S – F far more covalent than P – F
- Safer with carbon electrode
- more favourable low temperature phase diagram / σ

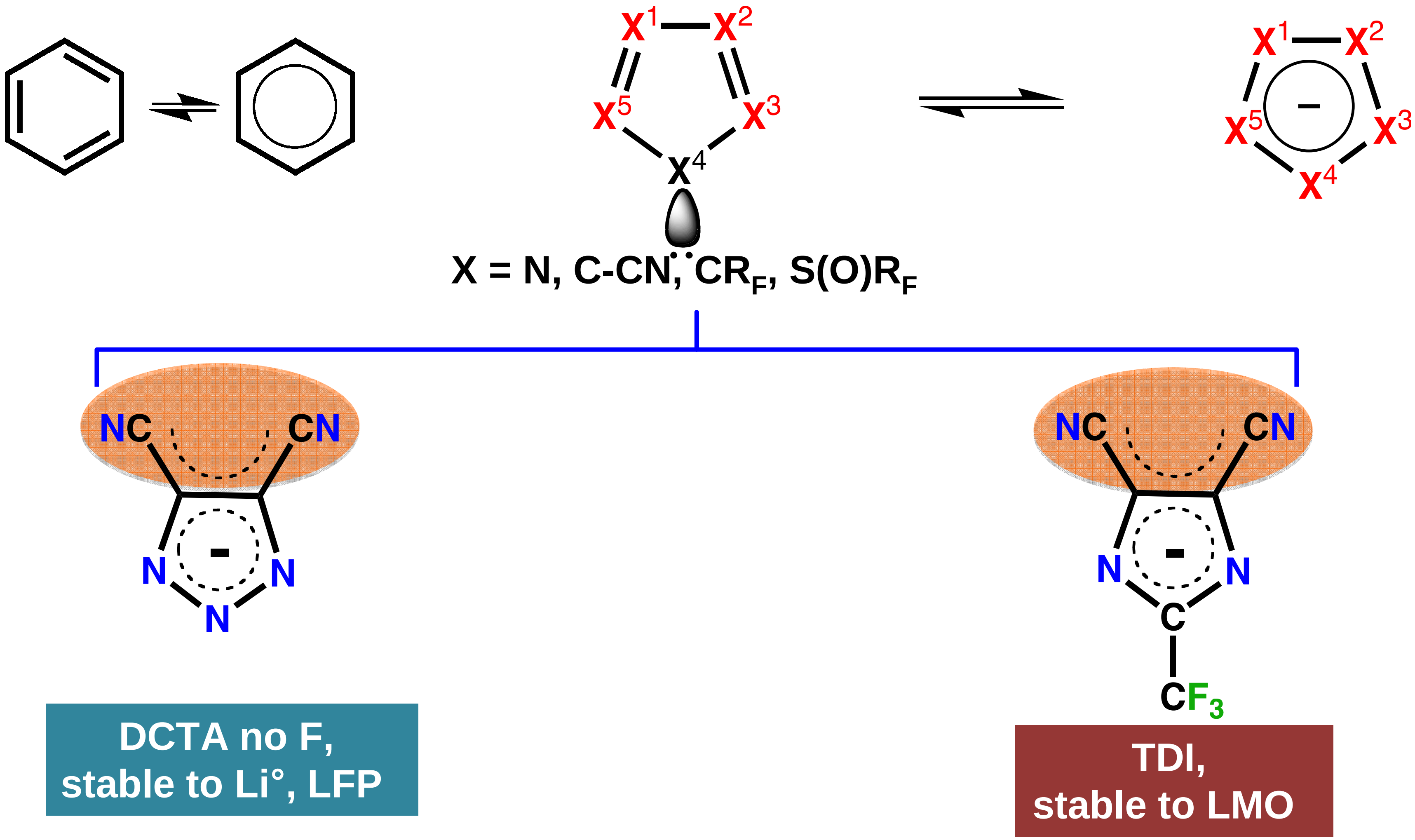


Hydrolysis at RT: LiFSI vs. $LiPF_6$



Hückel anions…

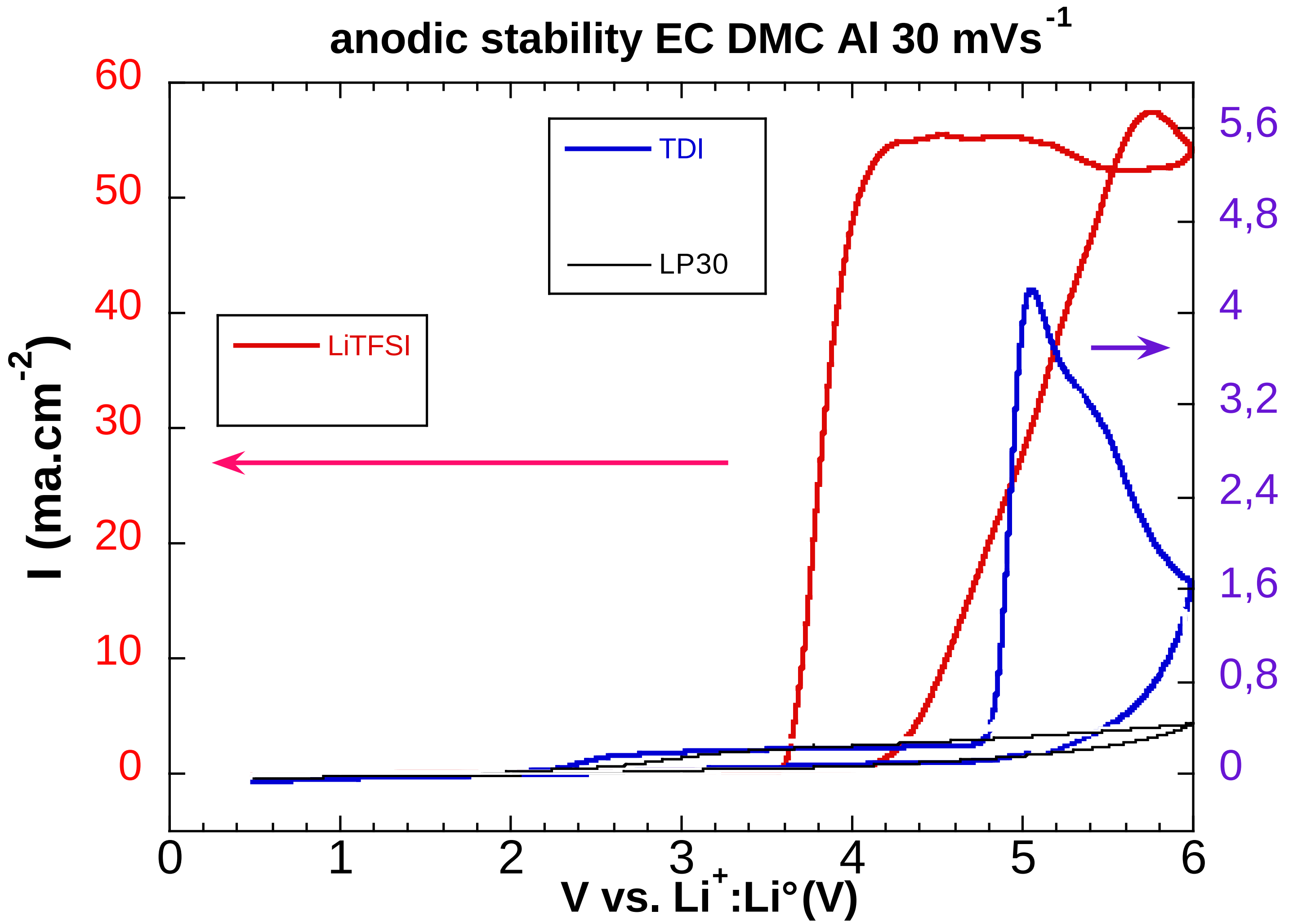
