Les rôles clés des polymères dans les électrodes composites de batterie Li ion

Bernard LESTRIEZ

Colloque du GFP du 18 Mai 2010, Paris

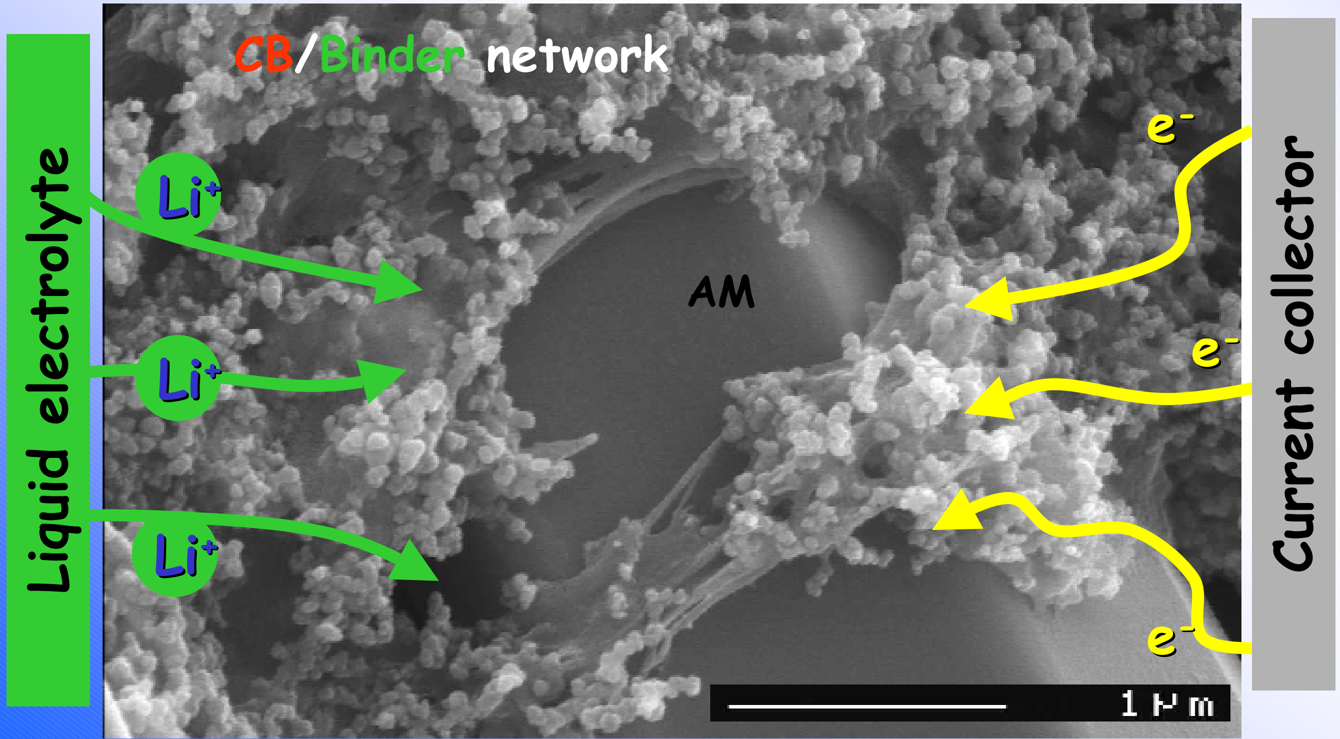
The (+) or (-) composite electrode.

Mixing the Active material with

Electron-conductive agent (CB powder) ⇒ e^- conductivity

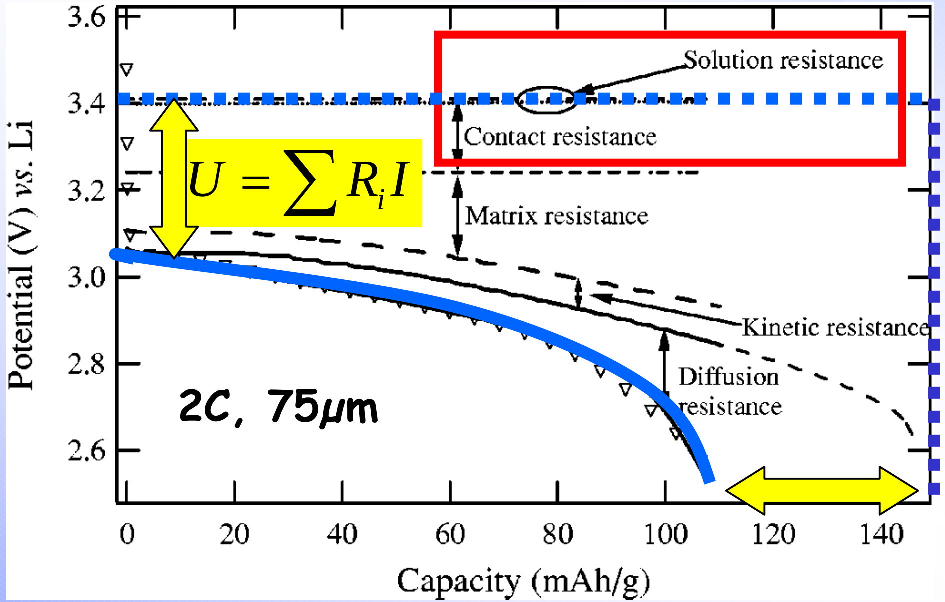
Liquid electrolyte within the porosity ⇒ Li^+ conductivity

Polymeric binder B ⇒ Cohesion and Adhesion



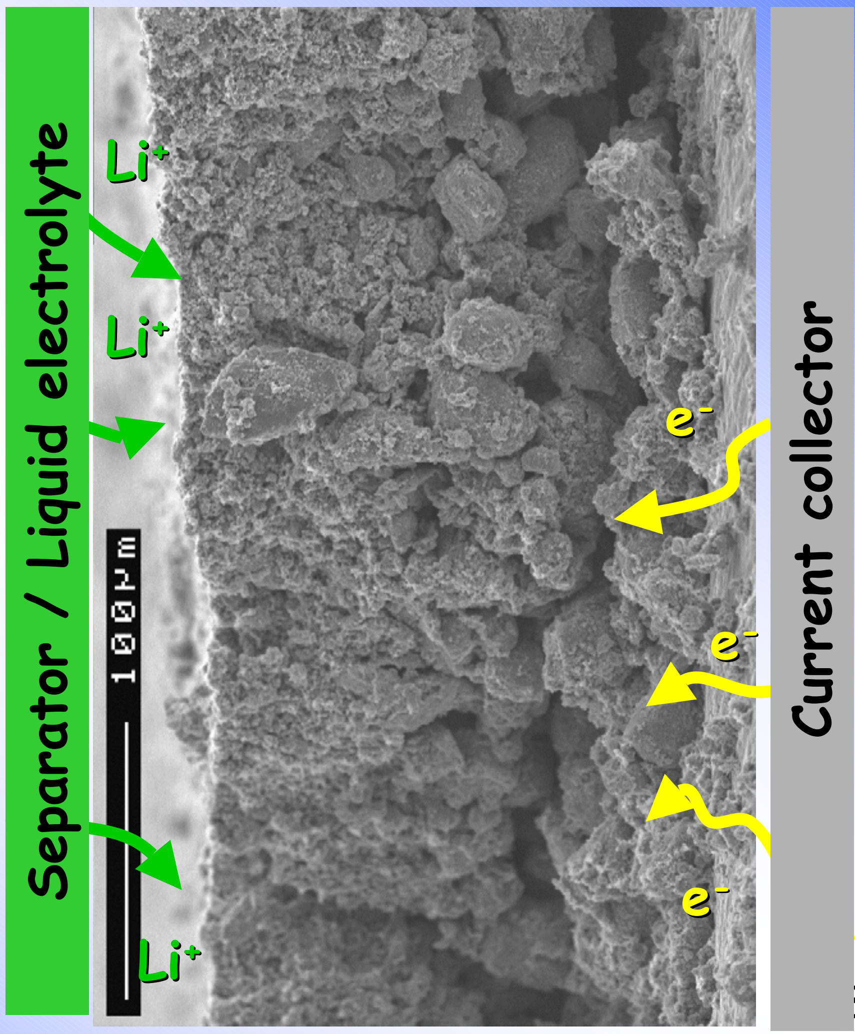
AM : 90 %w
CB : 5 %w
B : 5 %w
Porosity 30-40 %v
50-100 μm

The different contributions (simulation)



