

Apport de la microscopie électronique à l'étude des électrodes composites de batteries au lithium

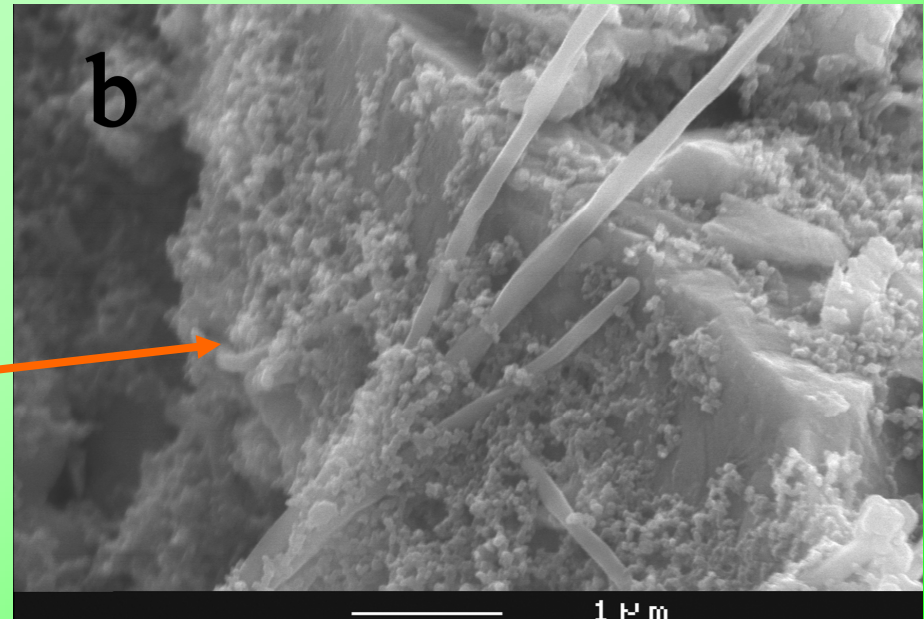
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2, rue de la Houssinière 44322 NANTES

Philippe.Moreau@cnsr-immn.fr

« Blue Car »



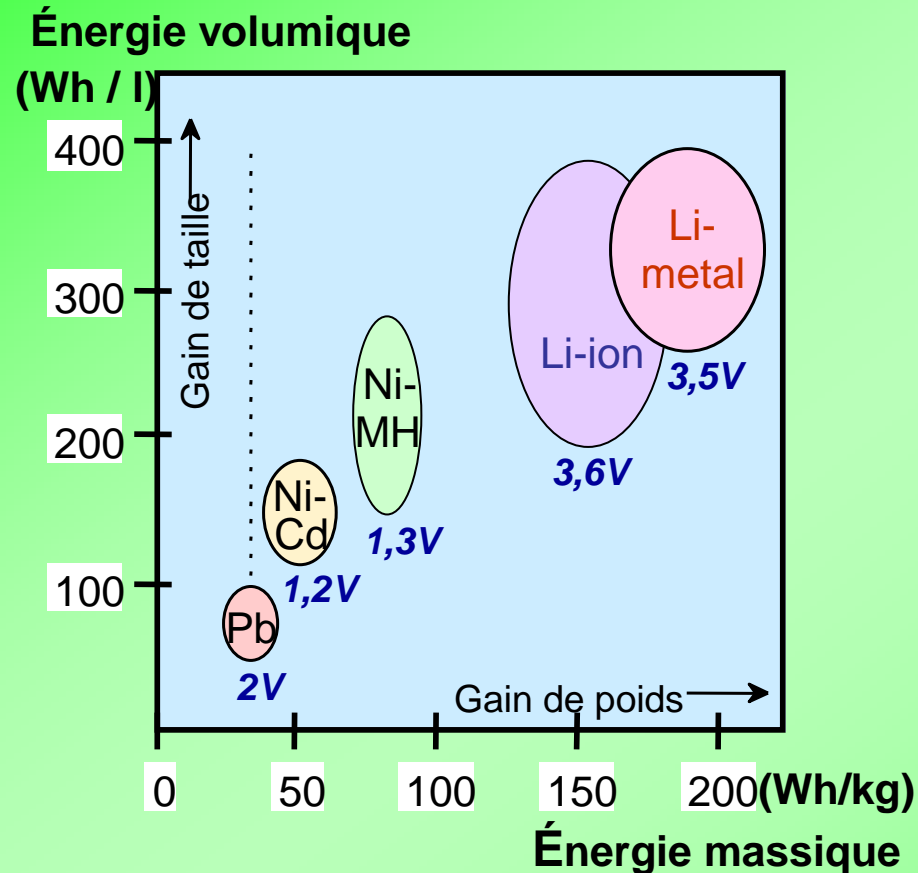
Plan :

- ▶ Introduction: contexte des batteries au lithium
 - Technologie
- ▶ Electrodes composites – Microscopie e^-
- ▶ Nécessité de l'EELS...

Contributions :

- ▶ Equipe ST2E (D. Guyomard, B. Lestriez,
J. Gaubicher, J. Danet)
- ▶ JM Tarascon (Université d'Amiens)

Bilan des différentes batteries existantes (pour VE)

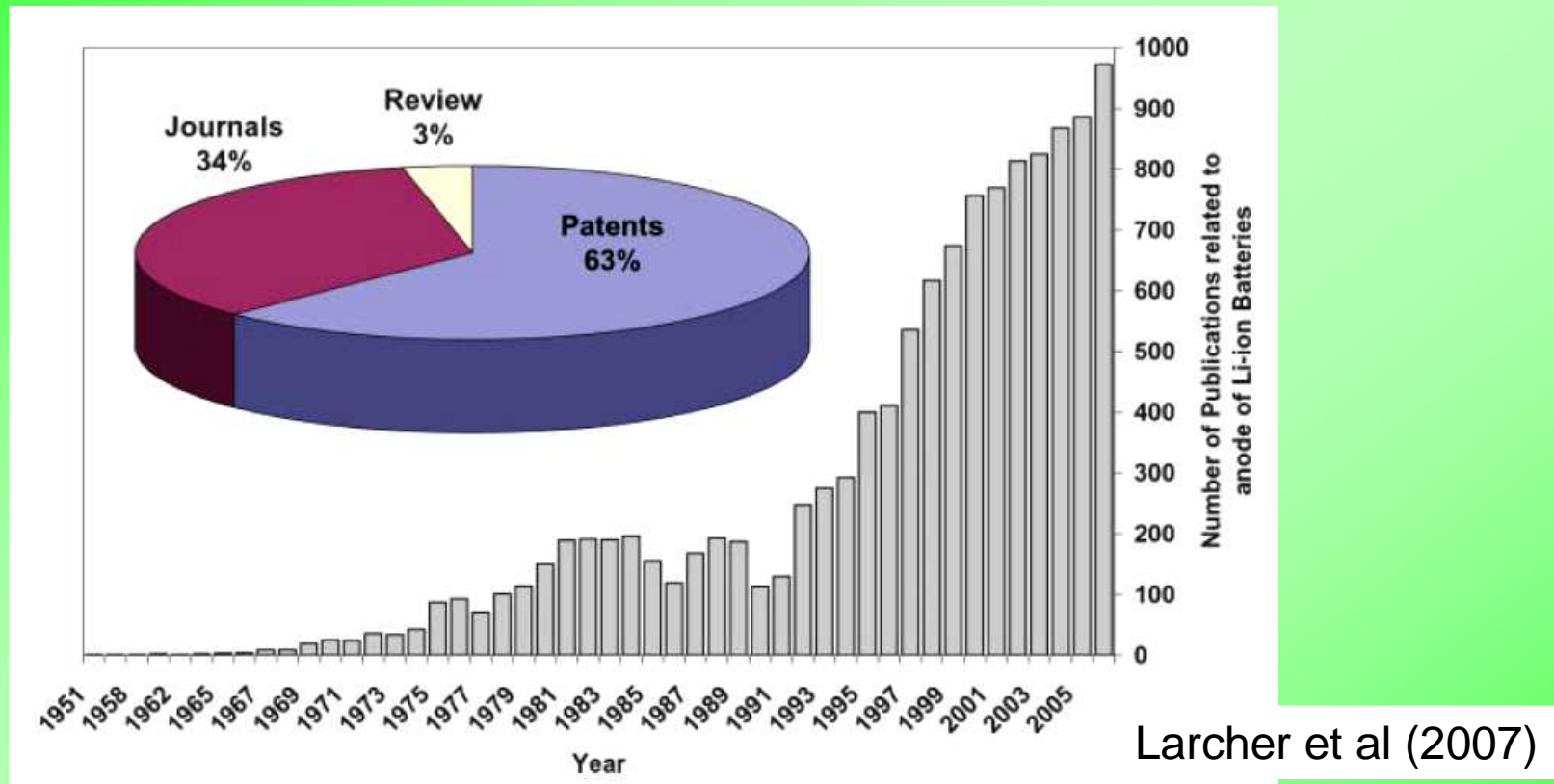


couples (état chargé)

- / ⊕

- «Pb» : Pb / PbO₂ (1859)
- «Ni-Cd» : Cd / NiOOH (1909)
- «Ni-MH» : H_xM / NiOOH (1980)
- «Li-ion» : LiC₆ / Li_{0,5}CoO₂ (1990)
- «Li-metal» : Li / LiFePO₄

Une recherche mondiale très active !