Aromaticity 4n + 2 « π » electrons



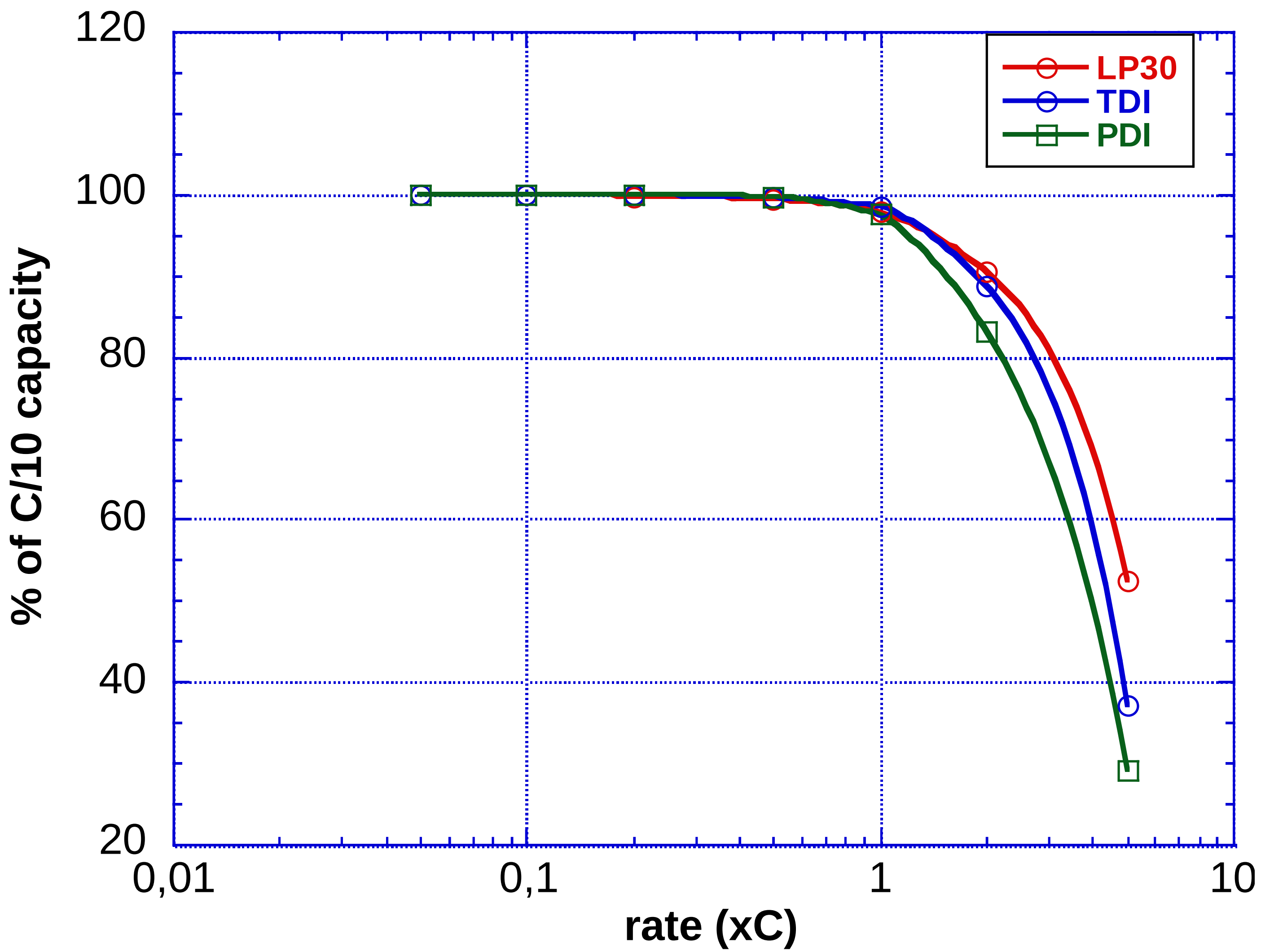
Conductivities (20°C)

Electrolyte	Formula	σ ($mS.cm^{-1}$)
LP30	$LiPF_6$ 1M in EC/DMC	10.8
LiFSI		12
LiTFSI		9.0
LiTDI	1M in EC/DMC	6.7
LiDCTA		2.7