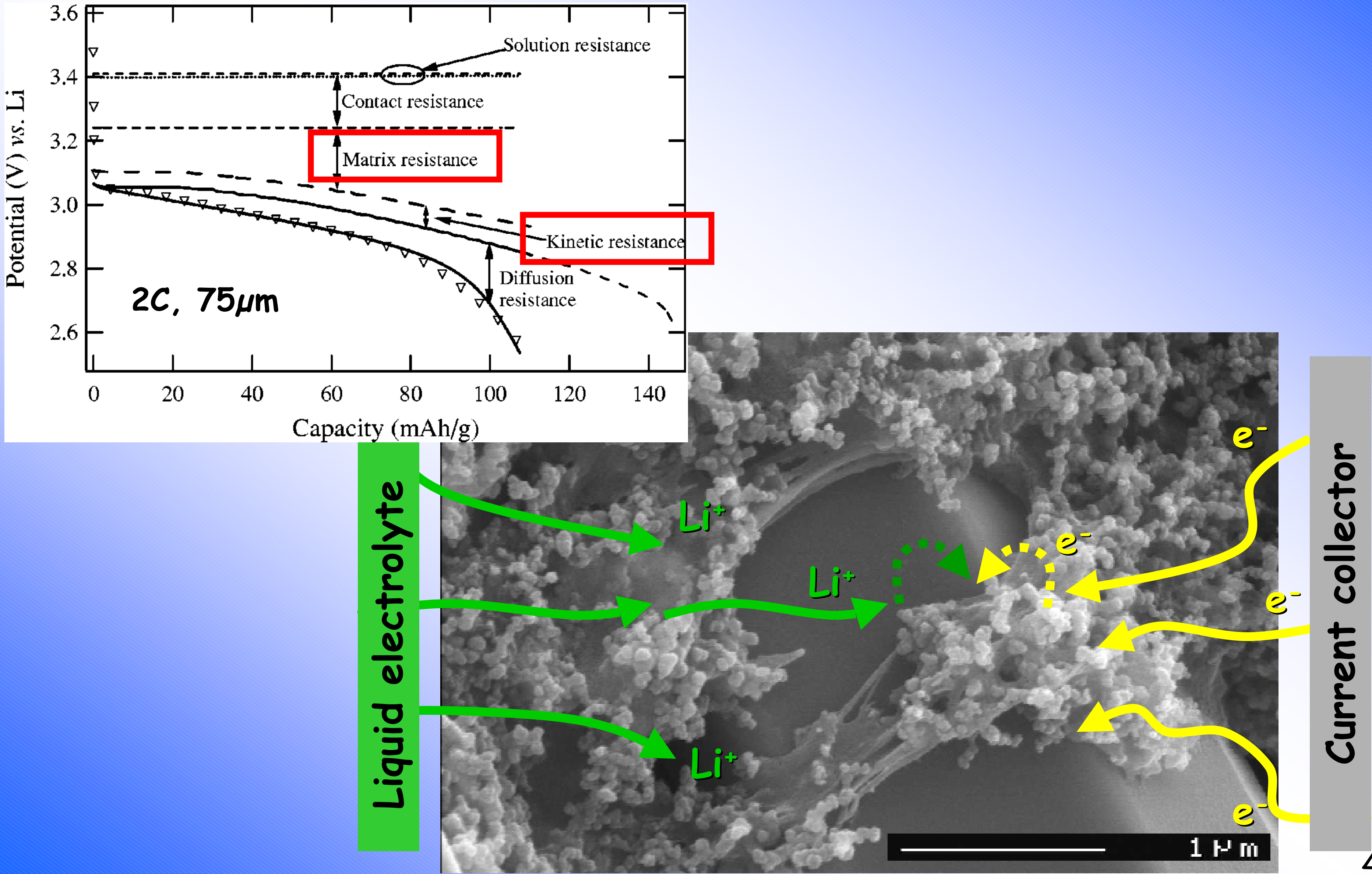
Li_xFePO_4 // Li cell

$x.Li^+ + FePO_4 + x.e^- \rightarrow Li_xFePO_4$

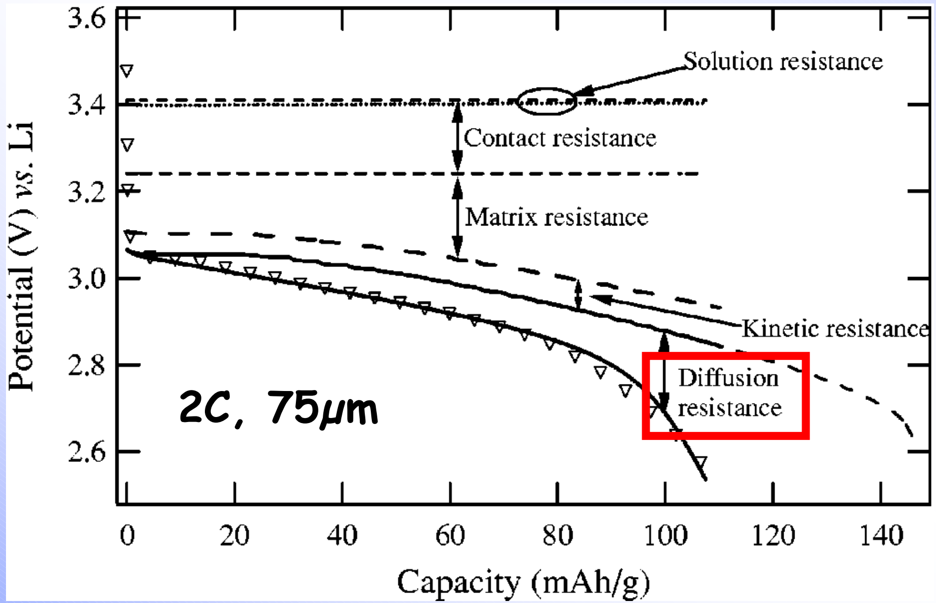


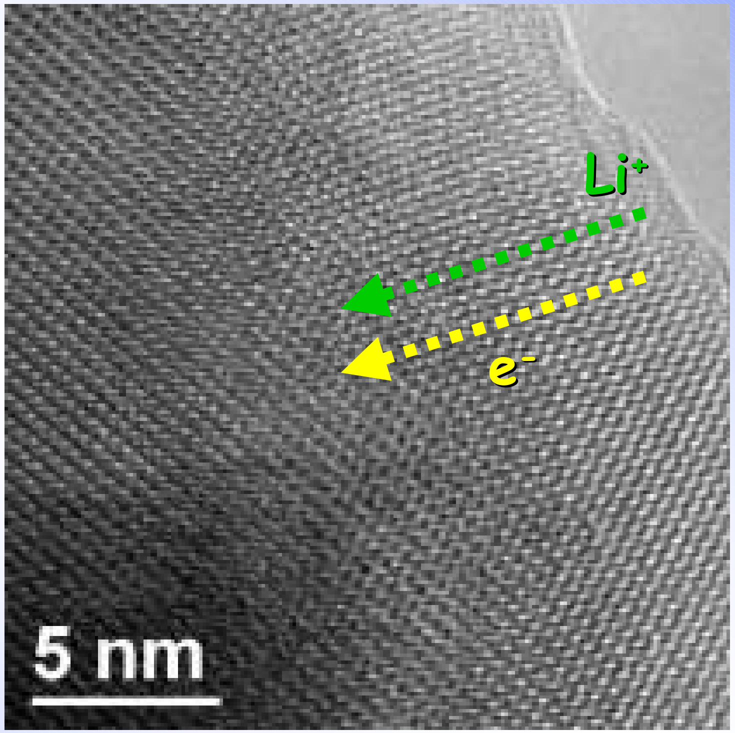
Srinivasan, V., and Newman, J. 2004, J. Electrochem. Soc.

The different contributions (simulation)

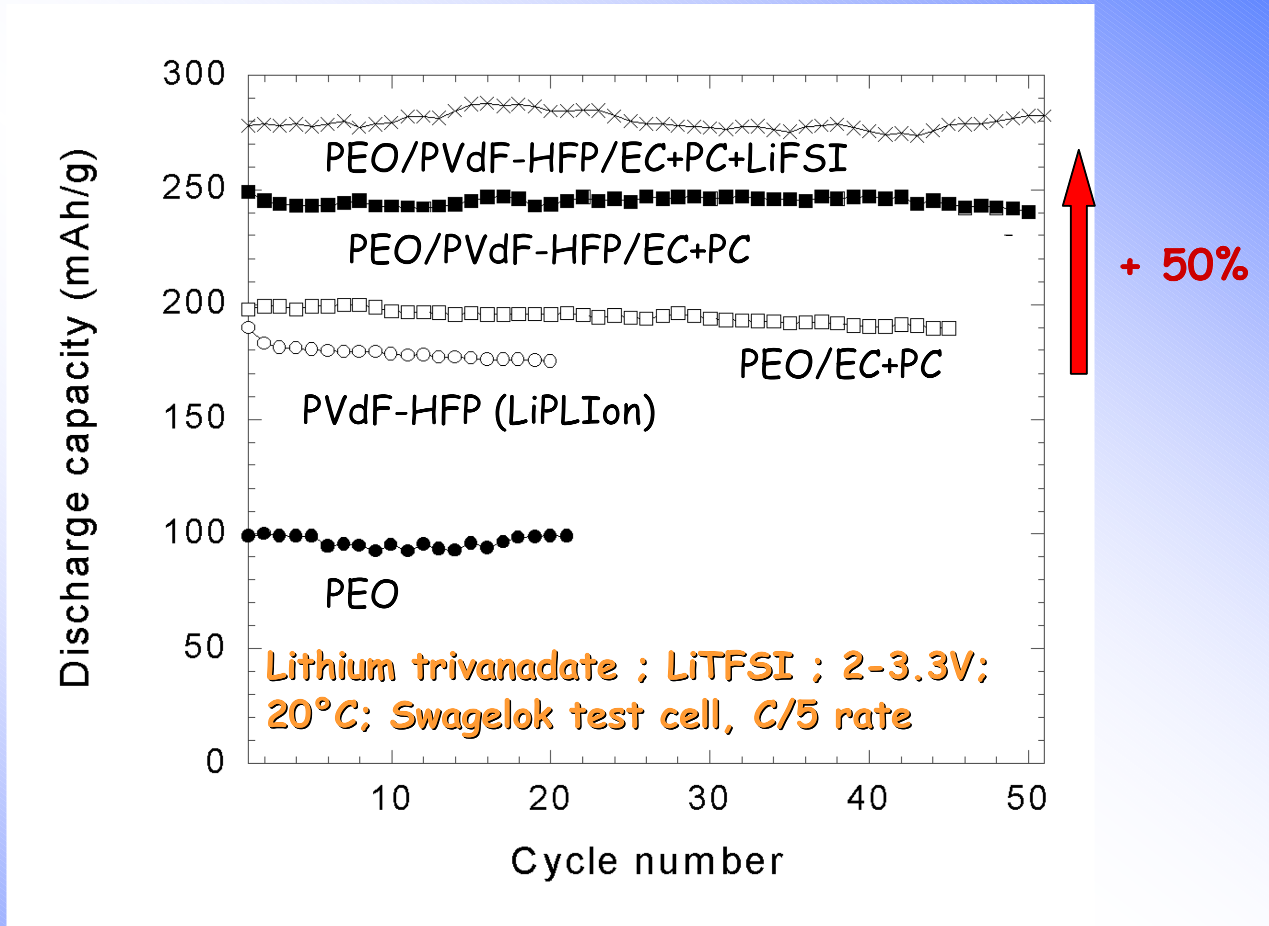


The different contributions (simulation)





What is the role of the binder ?



For a unique AM…

D. Guy, *et al.*, *Advanced Materials*, 2004.

Outline

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2. Role of the binder on the processing
3. Role of the binder on the electronic conductivity
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7. Conclusions and Prospects

1. Binders are polymers

Original (NON-aqueous) Binders

Poly(vinylidene fluoride) ⇒ standard industrial binder Li-Ion batteries, < 5 V

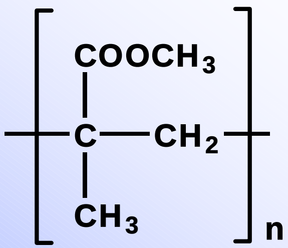
Poly(vinylidene fluoride–co-hexafluoropropylene) ⇒ Bellcore technology , < 5 V

Poly(tetra fluoro ethylene) ⇒ wet process for laboratory , < 5 V

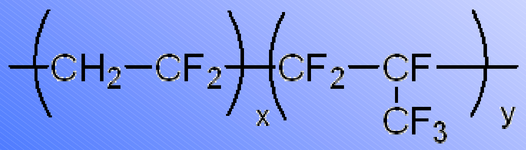
Poly(ethylene oxyde) ⇒ dry LMP batteries, < 4 V vs Li°/Li$^+$

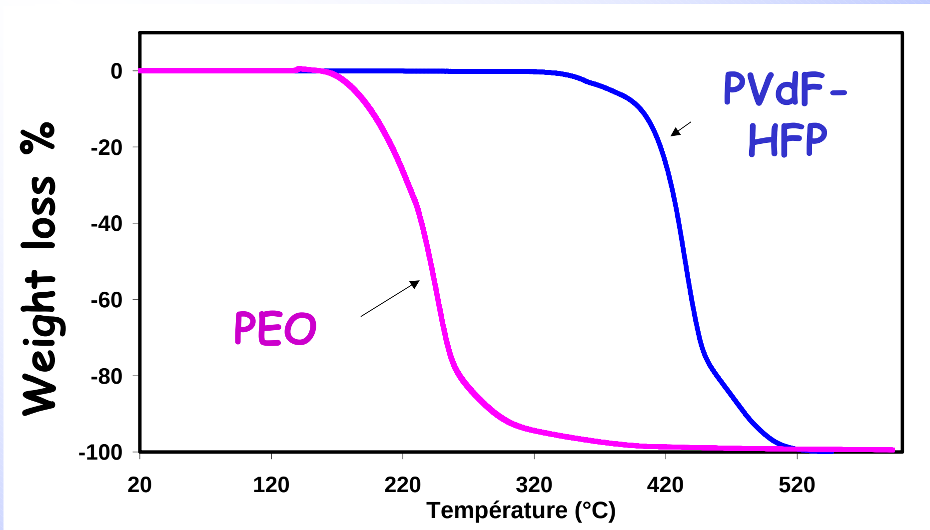
Poly(methyl methacrylate) ⇒ gel, < 4.6 V

$-(CH_2\text{-}CH_2\text{-}O)_n-$



$-(CH_2\text{-}CF_2)_n-$





Dias, F.B., *et al.*, 2000, J. Power Sources. Quatartone, E., *et al.*, 1998, Solid State Ionics. Tarascon, J.M., *et al.*, 1996, Solid State Ionics.

1. Binders are polymers

Aqueous Binders for aqueous processing

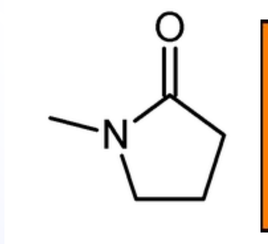
A big issue

Environment, cost, safety concerns => switch from **non-aqueous** to **aqueous** processing techniques

Drawbacks:

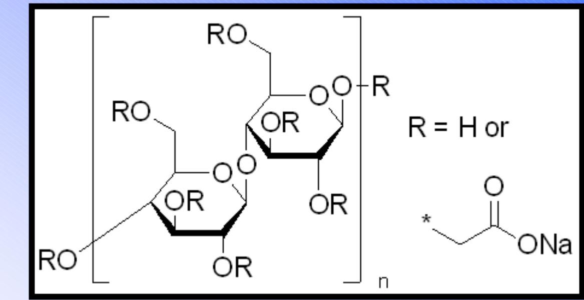
- Stability of the AM in water ?
- Water elimination

N-methyl-2-pyrrolidone



1. Binders are polymers

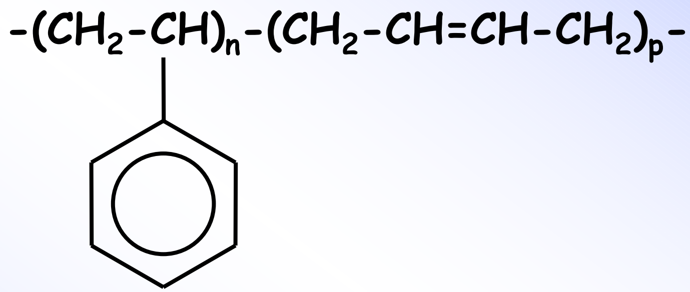
Carboxymethyl cellulose (CMC), rheological aid



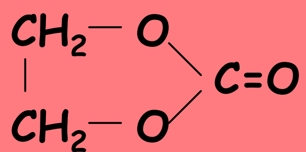
Polyacrylic acid (PAA), for adhesion strength to the current collector

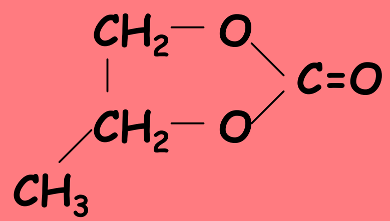
$$-(CH_2-\underset{\underset{\displaystyle HO-C{=}O}{|}}{CH})_n-$$

Styrene-butadiene rubber latex (SBR latex), elastomer (binder).