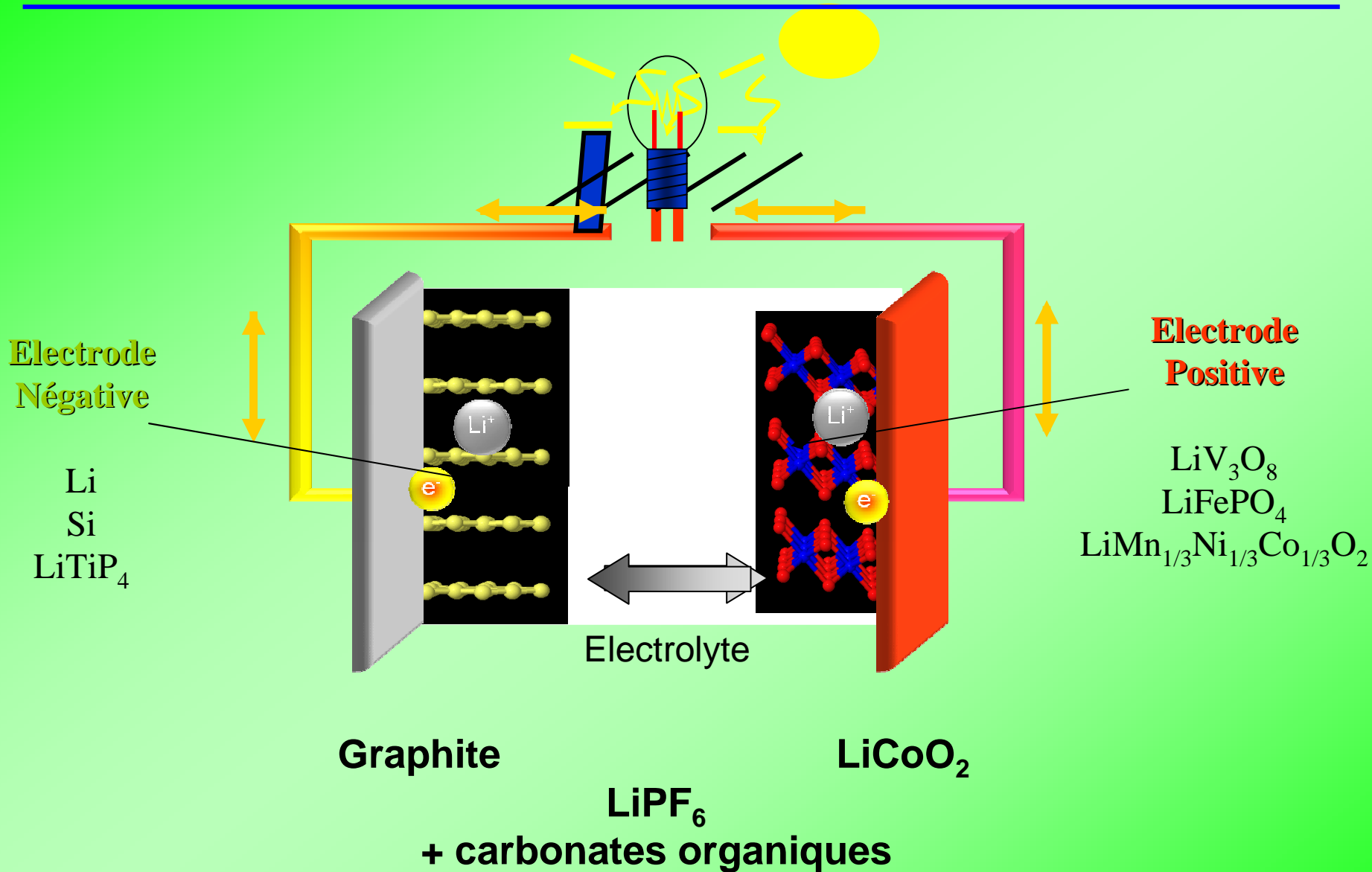


Financements

DOE : 25 milliards de dollars
+ 2 milliards (congrès américains, crise)

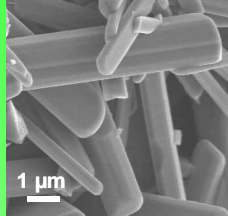
-250 millions d'euros Allemagne
-150 millions d'euros Japon

Principe de la batterie Li-ion



Batteries Lithium Métal Polymère (LMP) - BATSCAP

Matériau actif
(ex. LiFePO_4)



Polymère
Carbone (ex. POE)



Polymère Sel de lithium
(ex. POE) (ex. LiTFSI)



Matériaux
en poudres

*Les matériaux
sont
transformés
en films
minces
composites :*



Extrusion /
Laminage



Film de
cathode



Electrodes en
films minces
composites

Film d'électrolyte



Film de cathode



Film d'électrolyte

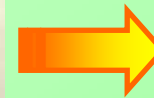
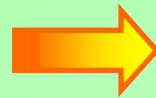


Les films sont assemblés en éléments :

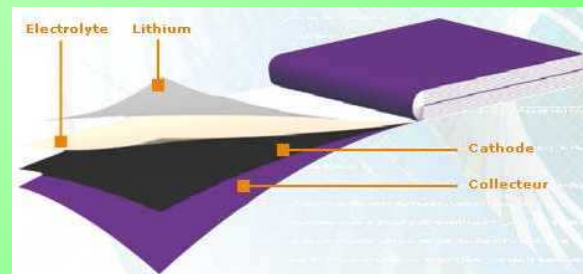
Film de lithium métal



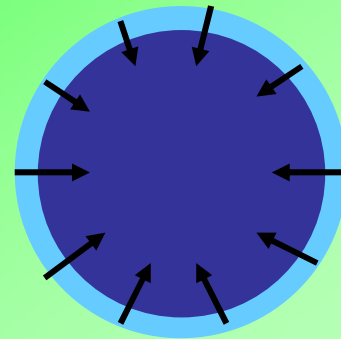
Film de cathode + électrolyte



Élément complet

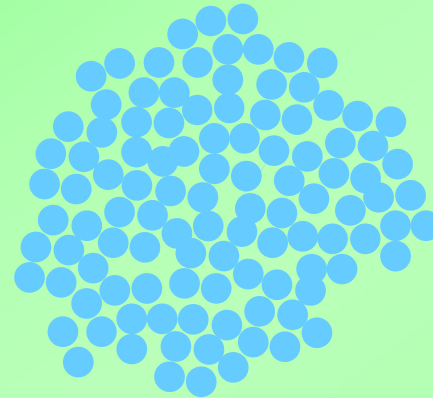


La microscopie car la puissance



e^- Li^+

Micro



Nano

Problèmes :

- grains non connectés
- réactivité de surface

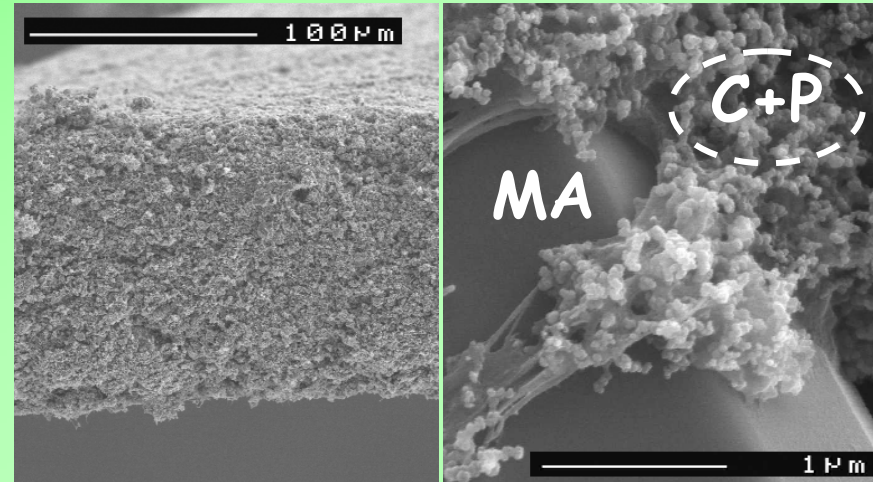
Solutions :

- formulation d'électrodes
- modification de la surface

Composition et Mise en œuvre

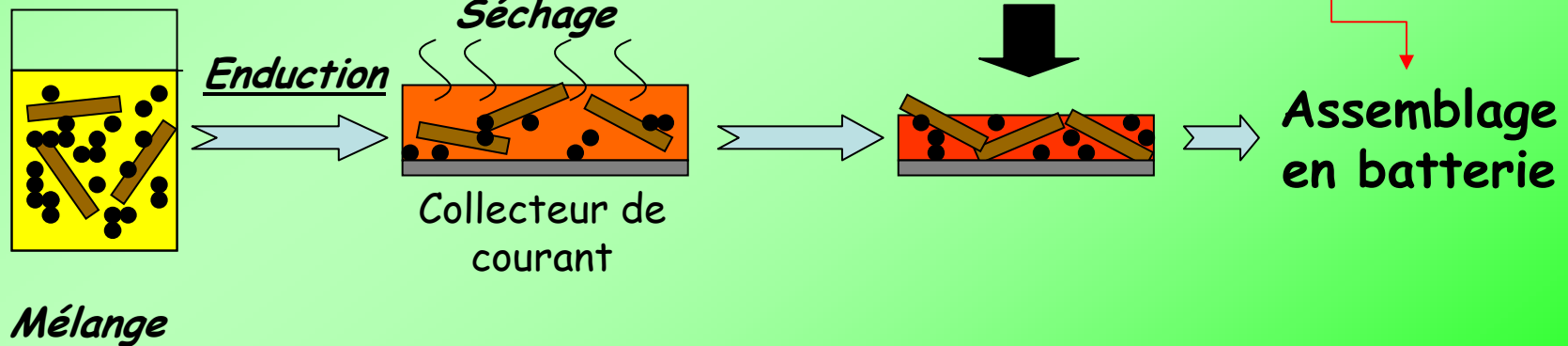
Bernard Lestriez (IMN)

<u>Electrode sèche</u>	%w/w
✓ Matériau actif	60-90
✓ Agent conducteur	15-5
✓ Liant polymère	25-5
✓ Porosité	30 - 40 %v/v