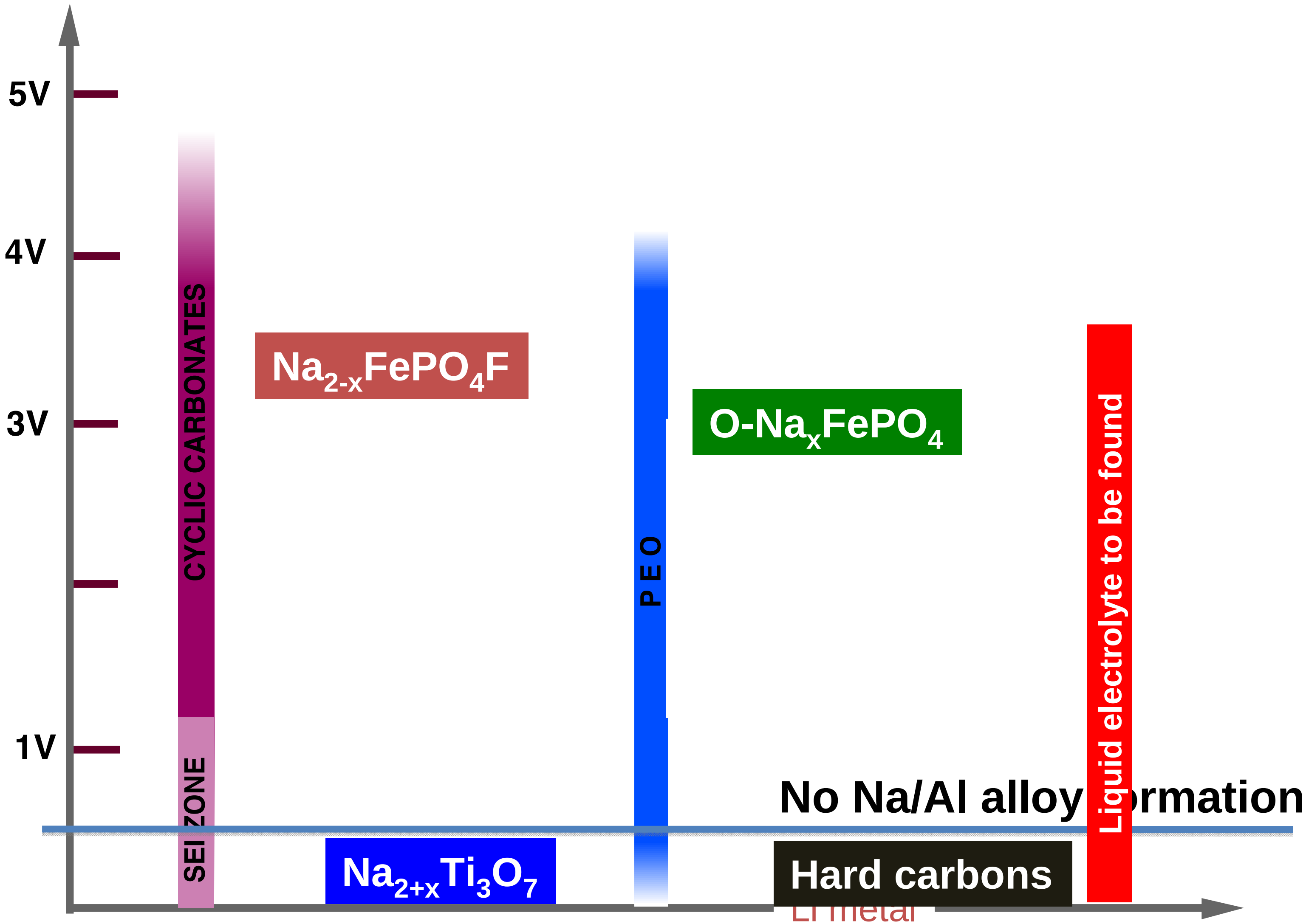
Anodic limit (Al, EC-DMC)