Liquid Electrolyte





$LiPF_6$

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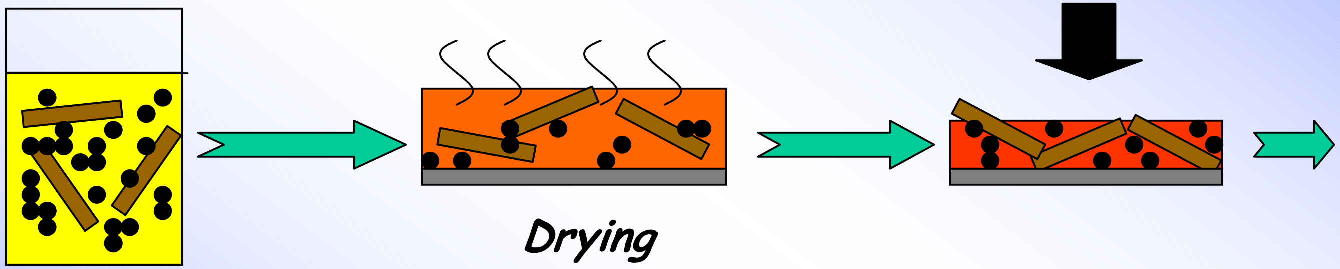
Processing

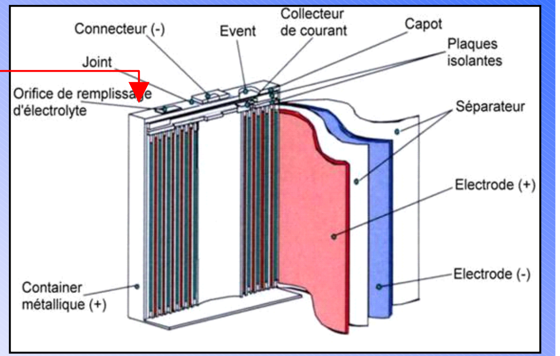
Liquid electrolyte

Mixing AM+CB+B in a solvent

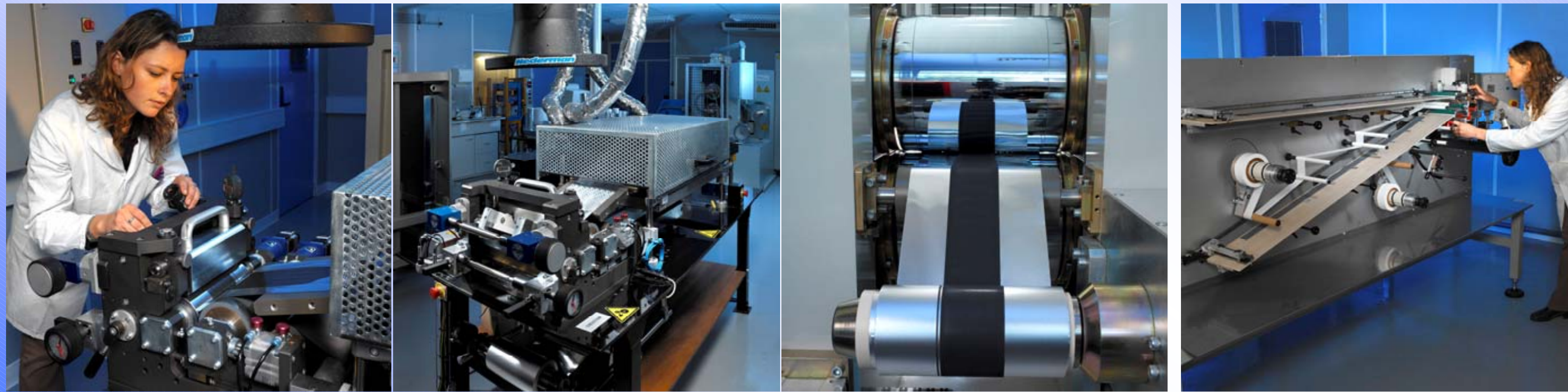
Calendaring



Drying



Battery assembly

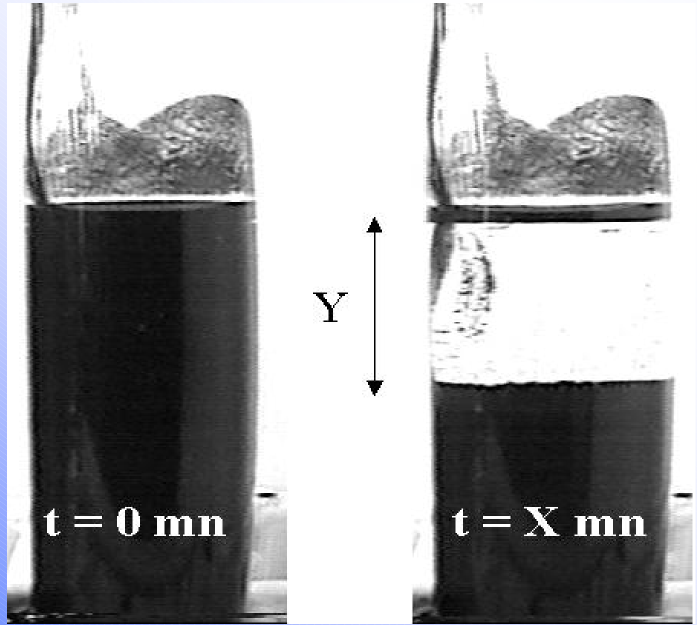


Typical speed for this machine: 5 m / min

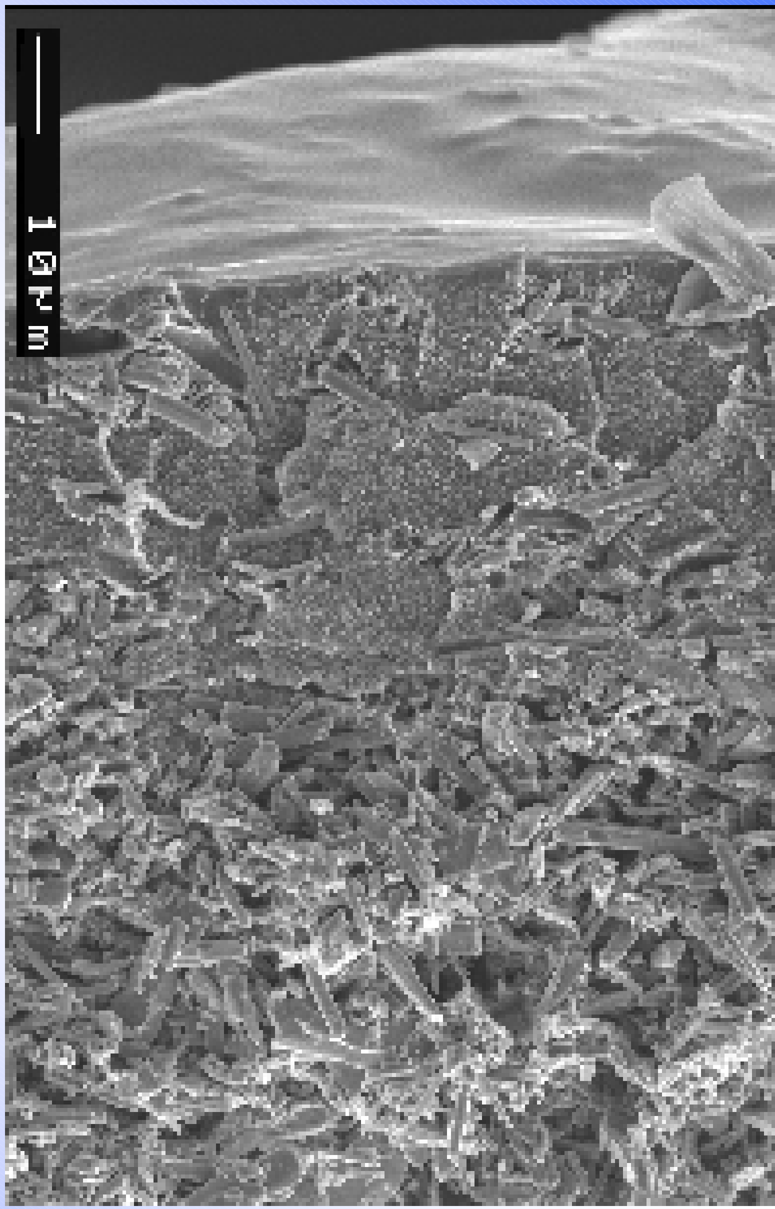
From CEA

Instabilities in electrode slurries

Settling

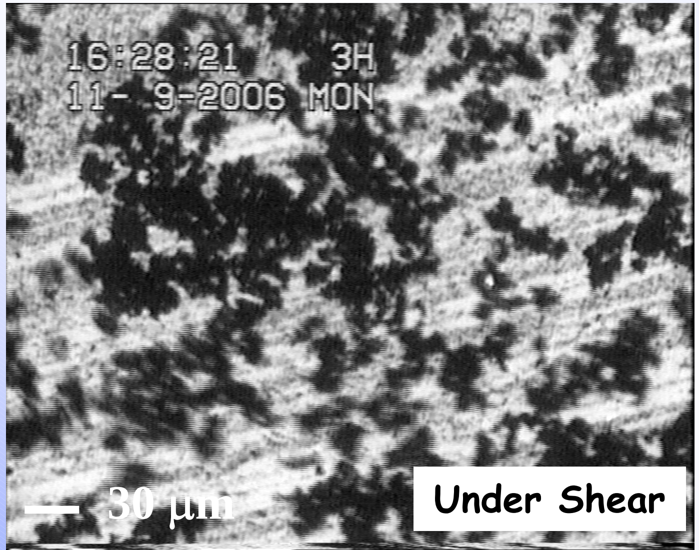


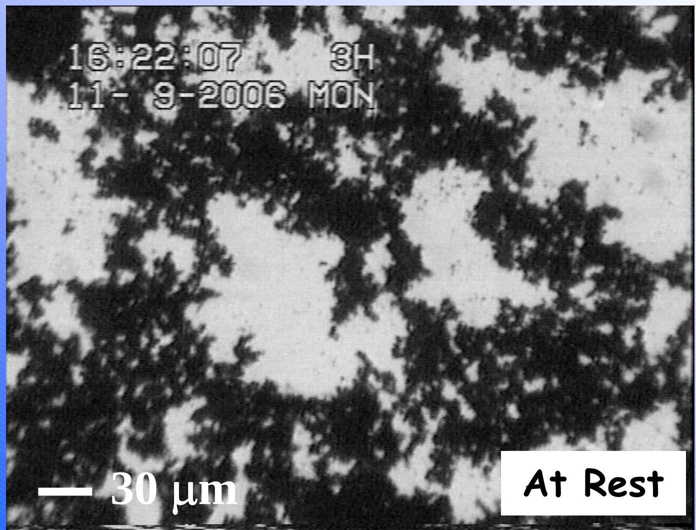
Measurement of settling rate
(closed tubes)



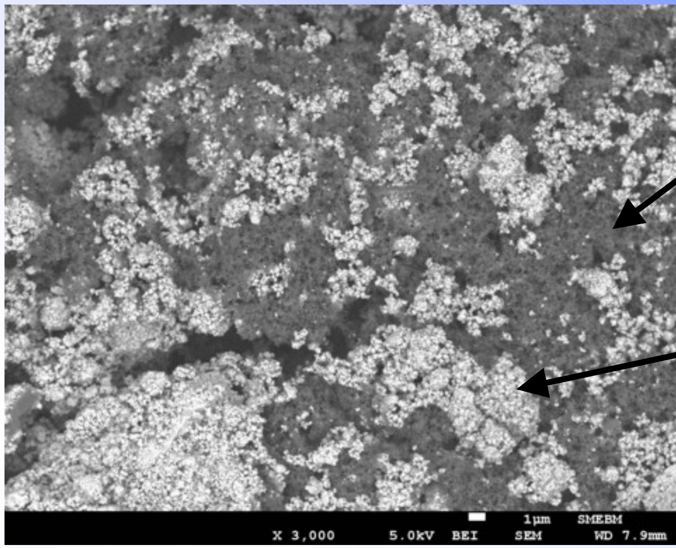
Instabilities in electrode slurries

Aggregation



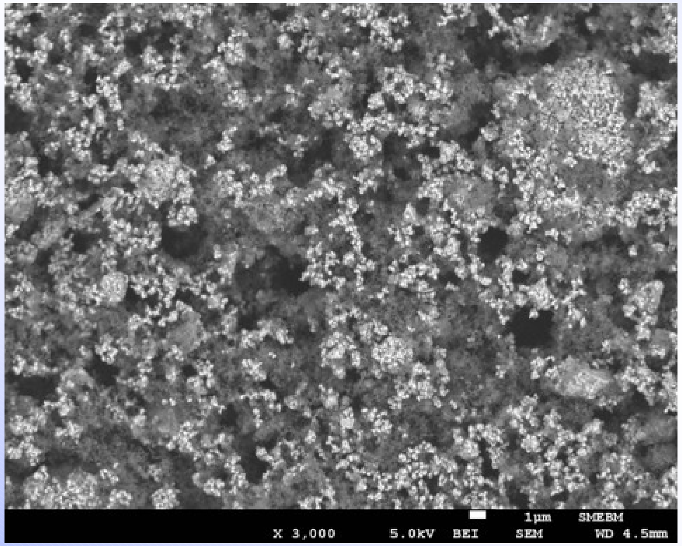


SEM (retrodiffusion mode)