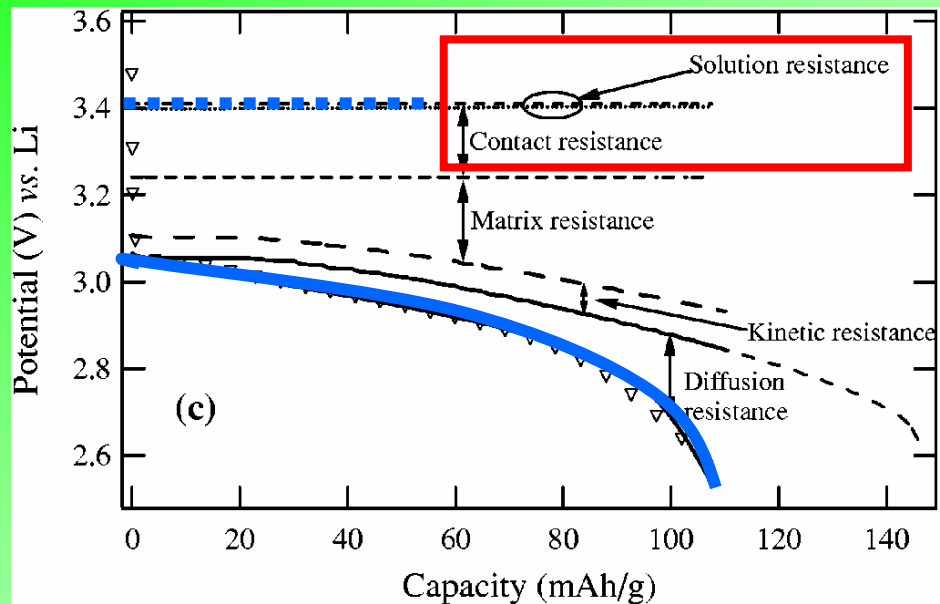


Encre:

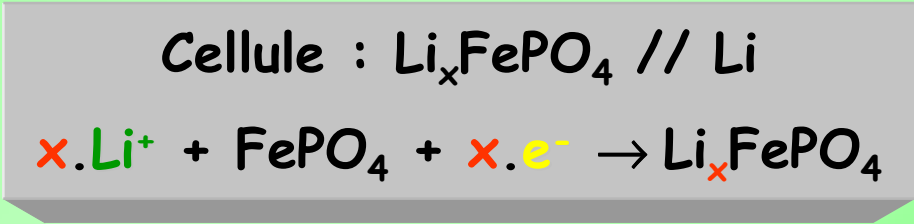
Matériau actif + agent cond. + liant + solvant



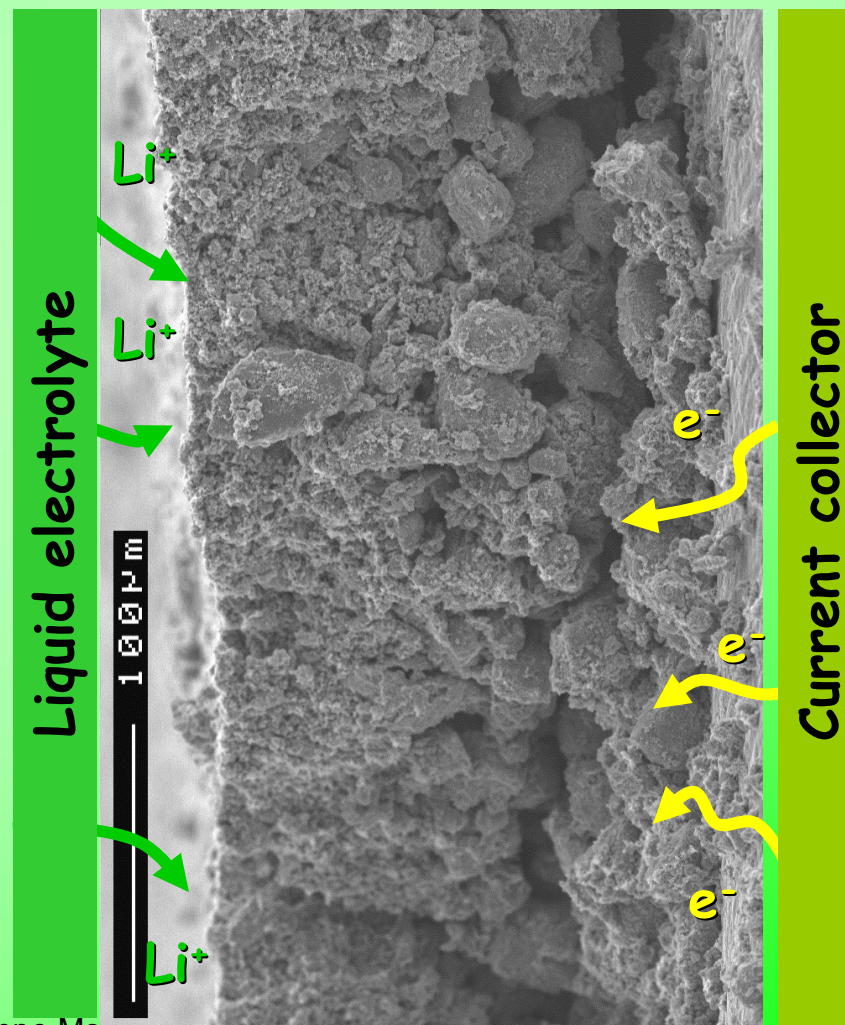
Les différentes contributions



Venkat Srinivasan, z and John Newman,
Journal of The Electrochemical Society, **151**, A1517-A1529 (2004)

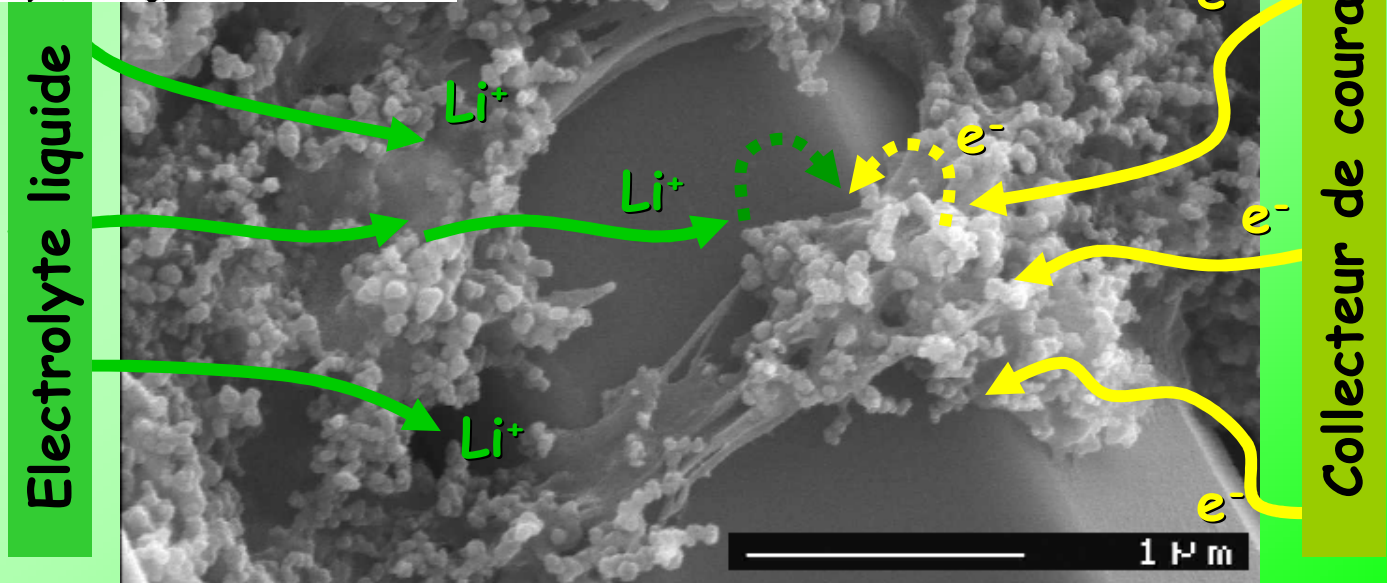
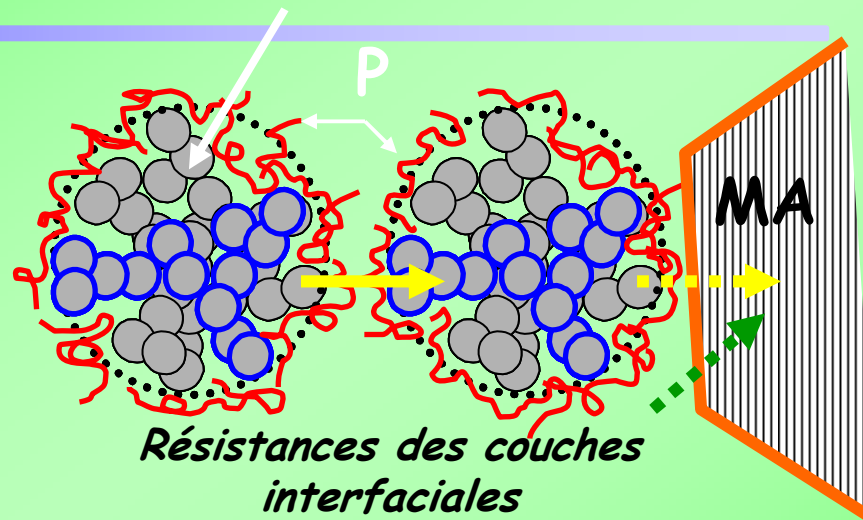
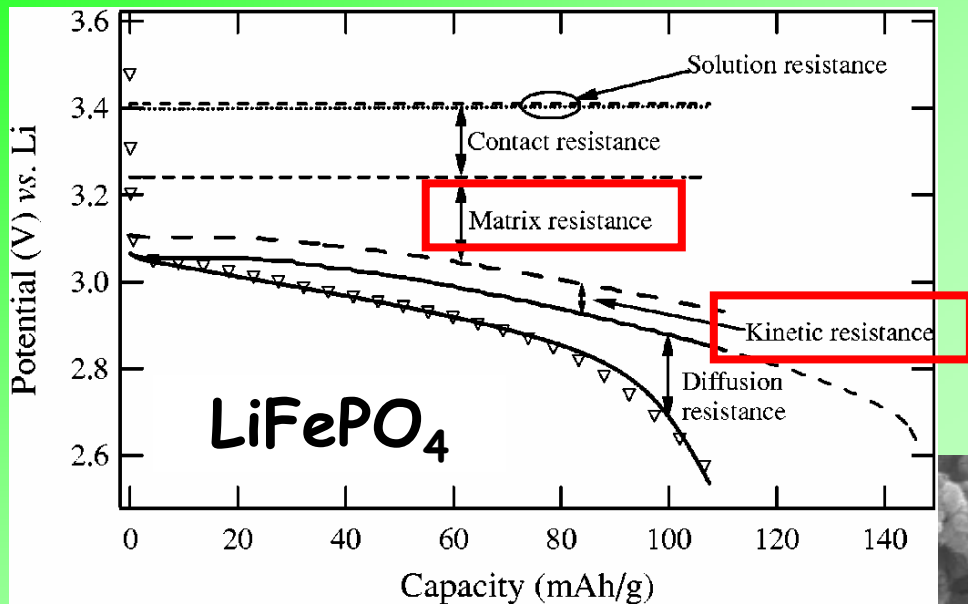