Ragone Signature

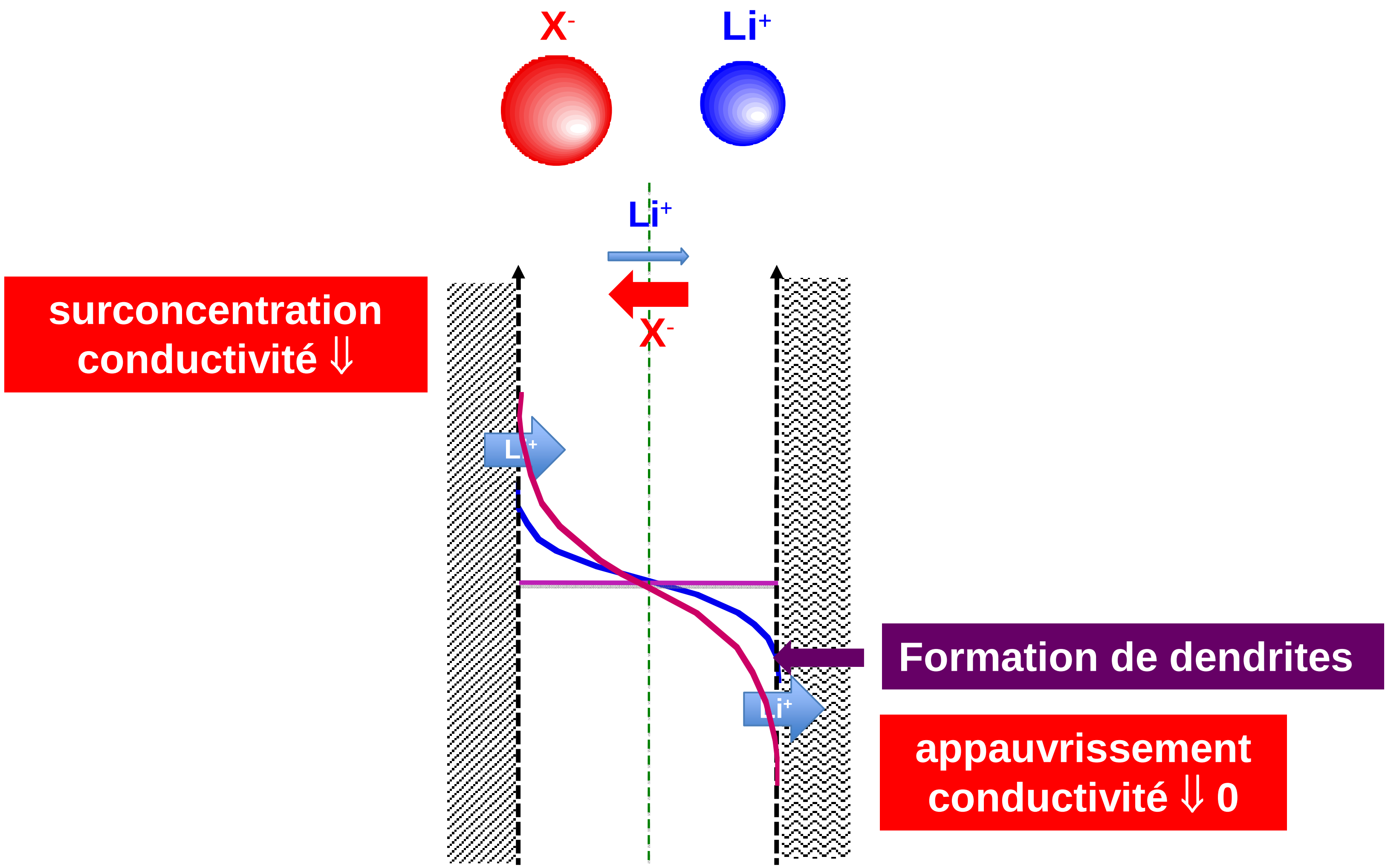


Sodium

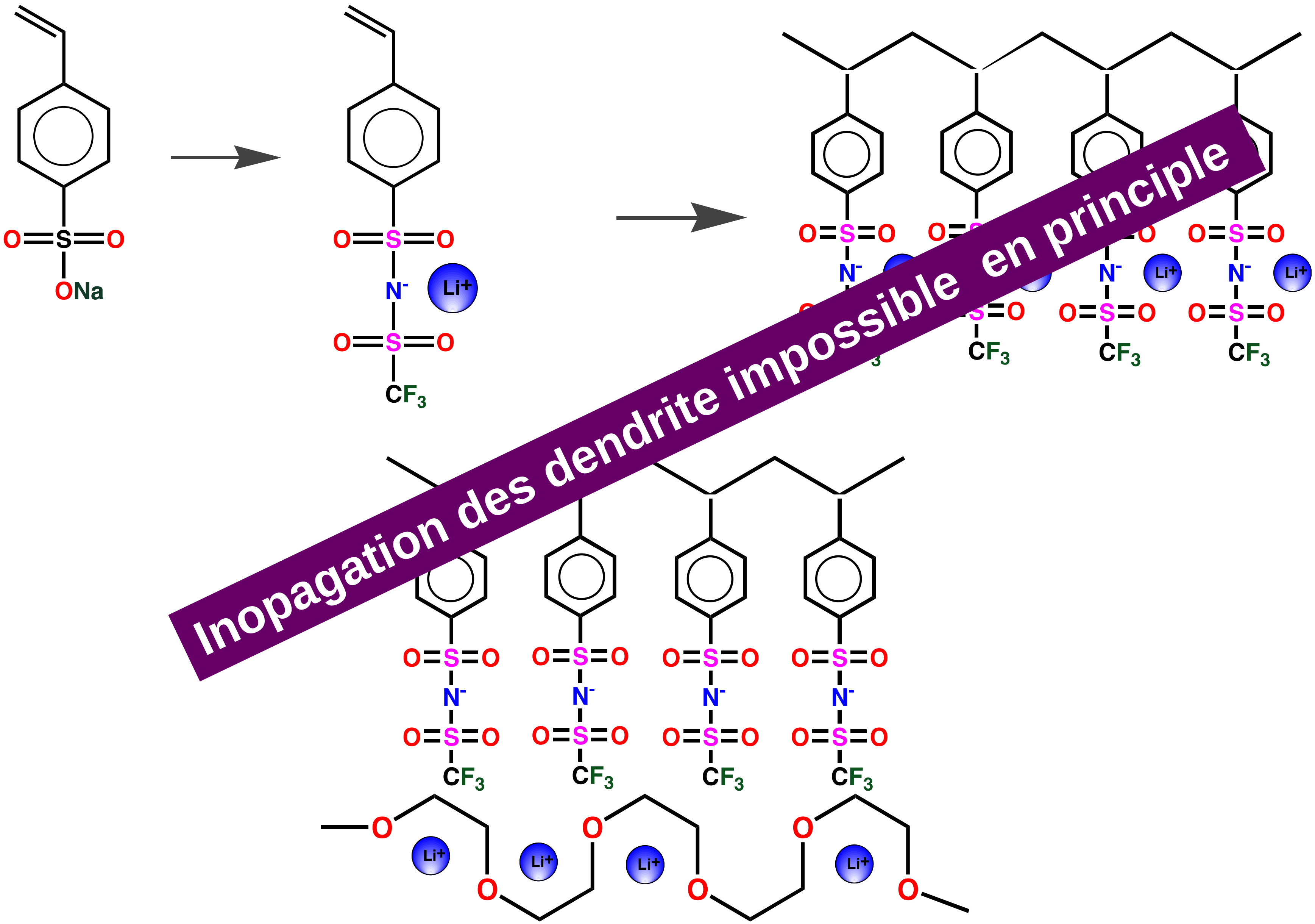


5V
4V
3V
1V
CYCLIC CARBONATES
SEI ZONE
$Na_{2-x}FePO_4F$
PEO
$O\text{-}Na_xFePO_4$
Liquid electrolyte to be found
No Na/Al alloy
$Na_{2+x}Ti_3O_7$
Hard carbons