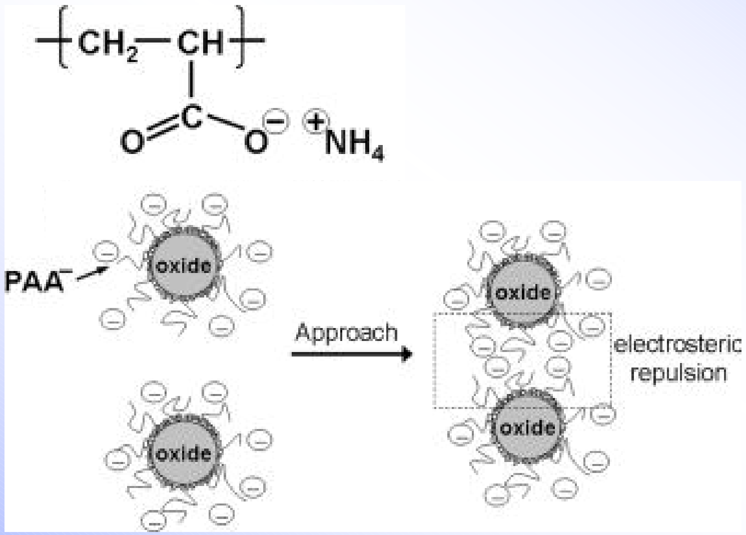
Carbon

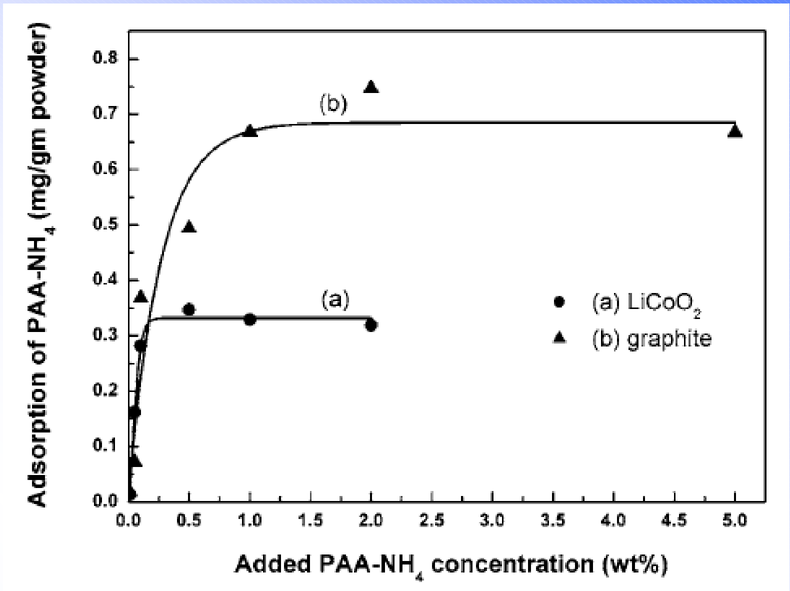
Active material

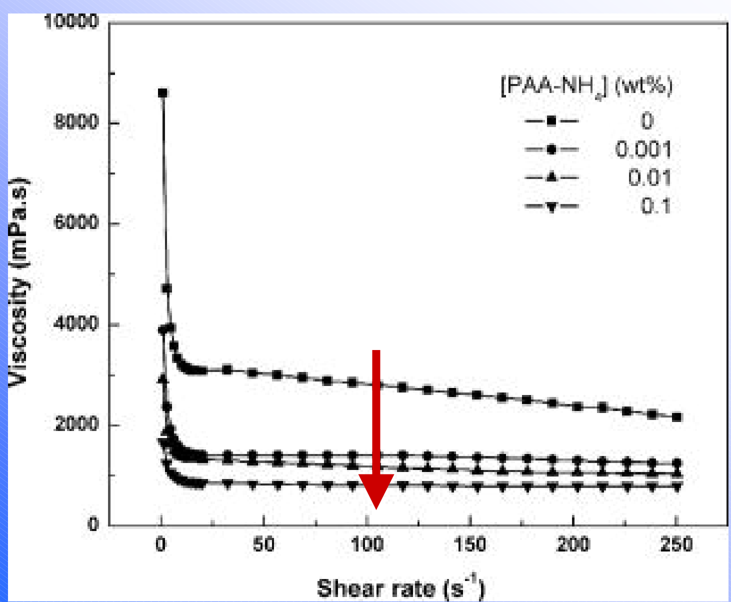


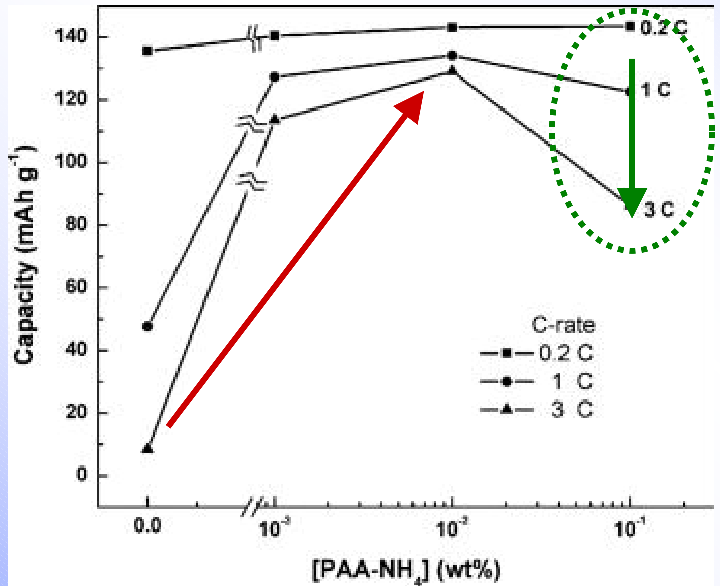
Dispersants for the aqueous processing

(6000 g/mol)





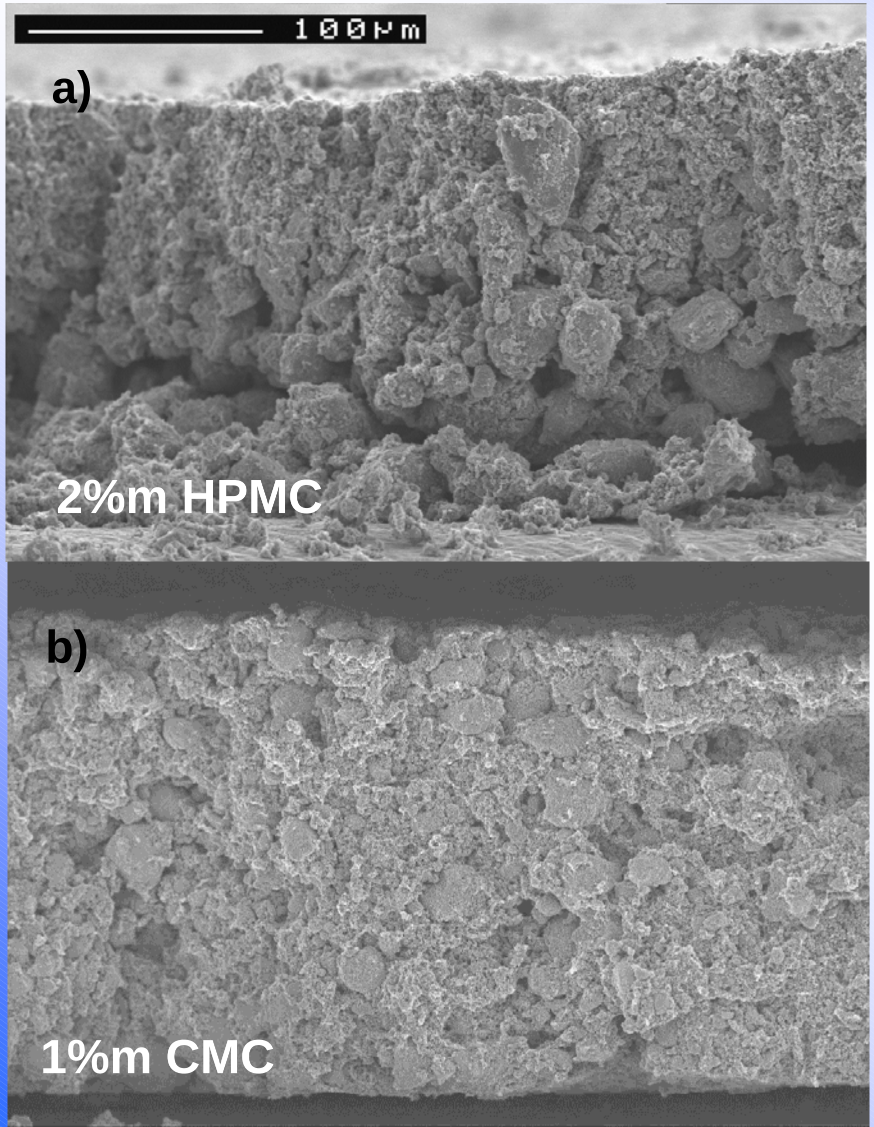


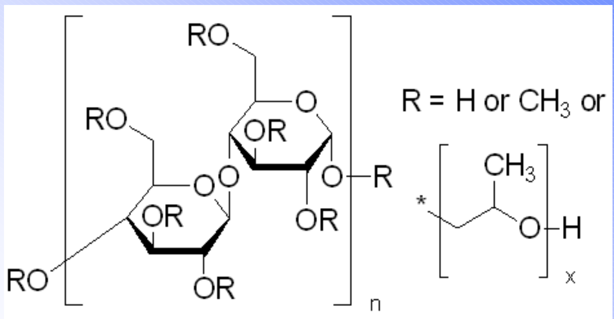


↘ Electronic conductivity

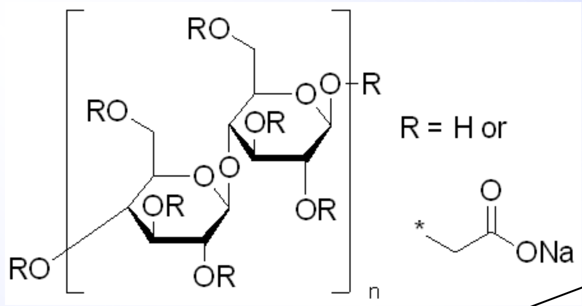
Li, C.C., *et al.*, 2006, J. Electrochem. Soc.

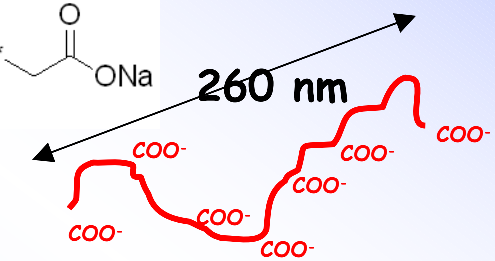
Thickeners





HPMC does not prevent settling

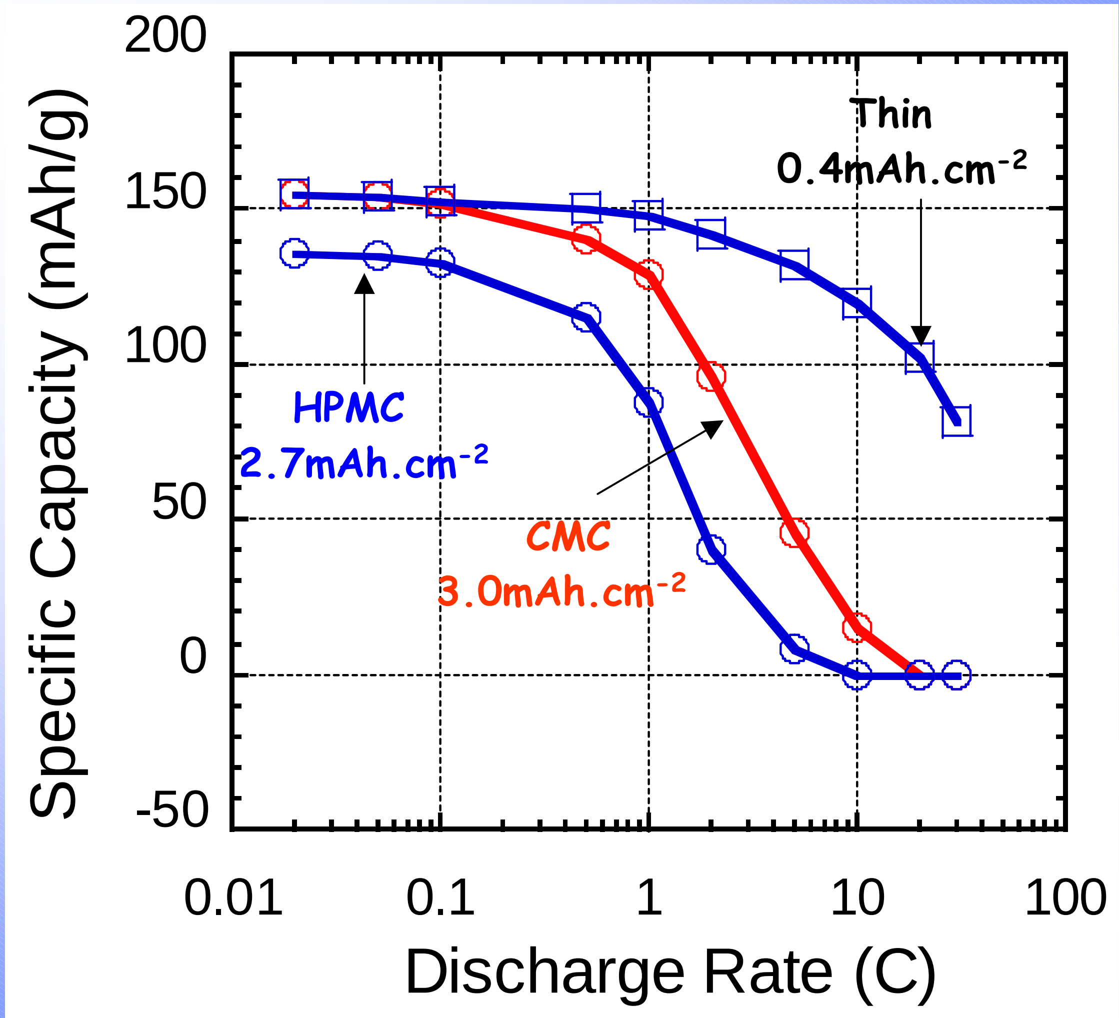




CMC (DS 0.7, 250.000 g/mol)