Bernard Lestriez (IMN)



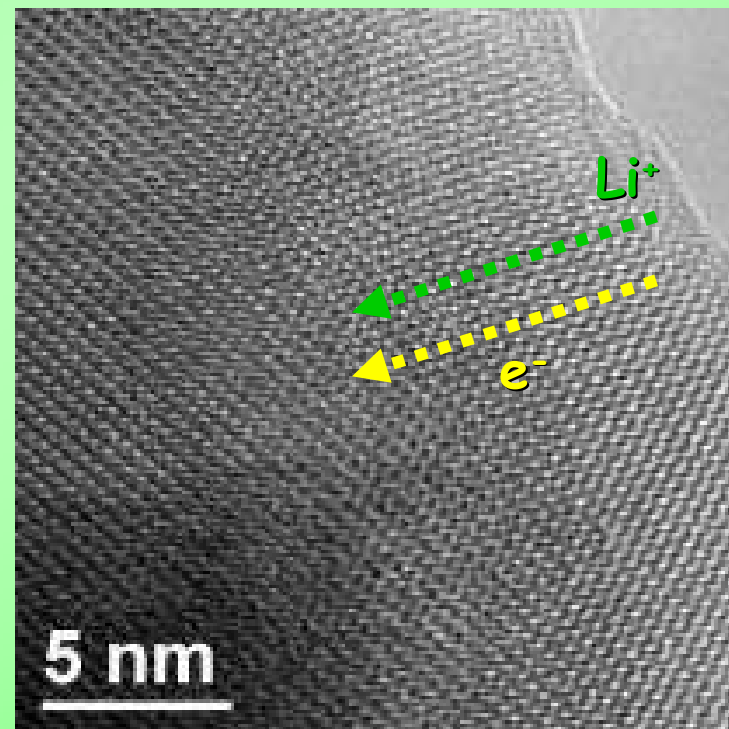
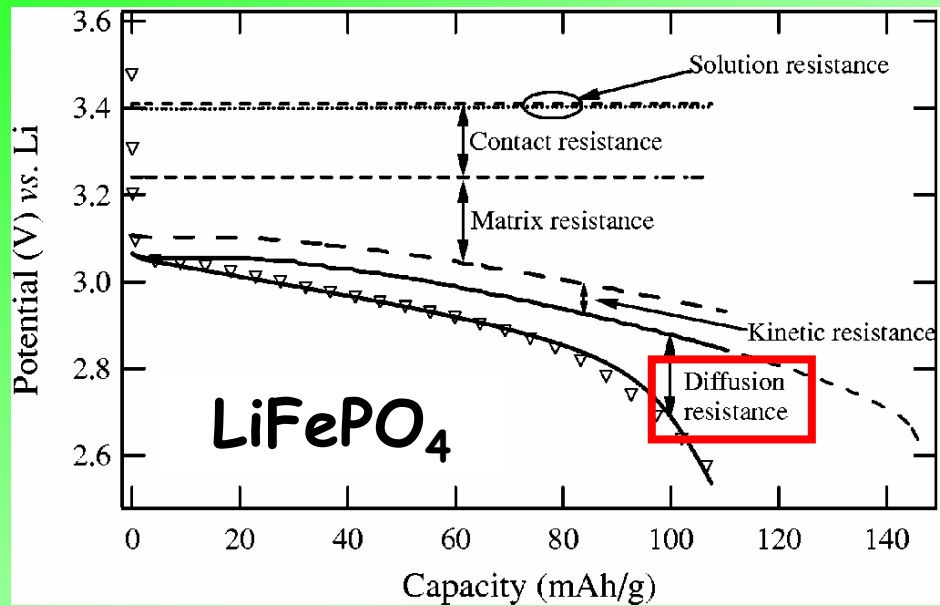
Les différentes contributions

Bernard Lestriez (IMN)

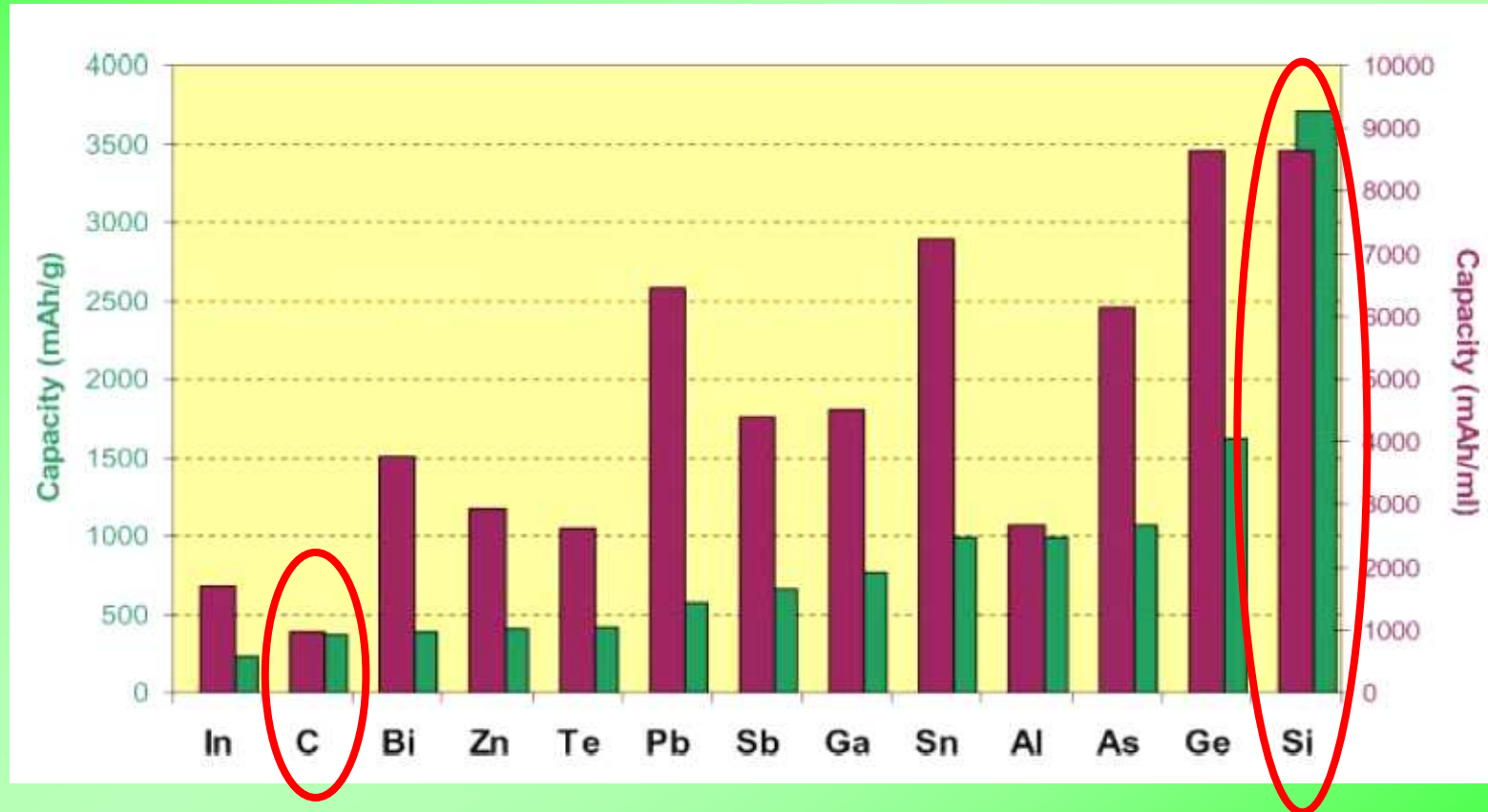


Les différentes contributions

Bernard Lestriez (IMN)