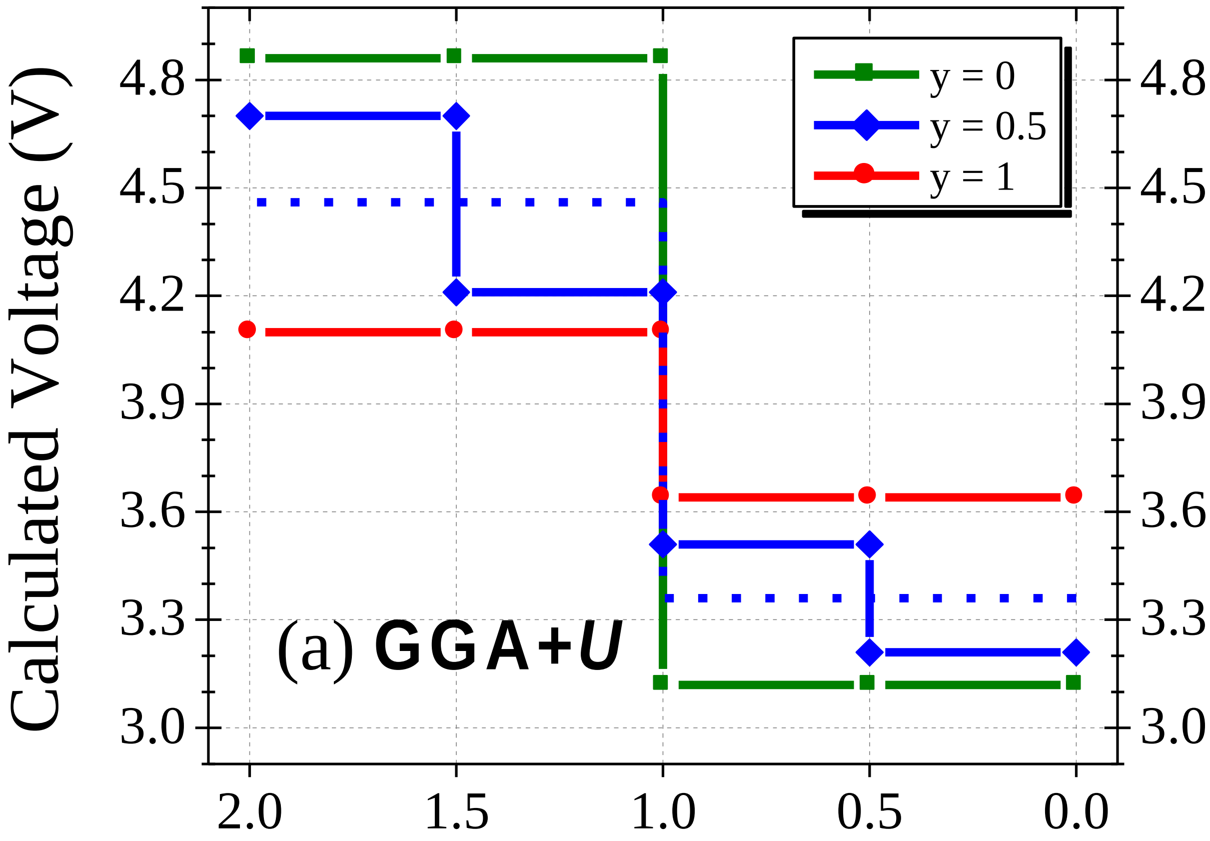
Conséquences du transport ambipolaire



électrolytes polymère avec t+ = 1 …



Vers 2 électrons / métal detransition …



Potential vs. composition for the system $Li_{2-x}FeSiO_{4-y}N_y$ for y = 0.5 and y = 1

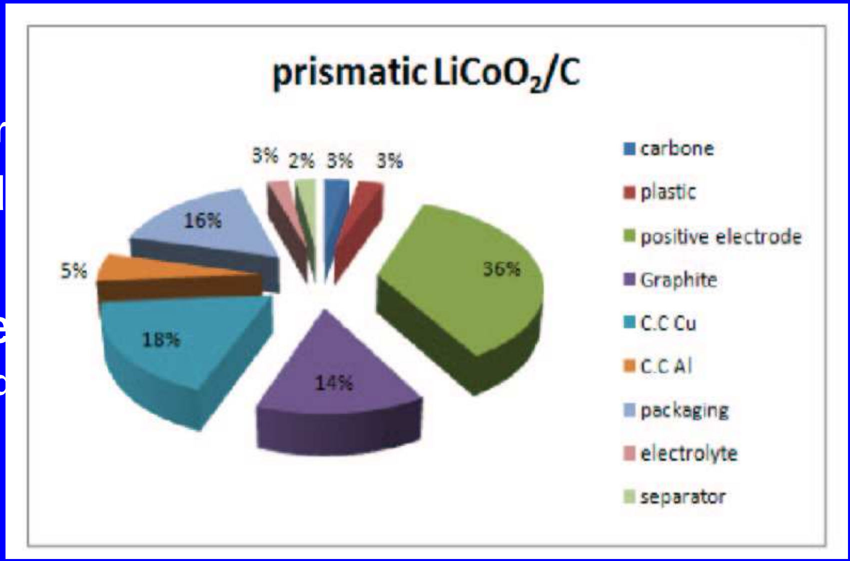
Conclusions…

- Les carbonates + $LiPF_6$ sont un miracle qui a permis le développement du Li-ion à 4V. S'il ne suffit pas pour les VE (HF et autre, vie calendaire et cyclage), il y a peu de démarches rationnelles pour respecter les hauts voltages.

- $LiFePO_4$ est "le pari de Pascal" dans la mesure où la technologie ne change pas pour les el. liquides et les densités d'énergies sont comparables (hélas @ 110- 130 Wh/kg).

- <3.9 V, il est possible de concevoir (≠ mi
peu ou pas de F, pas de corrosion Al, d

- Attention, le LMP est en embuscade ave
température est absurde (un batt non refroid
Mais Bolloré ne communique pas (plus) !