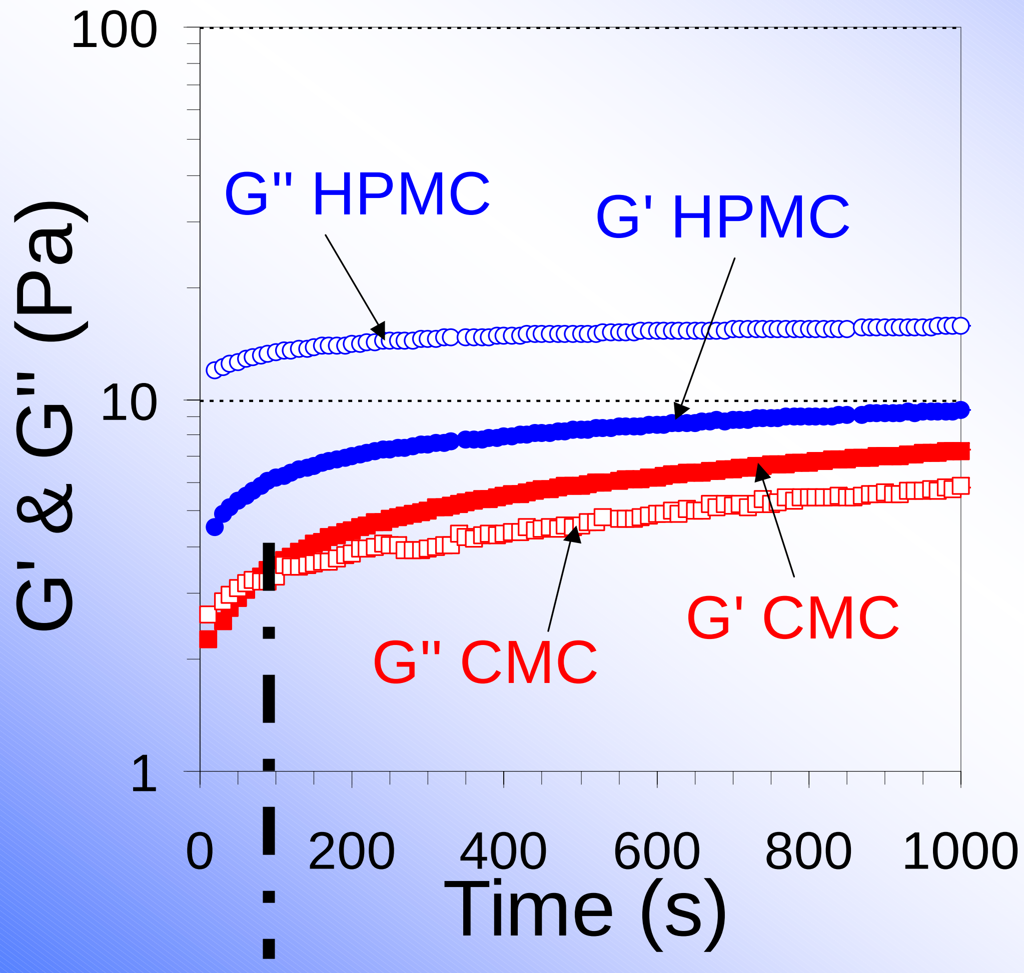
Porcher et al., J. Electrochem. Soc. 2009

Thickeners



Specific Capacity (mAh/g)
200
150
100
50
0
-50
0.01
0.1
1
10
100
Discharge Rate (C)
Thin
0.4mAh.cm-2
HPMC
2.7mAh.cm-2
CMC
3.0mAh.cm-2

Thickeners



t_f : G' = G"

Re-structuration of the slurries after constant shear.

HPMC ⇒ liquid-like

CMC ⇒ solid-like

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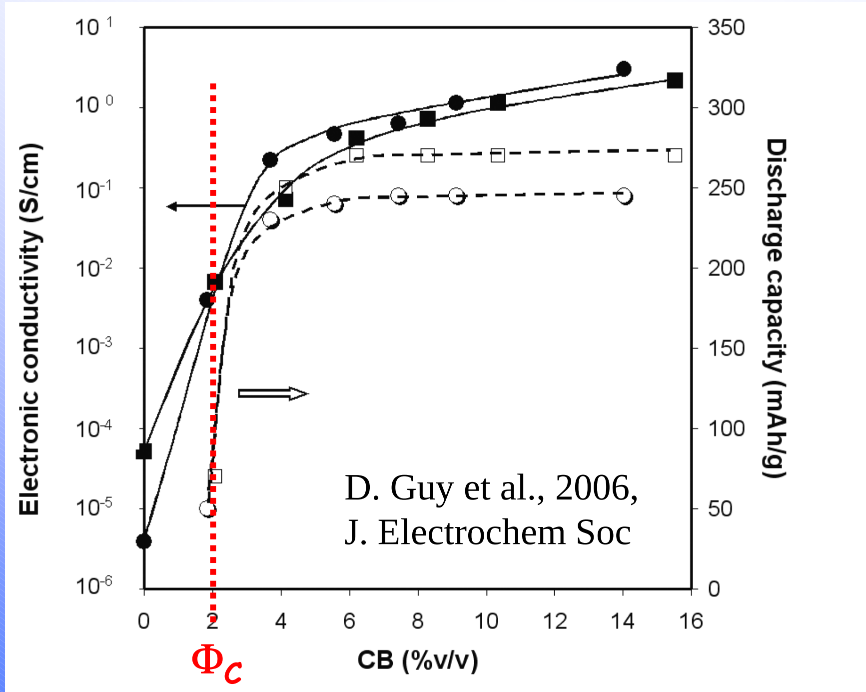
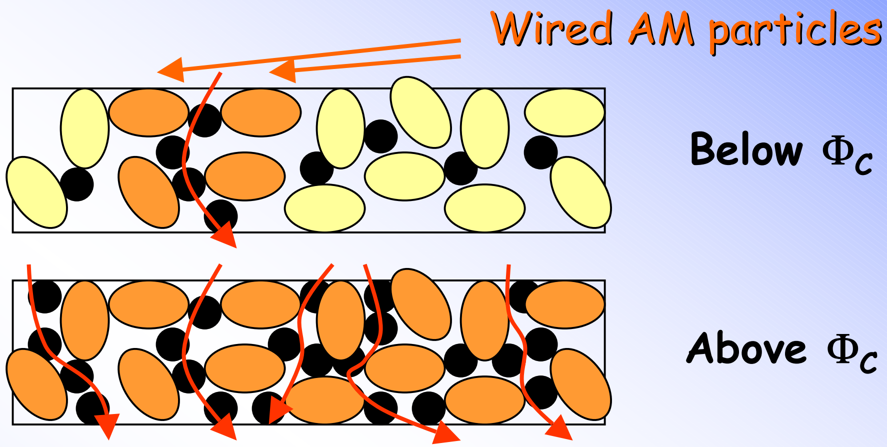
The electronic conductivity

e^- electronic conductivity follows a percolation (Φ_C) process

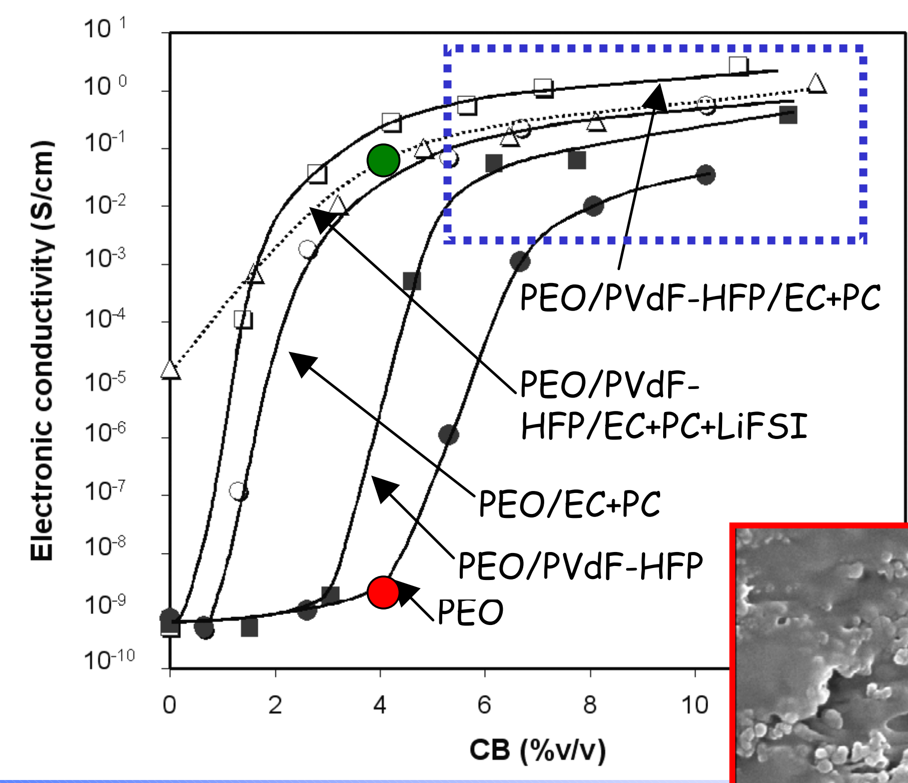


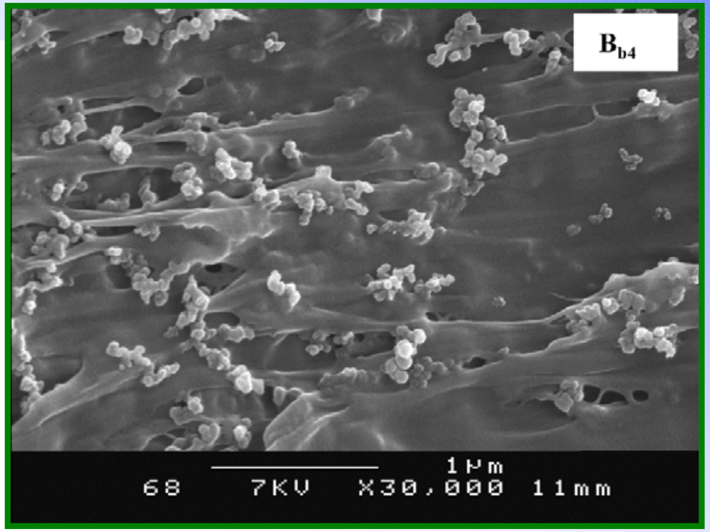


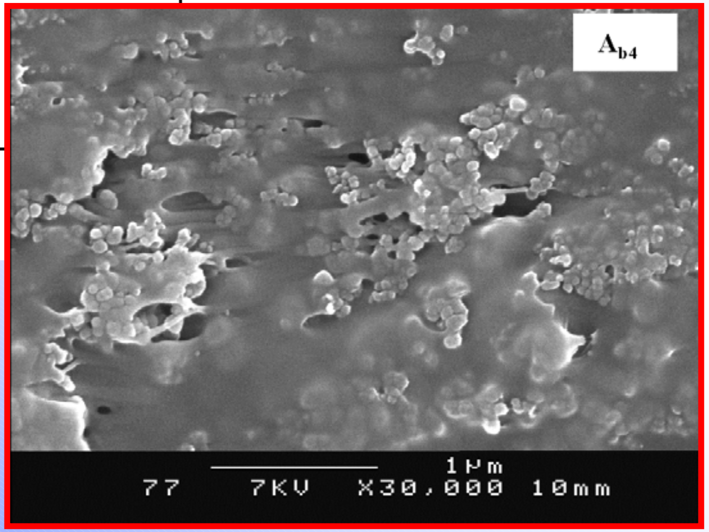
Dependence of Φ_C on processing and aspect ratio of the conductive additive.