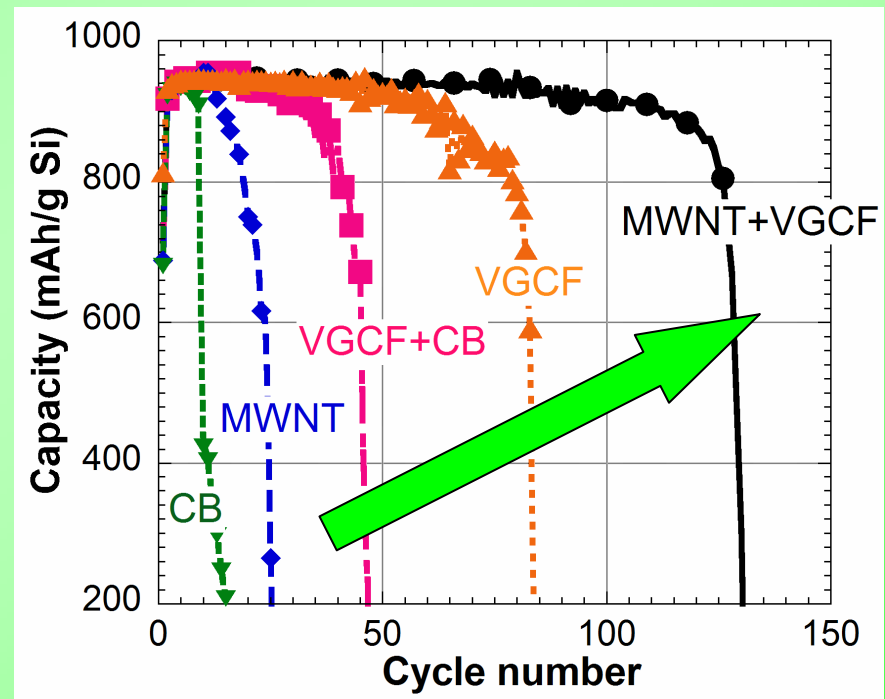
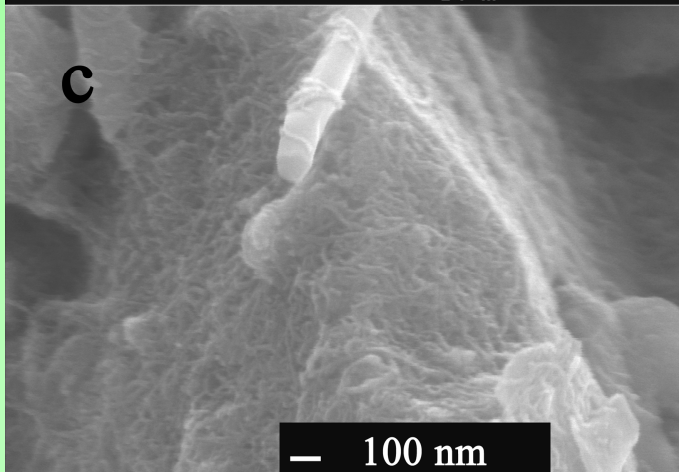
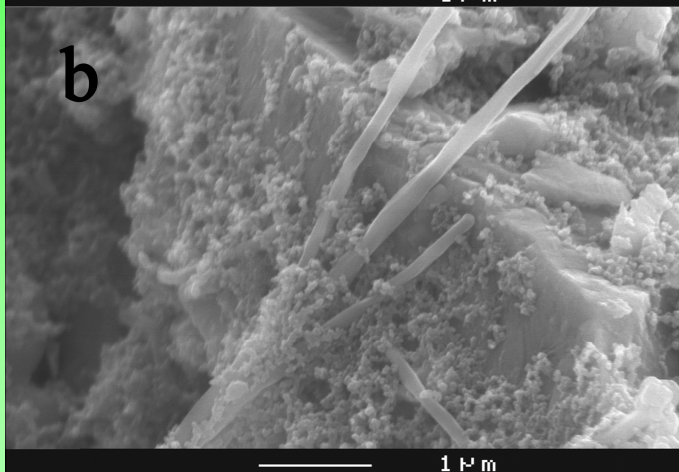
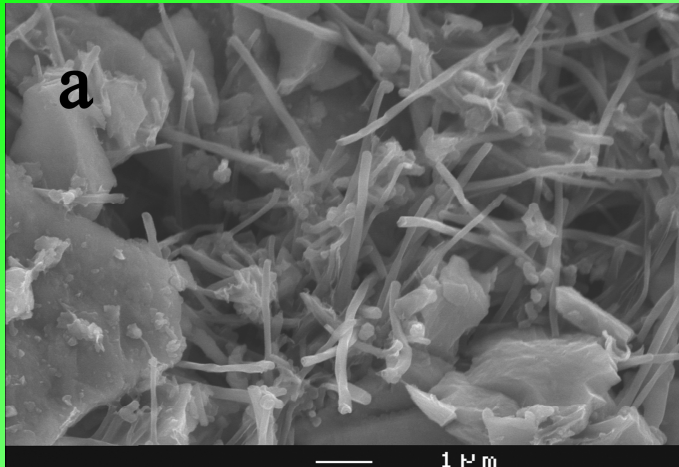
Le silicium : un candidat prometteur



Larcher et al (2007)

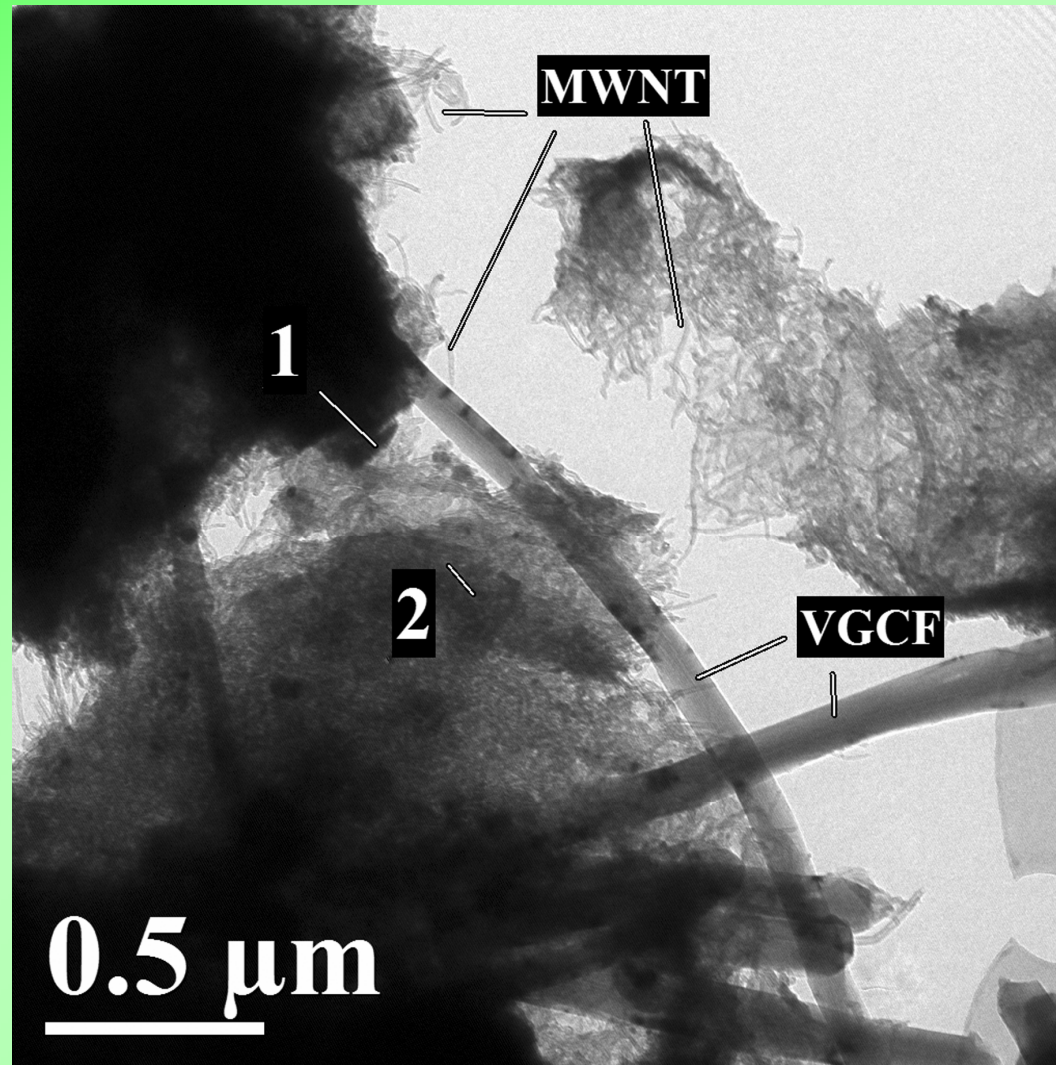
Mélange hiérarchisé de nanotubes de carbone et de fibres de carbone