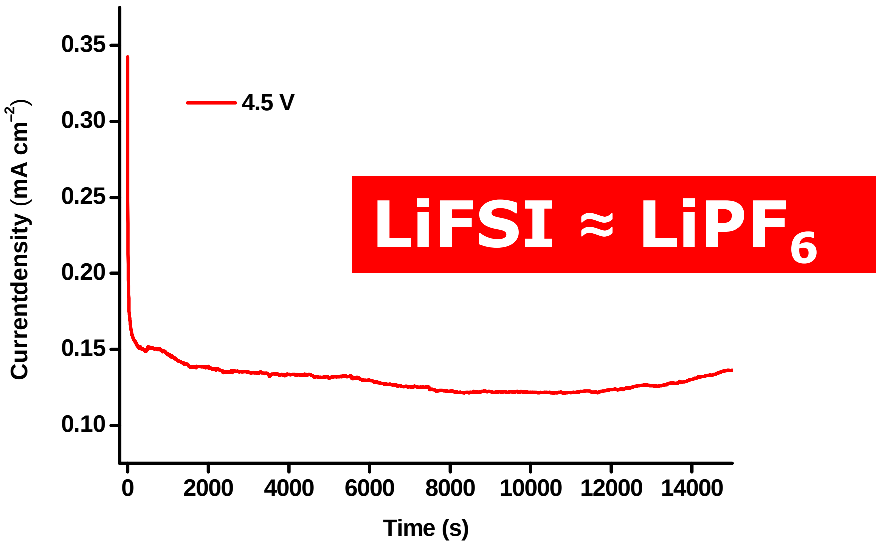


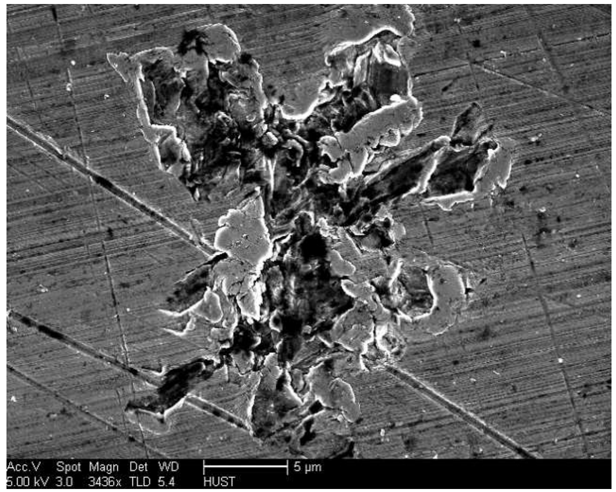
Merci de votre attention !

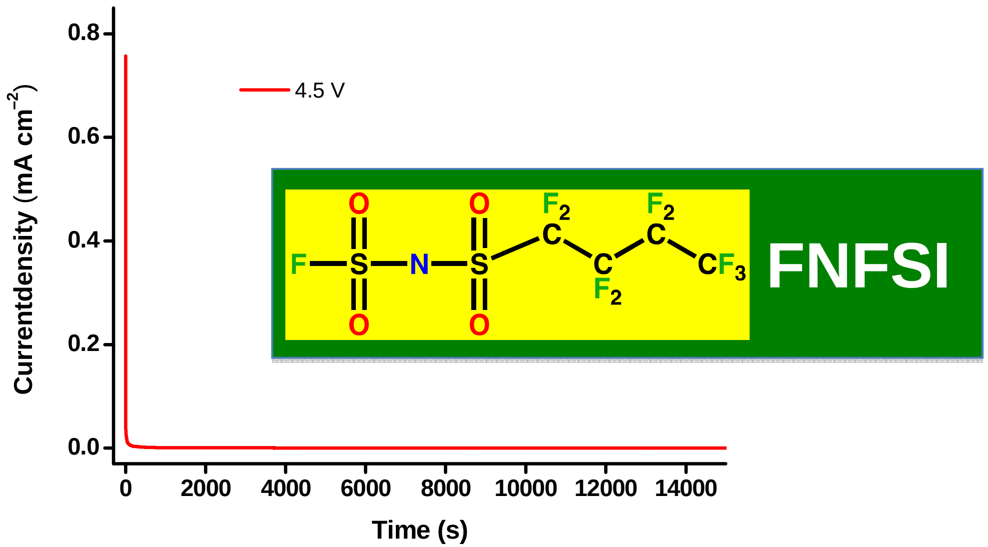
Merci !

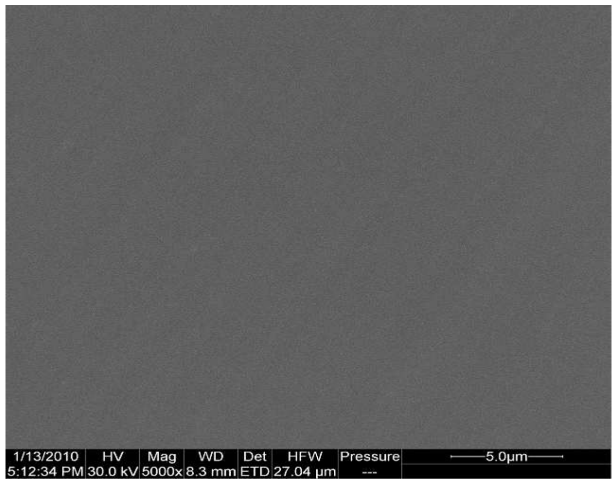
- **Sylvie Grugeon**
- **Stéphane Laruelle**
- **Grégory Gachot**
- **Devaraj Shanmukaraj**
- **Gebrekidan Gebreslase Eshetu**

Aluminium corrosion at 4.5 V vs Li^+/Li

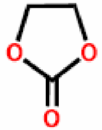
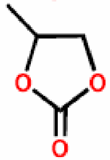
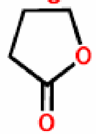
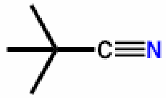
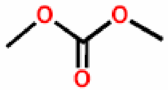
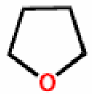
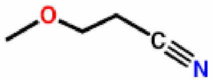