The percolation threshold

Φ_c dependence ⇔ role of the binder during the processing.



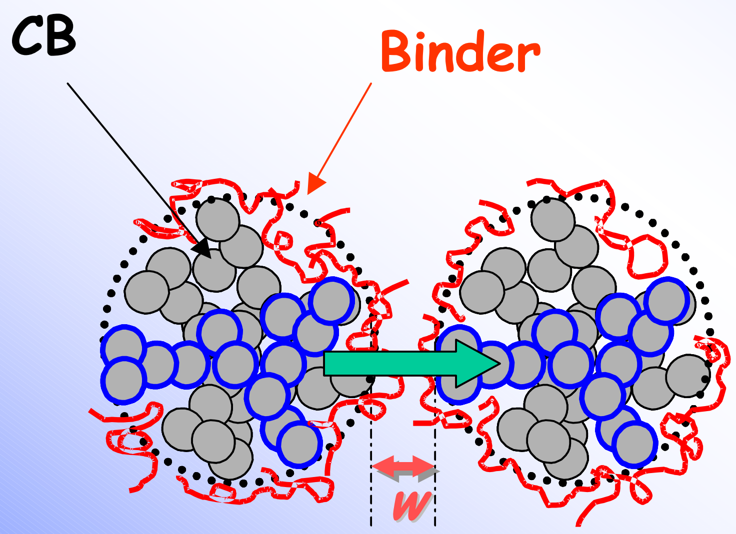




Guy, D., *et al.*, 2006, J. Electrochem. Soc.

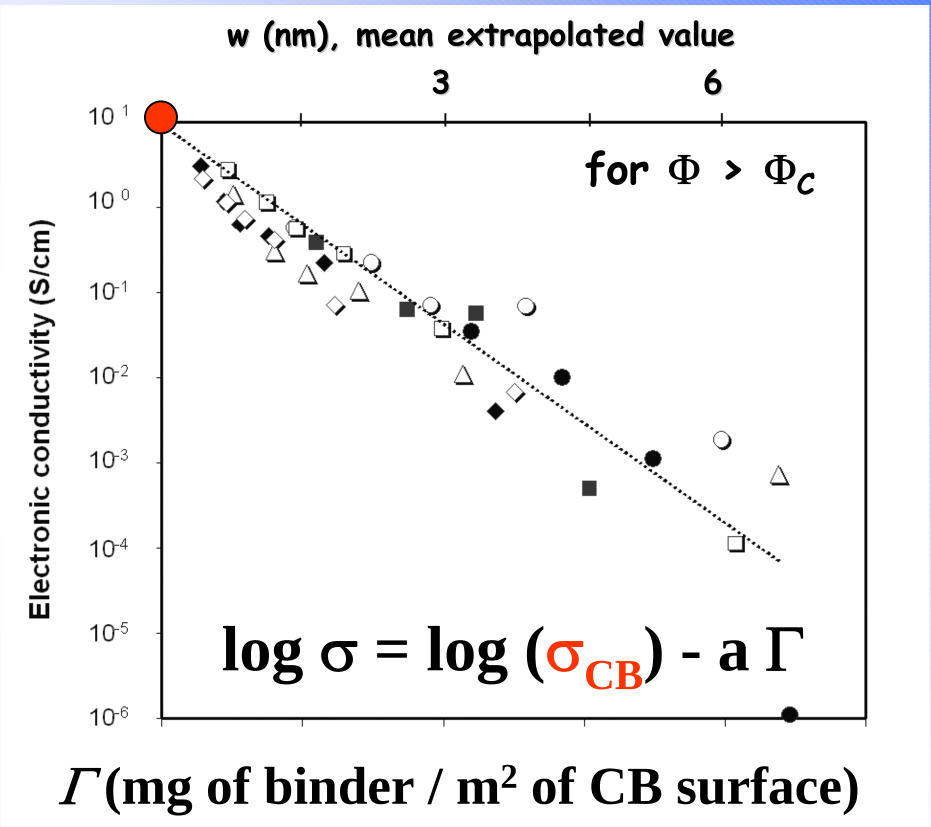
The tunneling mechanism

Tunnel junctions



$\text{Log}\rho \propto w \propto \Gamma$

Narrow distribution of insulating gaps



P. Sheng, Phys. Rev. B 1980. I. Balberg, Carbon, 2002 (**thermal fluctuation-induced tunneling model**).

D. Guy, *et al.*, 2006, J. Electrochem. Soc.

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The ionic conductivity

Li⁺ ionic conductivity κ_c

Influence the rate performance

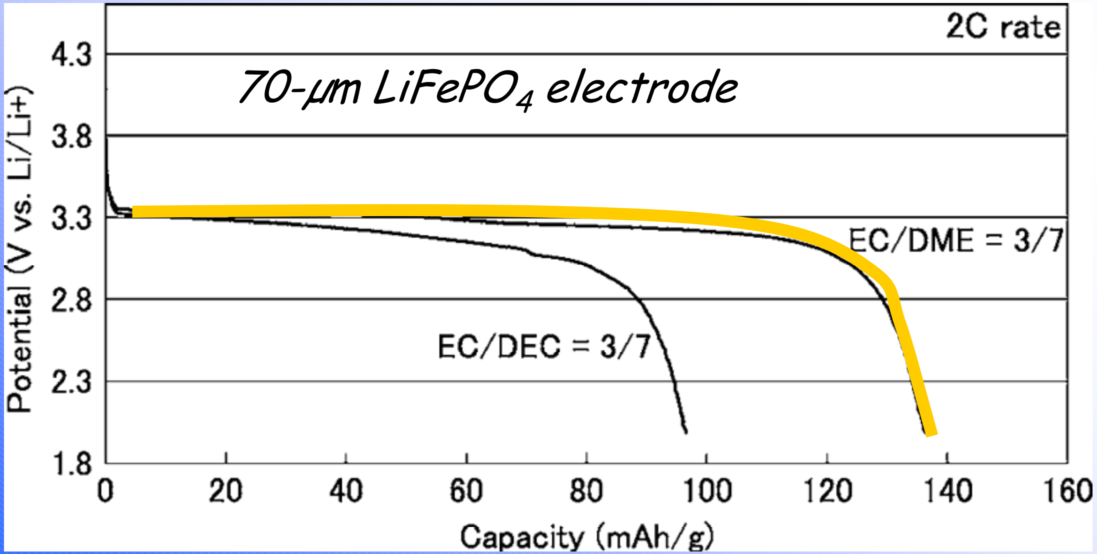
A property difficult to measure.

$$\kappa_c = \varepsilon^{\beta} \kappa_o$$

κ_0 bulk conductivity of the liquid electrolyte

ε void volume fraction of the porous electrode filled with electrolyte

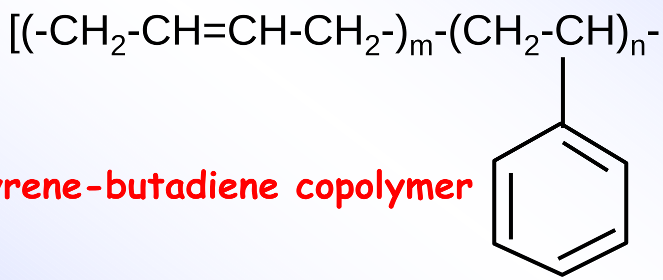
β pore tortuosity



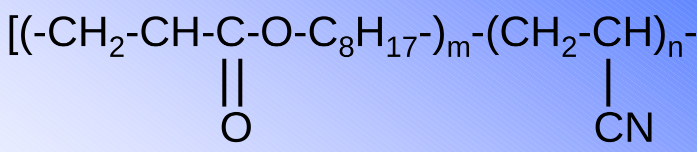
Viscosity and conductivity of electrolyte at 25°C.	η mPa s	κ_0 mS/cm
1 M LiPF6 in EC/DEC = 3:7	3.66	7.24
1 M LiPF6 in EC/DME = 3:7	1.96	18.72

Patel, K.K., *et al.*, 2003, J. Power Sources. Doyle, M., *et al.*, 1996, J. Electrochem. Soc. Arora, P., *et al.*, 2000, J. Power Sources. Doyle M., *et al.*, 2003, J. Electrochem. Soc. W. Yu et al., 2006, J. Electrochem. Soc.

The wettability

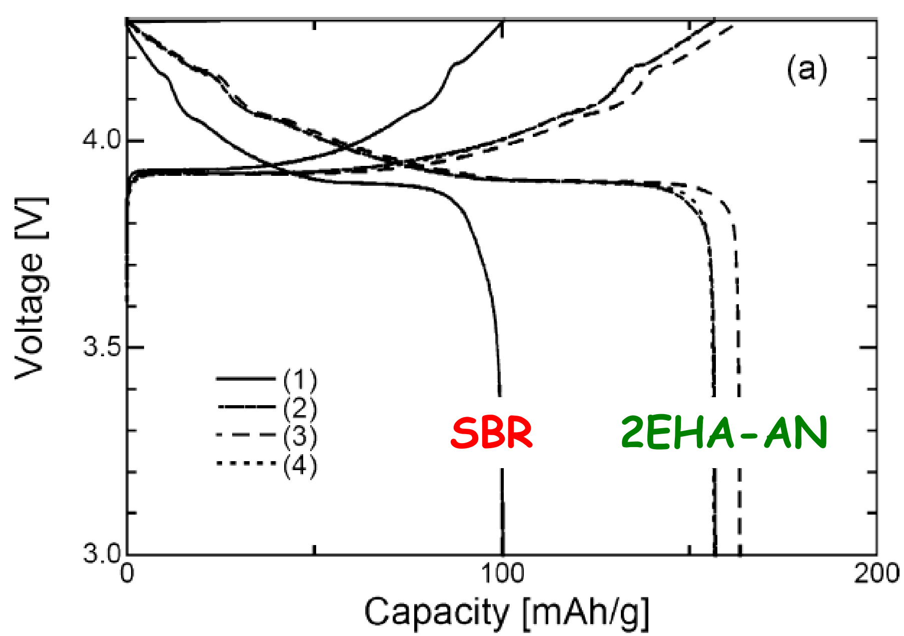


Styrene-butadiene copolymer



2-ethylhexyl acrylate-acrylonitrile copolymer

		Li concentration [μg/g]	σ [S/cm]	E_a [eV]
(a) Electrolyte			7.90E-03	0.093
(b) ST–BD copolymer	ST–BD= 60/40	810	9.40E-08	0.319
(c) 2EHA–AN copolymer	2EHA–AN= 85/15	3,300	1.20E-05	0.256
(d) 2EHA–AN copolymer	2EHA–AN= 75/25	3,000	8.00E-06	0.272



Kaneko M., *et al.*, 2007, J. Solid State Electrochem.