B. Lestriez, S. Desaeveer, J. Danet, P. Moreau, D. Plée, and D. Guyomard (2009)

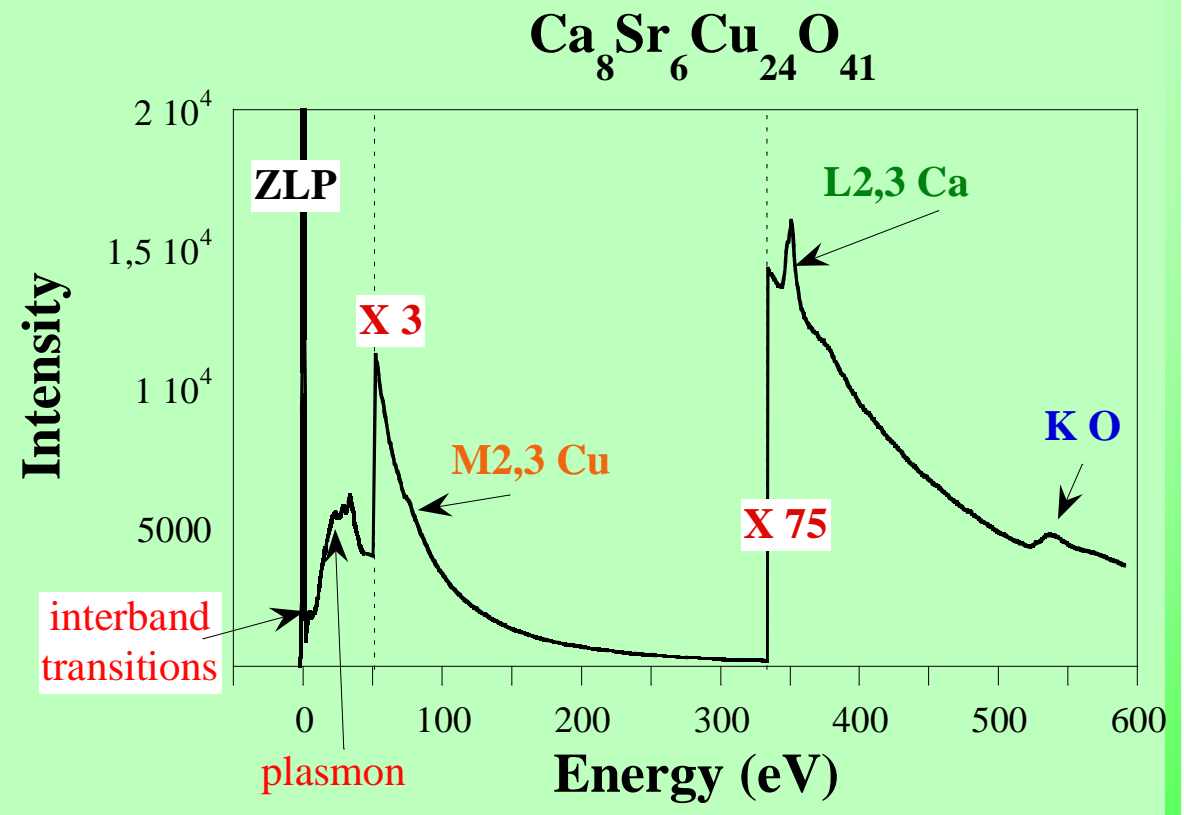


+ brevet en cours

Identification à l'échelle nanoscopique : la microscopie électronique à transmission (MET)



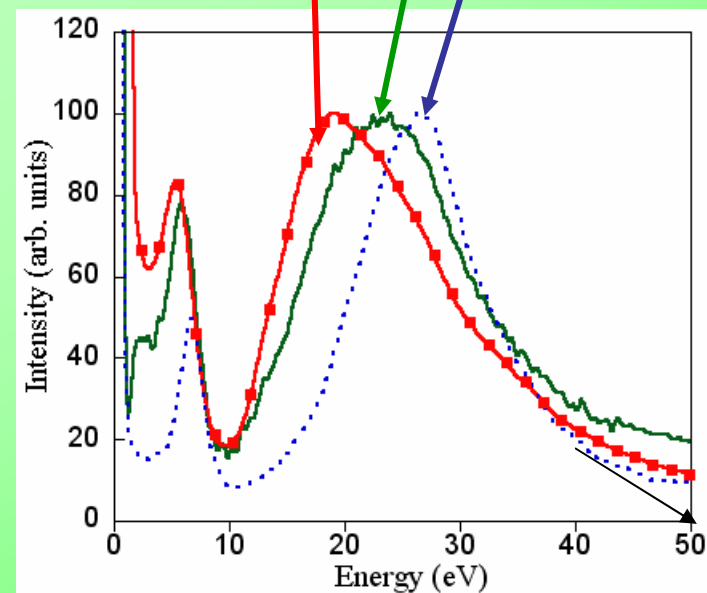
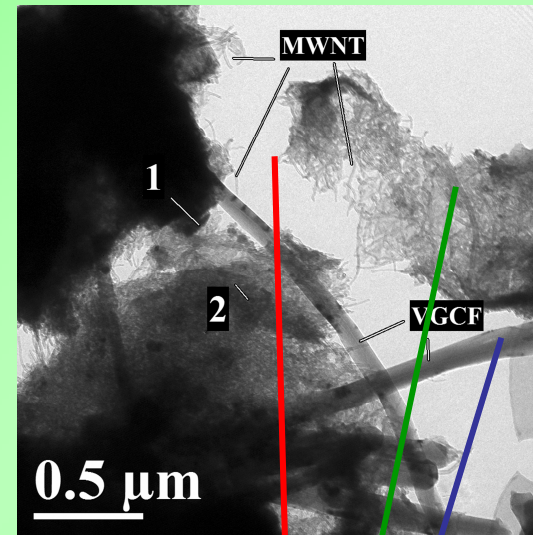
Spectroscopie de pertes d'énergie des électrons (EELS)



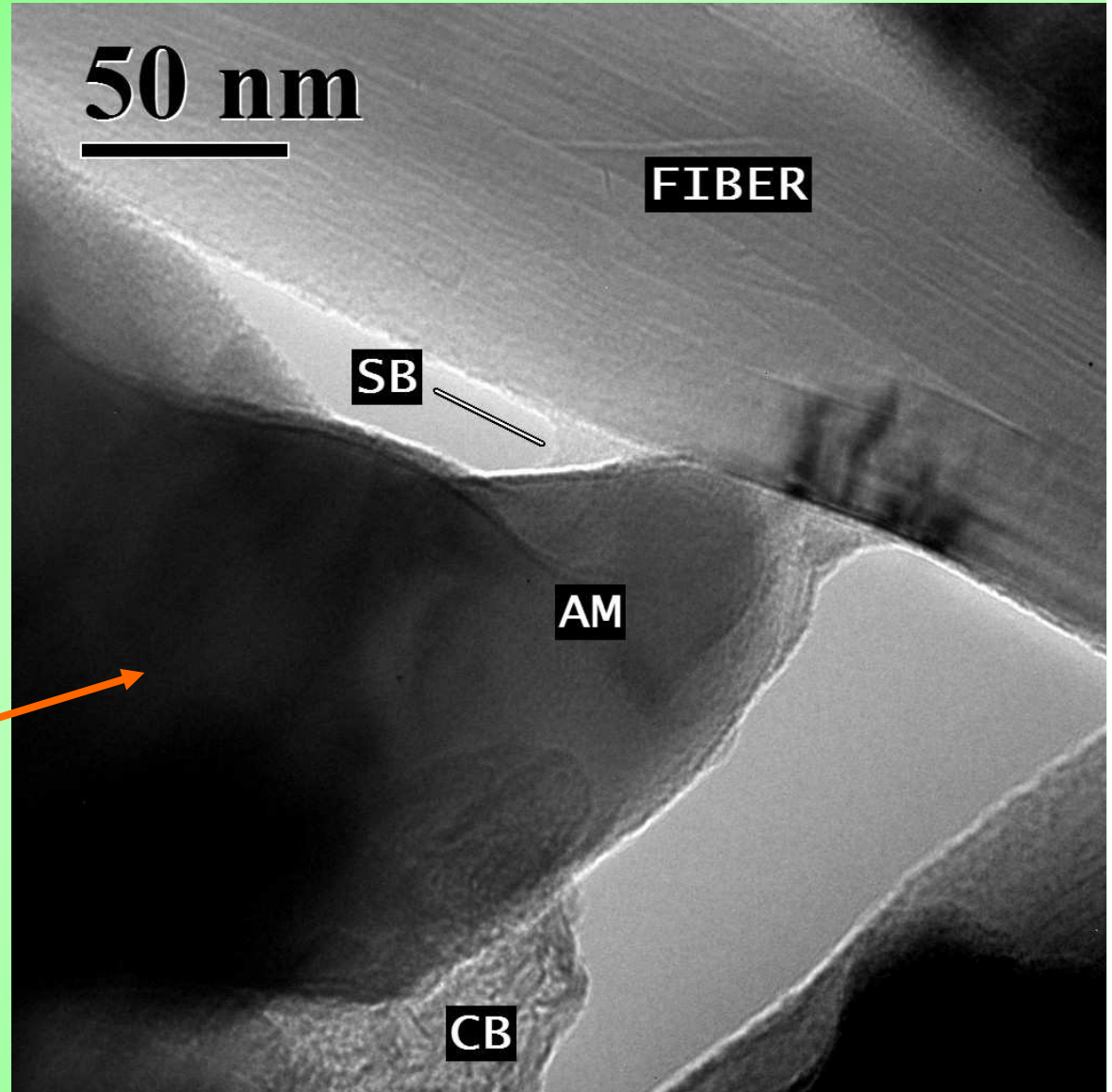
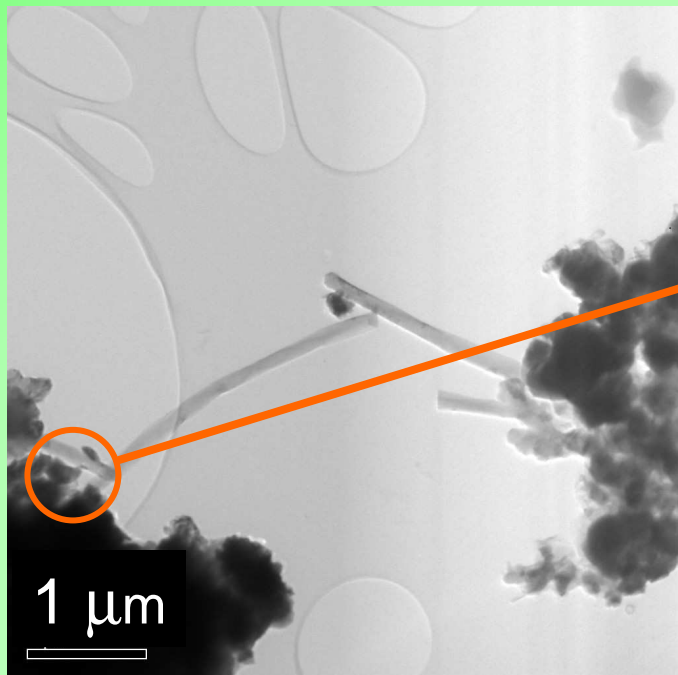
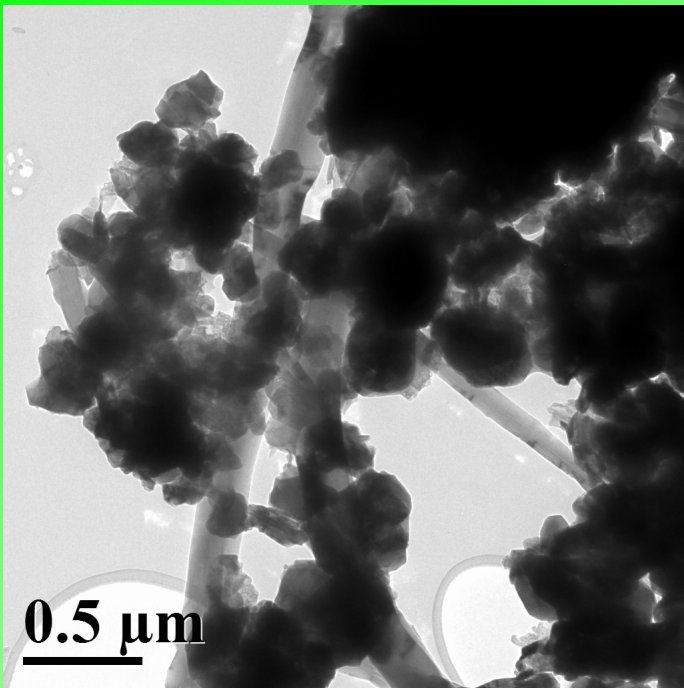
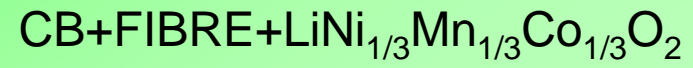
Résolution spatiale : 2 nm
Résolution en énergie : 0.7 eV