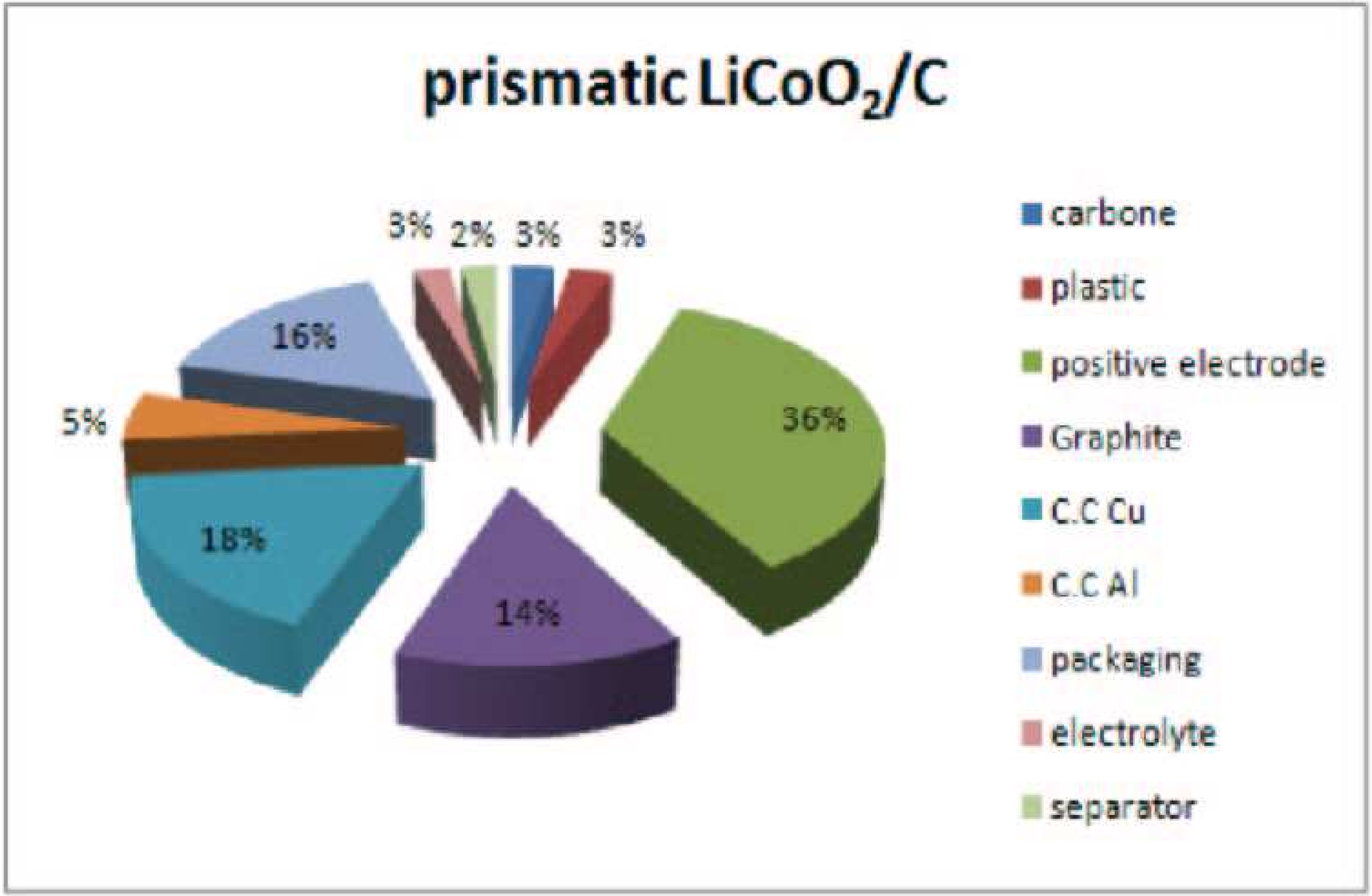


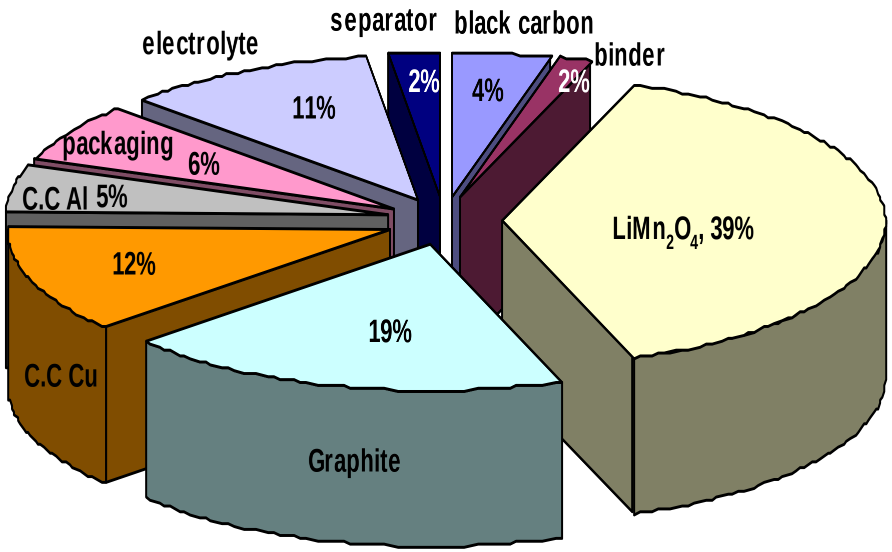


Solvent properties

Solvent name and **abbrev**.	Developed formula	T_m (°C)	T_{eb} (°C) *(Flash pt)*	Dielectric constant ε	Viscosity cP (25°C)
Ethylene carbonate **EC**		36	248 *(160)*	90	1.85
Propylene carbonate **PC**		-49	242 *(123)*	65	2.53
γ-butyrolactone **γ-BL**		-44	204 *(60)*	39	1,7
Acetonitrile **ACN**		-48	81 *(5)*	37.5	0.369
Glutaronitrile **GL**		-29°	286 *(> 110)*	-	5.3
Dimethyl carbonate **DMC**		5	95 *(18)*	3.1	0.6
tetrahydrofuran **THF**		-108	66 *(-17)*	7.2	0.48
Methoxy propionitrile **MPN**		-57	165 *(61°)*	36	1.1