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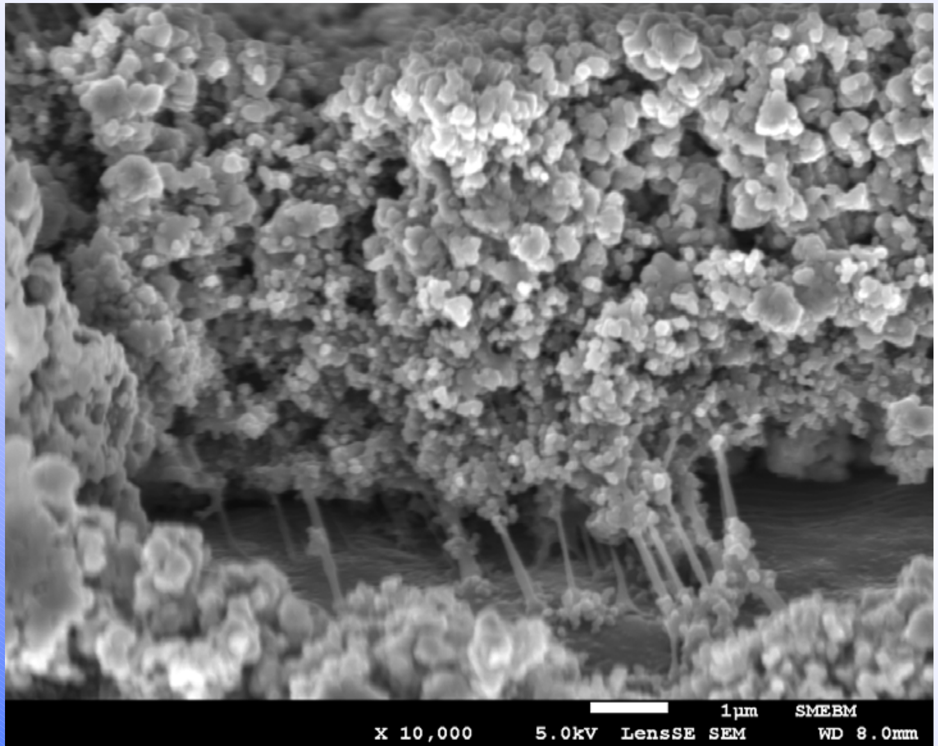
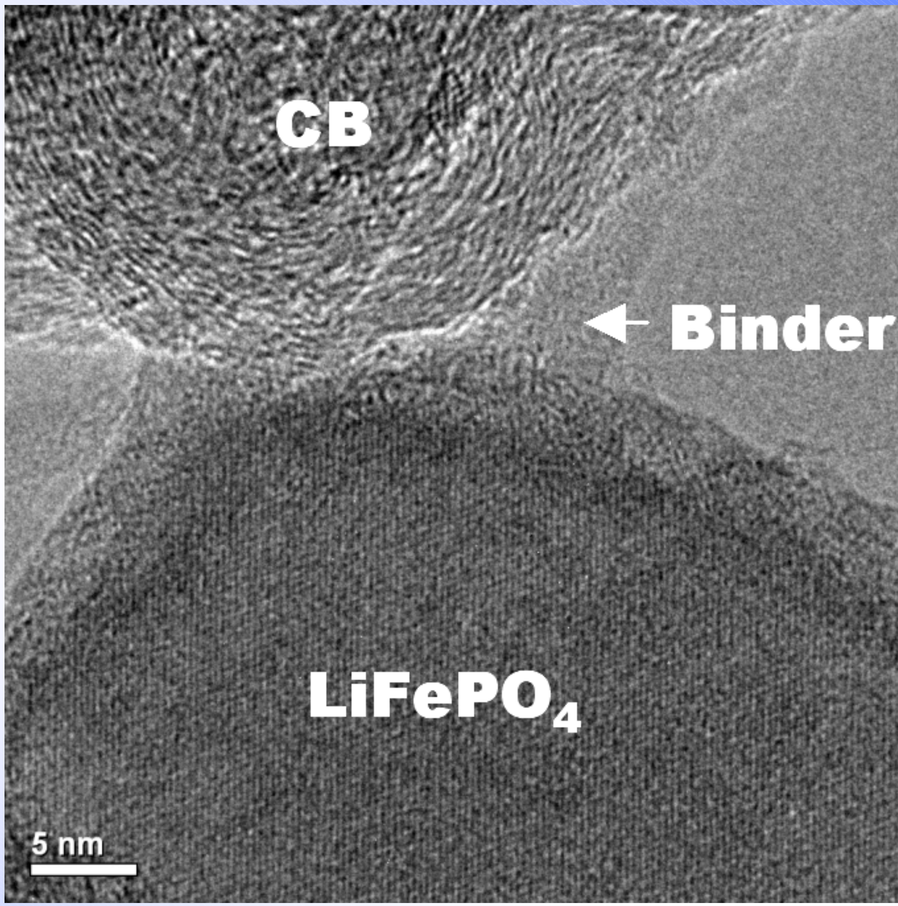
Mechanical properties: the binder's job

Adhesion to the current collector

Cohesion of the composite electrode by particle-to-particle bridging





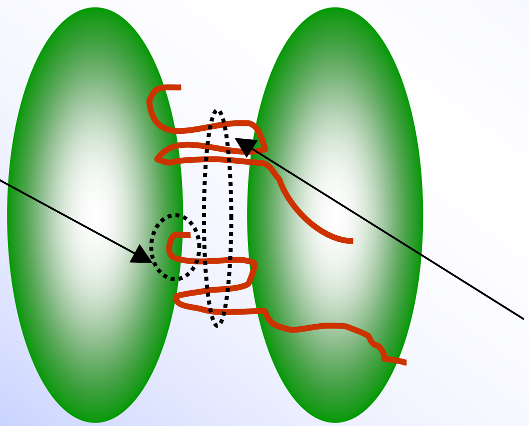
TEM image : Anne-Claire GAILLOT (IMN)

Modelling ?

Model of the Mechanical toughness in polymer-based composite materials for aeronautics, automotive… applications:

Strength of composite ⇔ Strength of interface

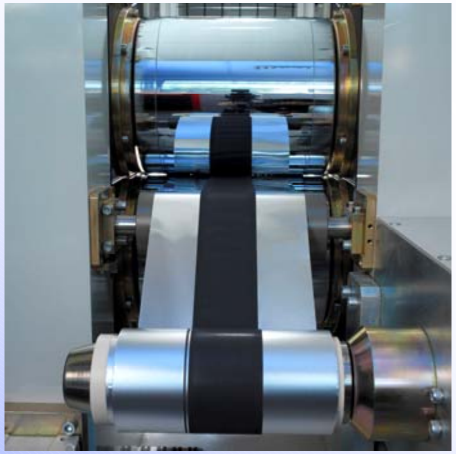
$$\boxed{\sigma = f\,\Sigma}$$

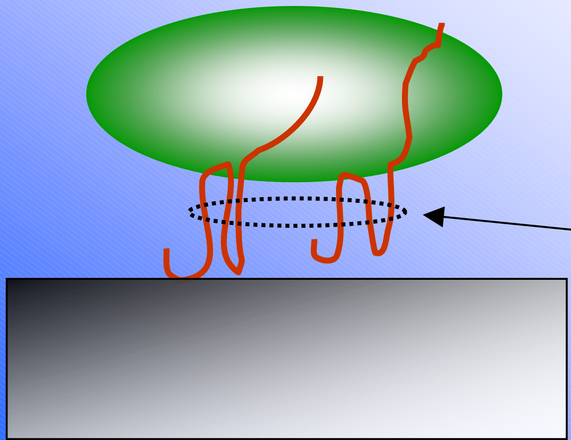


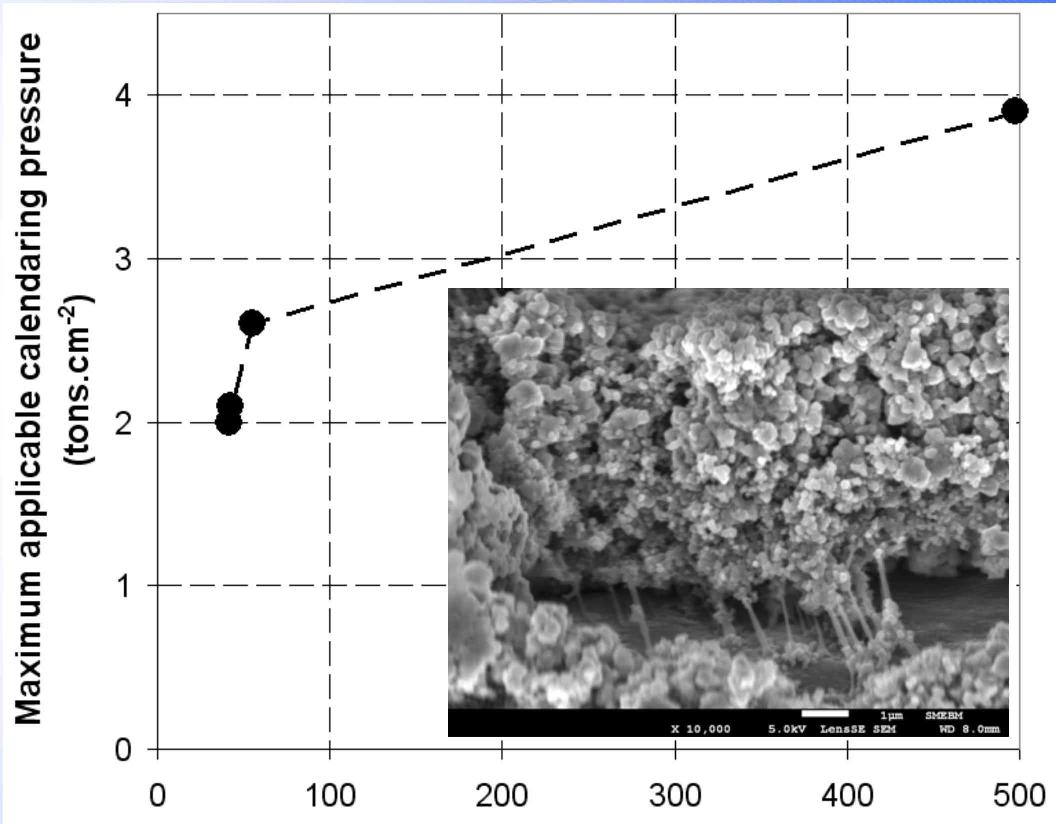
C. Creton (ESPCI), J.F. Gérard (INSA Lyon), L. Léger (Coll. France),

Role of the binder on the mechanical properties

The <u>calendaring</u>



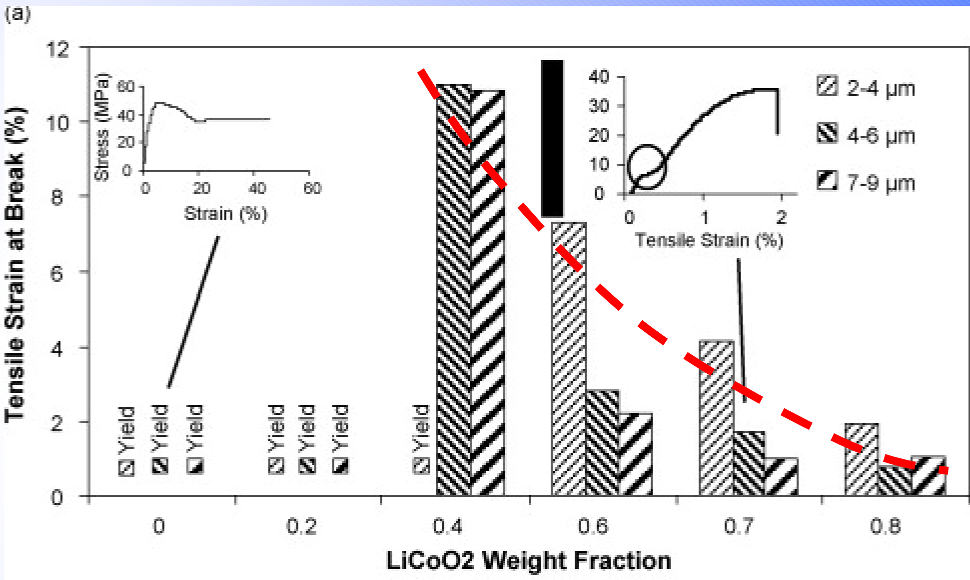




W. Porcher., *et al.* 2010, J. power Sources.

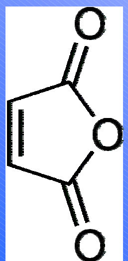
Role of the binder on the mechanical properties

The assembly

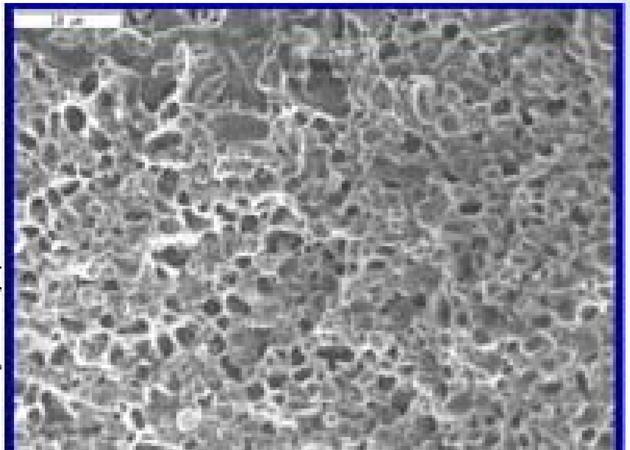


Strain at break is less than 2% with PVdF.

Particle delamination from the PVdF matrix is a mechanism for stress relief.