HF2000, FEG, 100kV, EDX

MET : imagerie et analyse à l'échelle du nanomètre



Collaboration avec General Motors



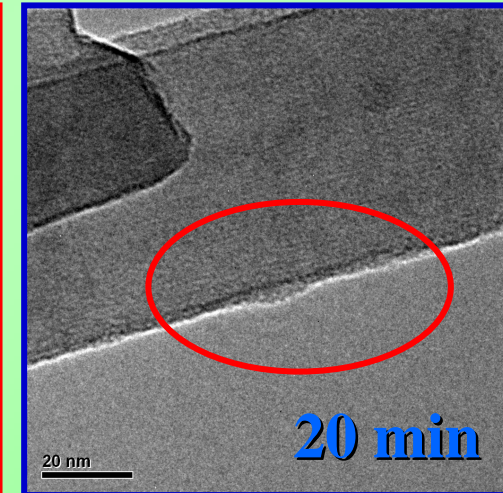
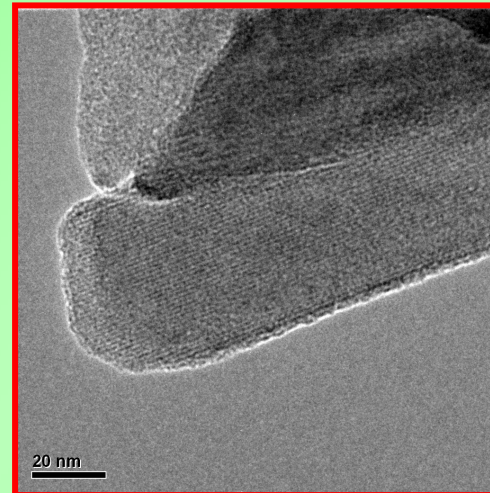
Modifications de surface

Electrogreffage *in situ*

J. Gaubicher (CR, IMN)

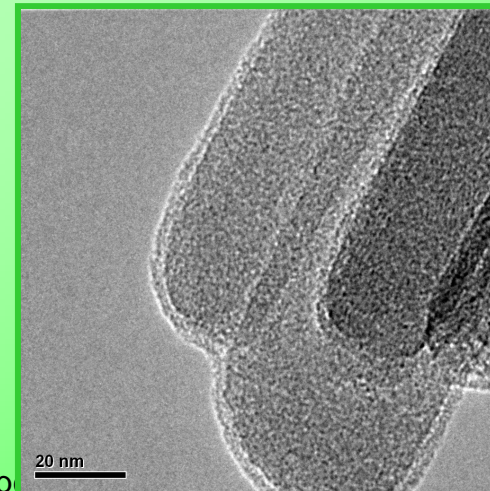


3 min



F. Tanguy, J. Gaubicher, AC Gaillot, D. Guyomard and J. Pinson, *J. Mater. Chem.*, 2009, *DOI:* 10.1039/b901387c

60 min
2 nm



Etude de Li_xFePO_4

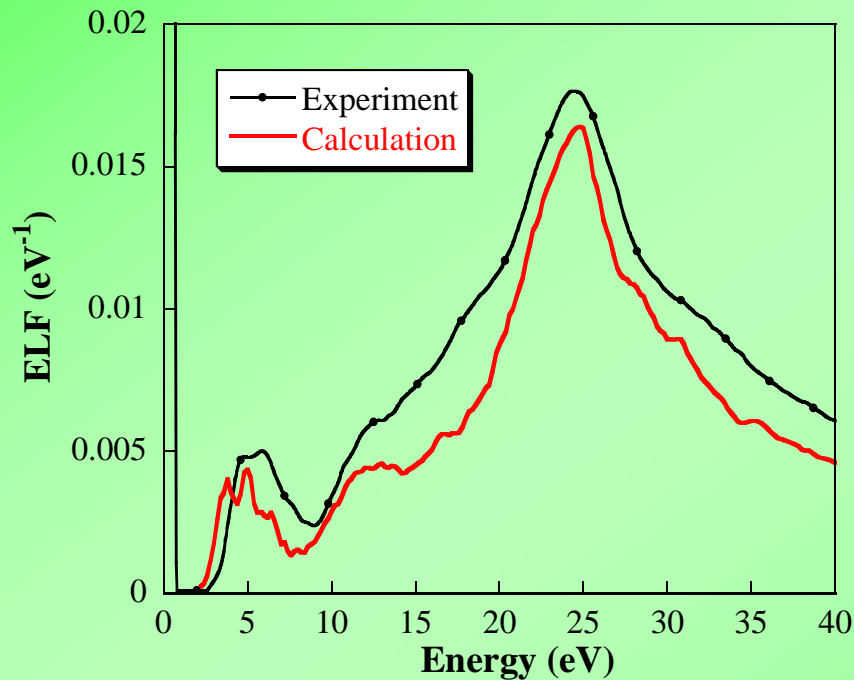
P. Moreau, V. Mauchamp, F. Pailloux, and F. Boucher, Applied Physics Letters **94**, 123111 (2009)

WIEN2k, V_{xc} : **GGA+U** with $U=4.3$ eV

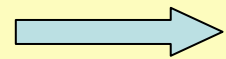
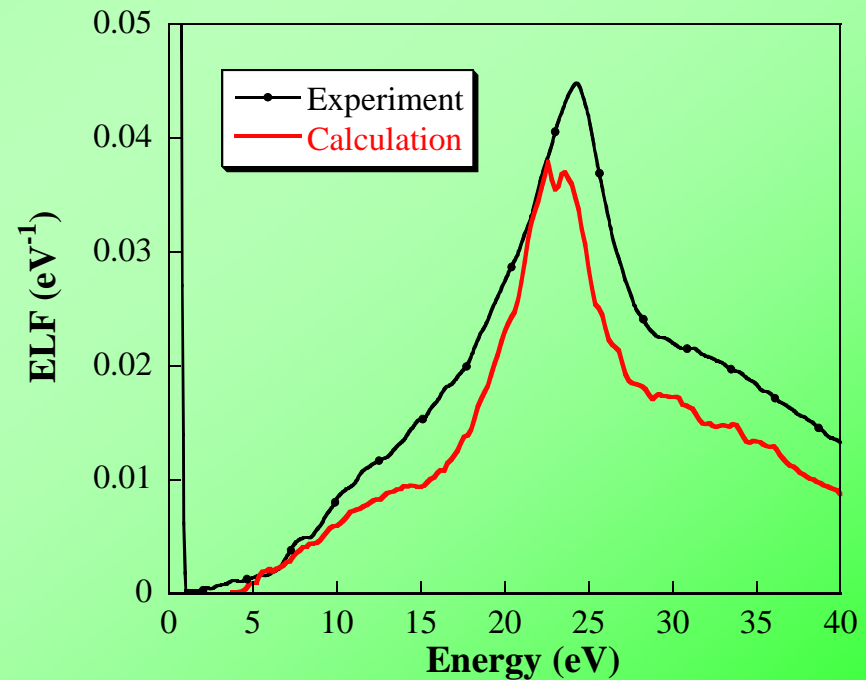
Spin polarisé / Ordre anti-ferromagnetique