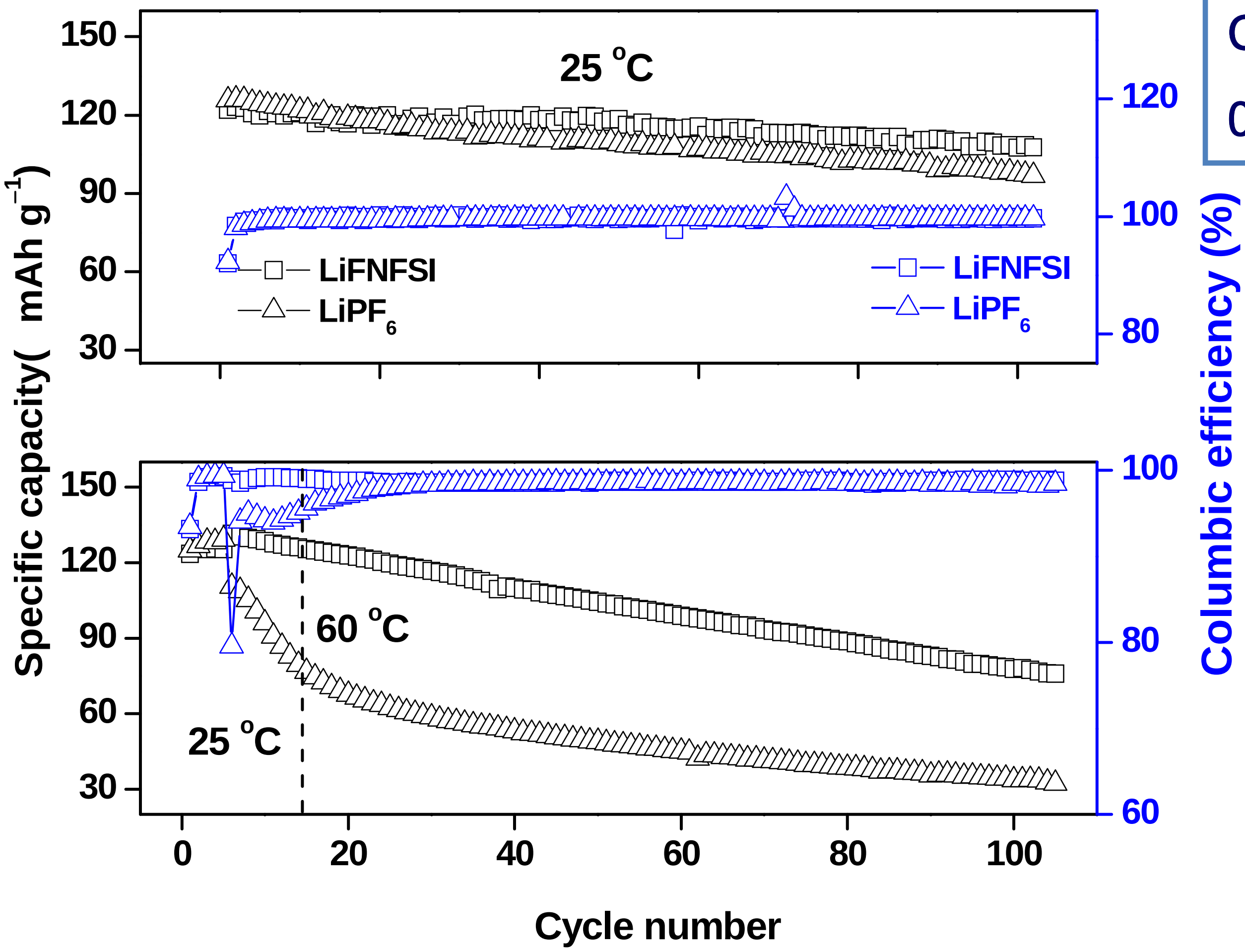
Materials weight break-down





electrolyte
separator
black carbon
binder
11%
2%
4%
2%
packaging
6%
C.C Al 5%
12%
LiMn2O4, 39%
19%
C.C Cu
Graphite

Cycling (LiFNFSI vs $LiPF_6$)



Charge/discharge rate

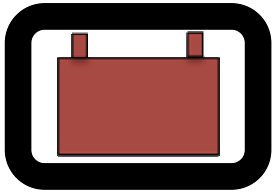
0.5/0.2 C

- The cells with LiFNFSI display much better cycling performances than those with $LiPF_6$ at both room temperature and elevated temperature (60 °C)

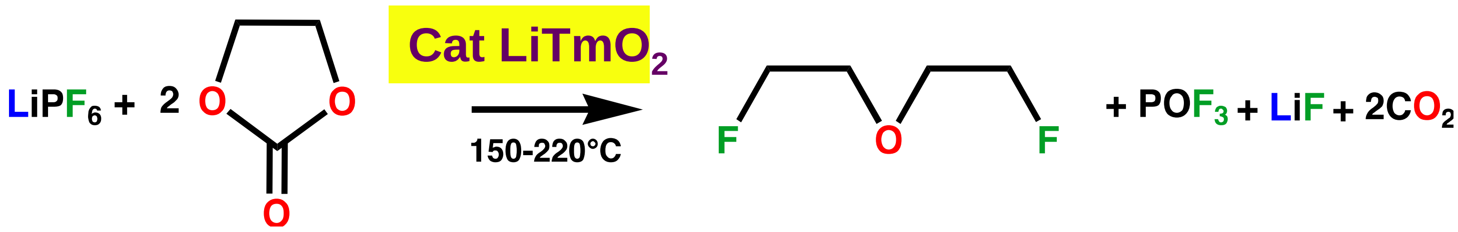
Touchy Science!

FIRE! →

Either lethal or permanent lung damage!



SMOLDERING!



LD50 = 0.1 mg.Kg^{-1} for mice!!!!

A. Hammami, N. Raymond & M. Armand, *Nature*, 424 (6949), 635-636, (2003).