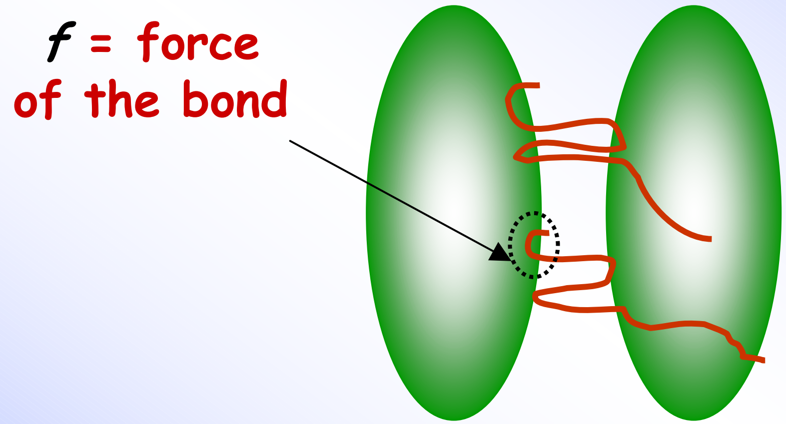
Degree of functionality of PVDF	Peel strength 180° (g/25 mm)
Low	20
Medium	80
High	330

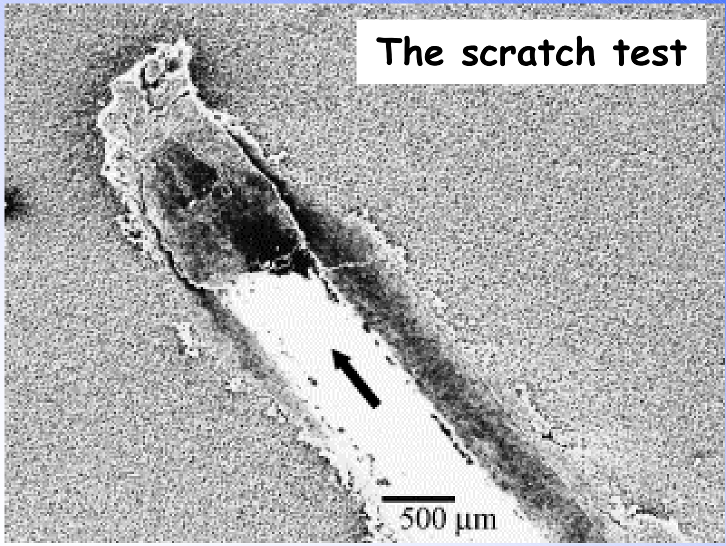


(SEM of fractured surface ⇔ Particle delamination)

S. Babinec., *et al.* J. power Sources, 174 (2007) 508.

Role of the binder on the mechanical properties





Graphite and amorphous carbons negative composite electrode

weak hydrogen bonds

PVdF F atoms ⟷ H atoms from graphite ⇒ scrapping load < 1,000g

semi-ionic / covalent bonds

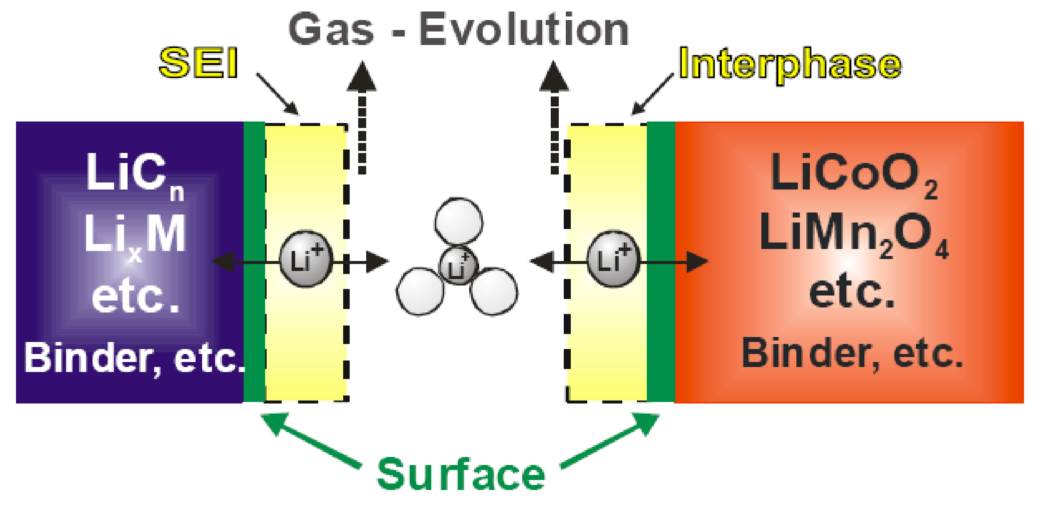
PVdF F atoms ⟷ C atoms from amorphous carbon ⇒ scrapping load > 10,000g

Yoo, M., *et al.* 2003, Chem. Mater. Yoo, M., *et al.* 2004, Chem. Mater. Yoo, M., *et al.* 2003, Polymer.

Outline

1. The usual and new binder combinations
2. Role of the binder on the processing
3. Role of the binder on the electronic conductivity
4. Role of the binder on the ionic conductivity
5. Role of the binder on the mechanical properties
6. **Role of the binder on the SEI layer**
7. Conclusions and Prospects

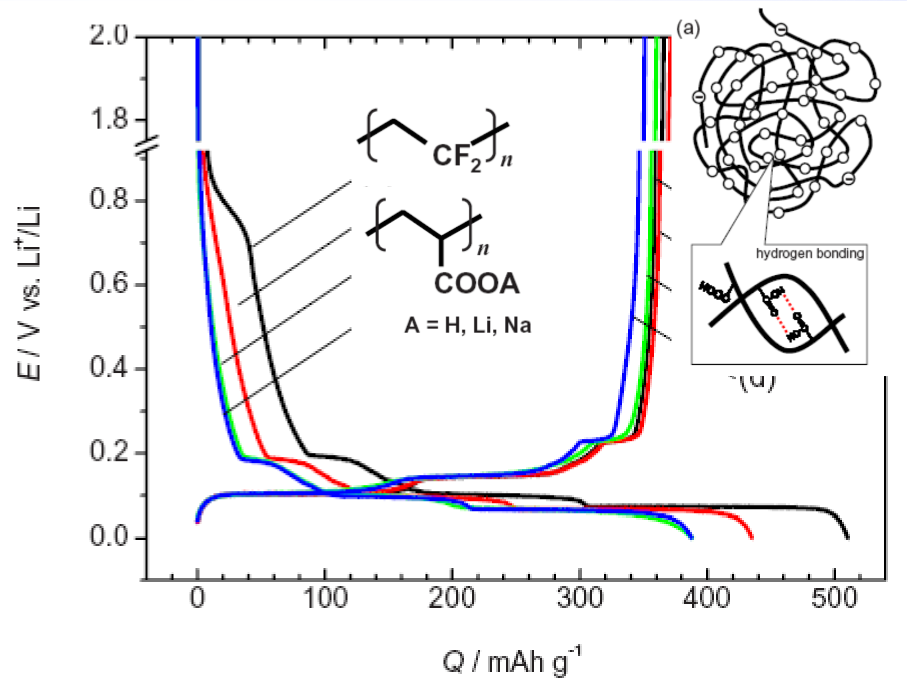
The SEI / interphase layer (5 - 10 nm)

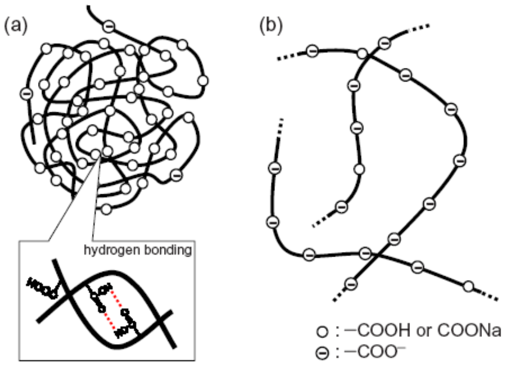


Decomposed Species	Origin	Effect on Performance
CH_2=CH_2, H_2, CO	Solvent(s)	Increase of cell pressure, EL loss (drying out)
Polymers, e.g., PEO	Solvent(s)	SEI contribution, cell resistance, EL loss (drying out)
LiF	$LiPF_6$	Change of EL conductivity, SEI contribution, cell resistance
Li_2CO_3, $(CH_2OCO_2Li)_2$, CH_3OLi	Solvent(s) Li (c/o cathode)	SEI contribution, cell resistance, Li capacity loss ⇒ Change of material balance in cell

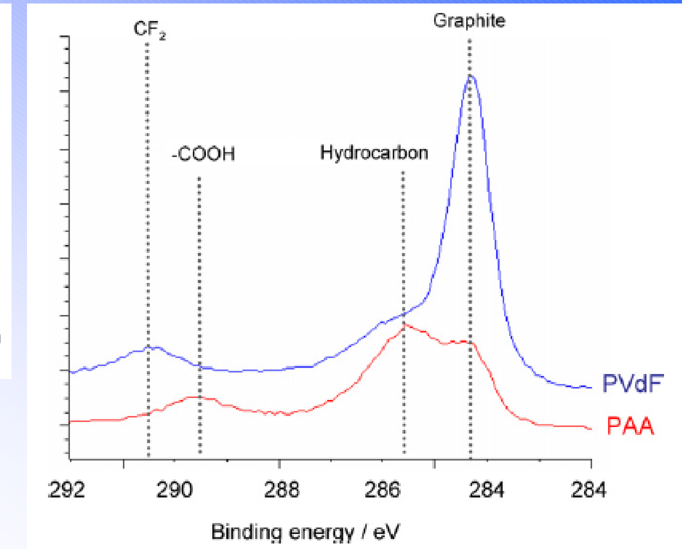
From M. Winter

Improvement of efficiency with aqueous binders

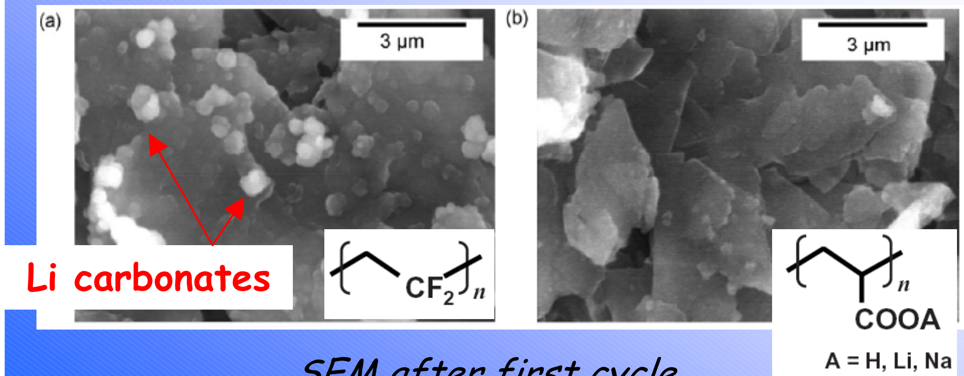




Graphite in 1 mol dm^{-3} LiClO$_4$ EC:DMC



XPS of Graphite before cycling



SEM after first cycle

Improvement of efficiency:

- more uniform covering of graphite grains with Polyacrylate than with PVdF

- COO^- groups enhancement of the de-solvation / intercalation of Li^+ ions

Komaba S. et al., Electrochem. Solid-State Lett., 2009 ; J. Power Sources, 2009.

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Conclusion

Polymers for Li-Ion electrodes

5%w ⇔ 1-2%v

- Binder
- Processing aid (dispersant, thickener)
- Participate in the electronic wiring
- Participate in the ionic wiring
- Participate in SEI formation and efficiency

Critical dependence on the nanometer scale,

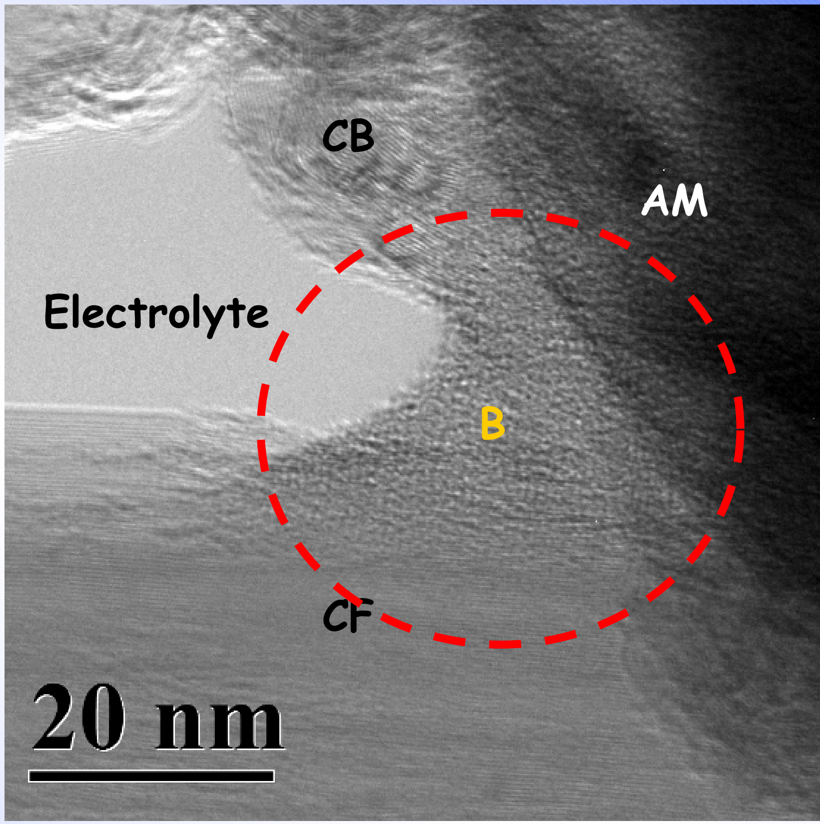
-Poorly defined !

-Properties of polymers in ultra thin layers are different from the bulk !

-Studies to be done on well defined polymers

⇒Strong need for fundamental research

"TODAY" !



TEM image : Philippe MOREAU (IMN)

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Functions of polymers in composite electrodes of lithium ion batteries

Bernard Lestriez

CNRS, institut des matériaux Jean-Rouxel (IMN), université de Nantes, 2, rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France

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ABSTRACT

The different functions of polymer binders on the processing of the electrode, the electrical (electronic and ionic) and mechanical properties of the electrode, and as a consequence on the electrochemical performance are discussed. The role of the polymer binder on the solid–electrolyte interface (SEI) layer and the cyclability of the graphite- and silicon-based negative electrodes is also addressed. All these properties critically depend on the very thin layer formed by the polymer at the surface of the active and conductive particles. That is where research efforts have to focus on, now, for further optimization of electrodes through tailoring of the binder combination.

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