+ Expériences à la température de l'azote liquide

FePO_4



LiFePO_4



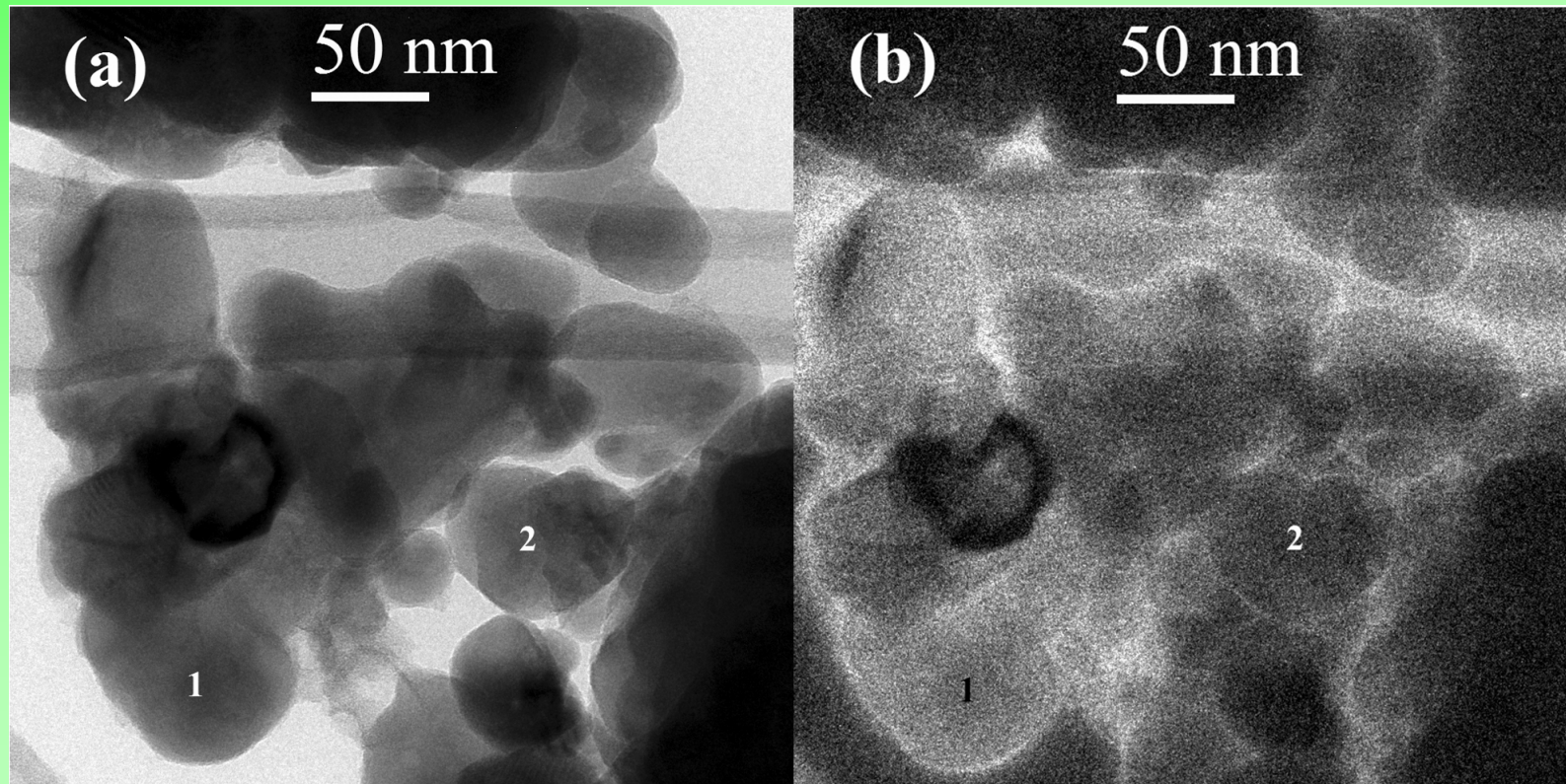
Images chimiques: local et rapide

Images EFTEM sur Li_xFePO_4

(JEOL 2200FS, 200 kV, à Poitiers)

Image en champ clair d'une région avec de multiples nanocristaux

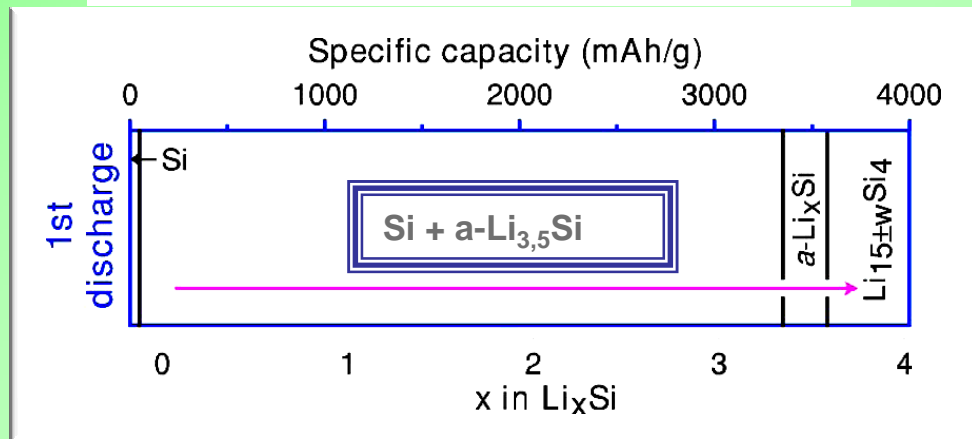
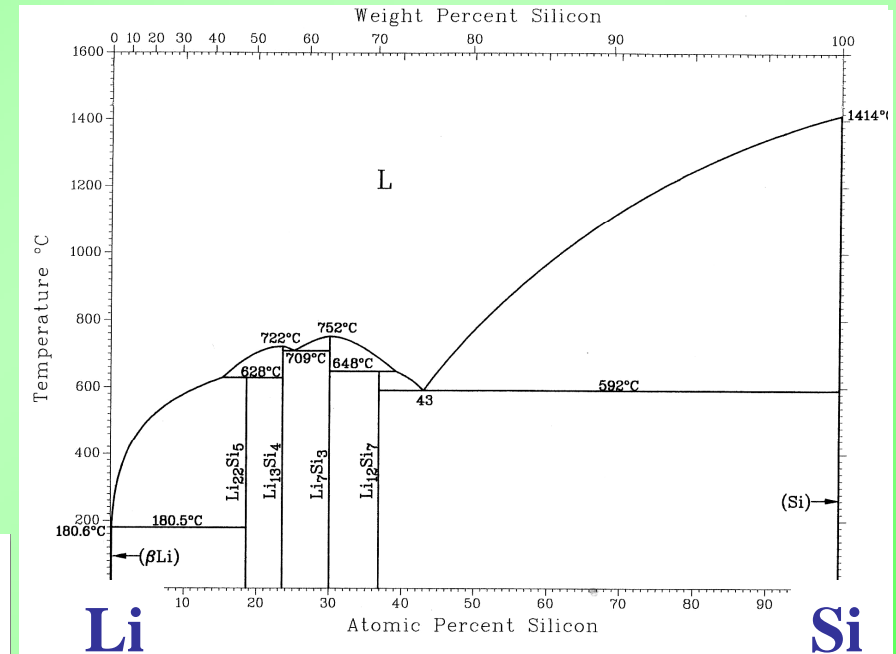
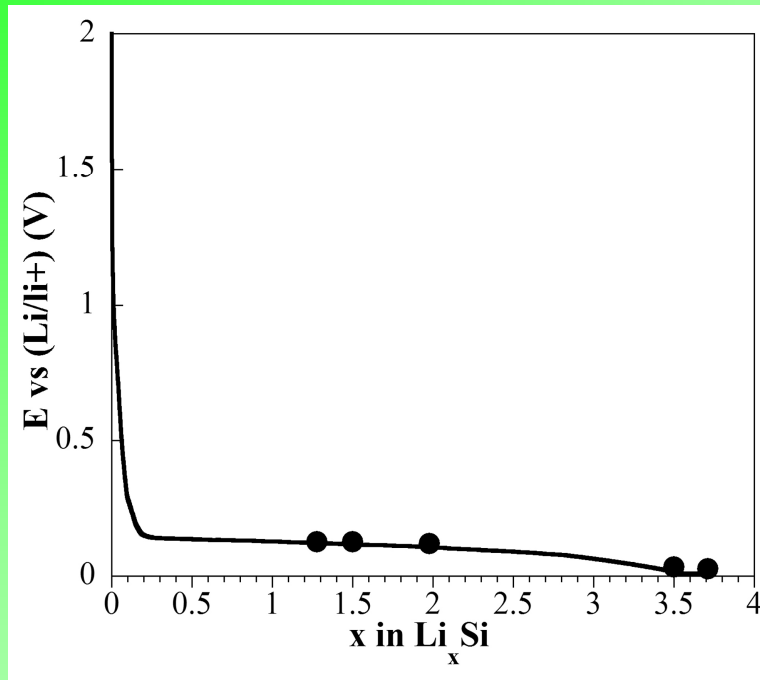
Image EFTEM de la même région pour une fente centrée à 5 eV



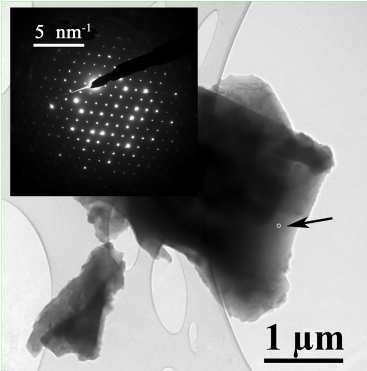
P. Moreau, V. Mauchamp, F. Pailloux, and F. Boucher, APL **94**, 123111 (2009)

Etudes d'électrodes négatives au silicium

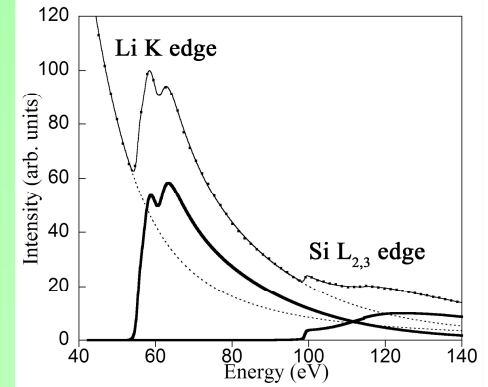
J. Danet, T. Brousse, D. Guyomard and P. Moreau, soumis JPCC



J. Li et J. R. Dahn, *Journal of The Electrochemical Society* **154** (2007): A156.

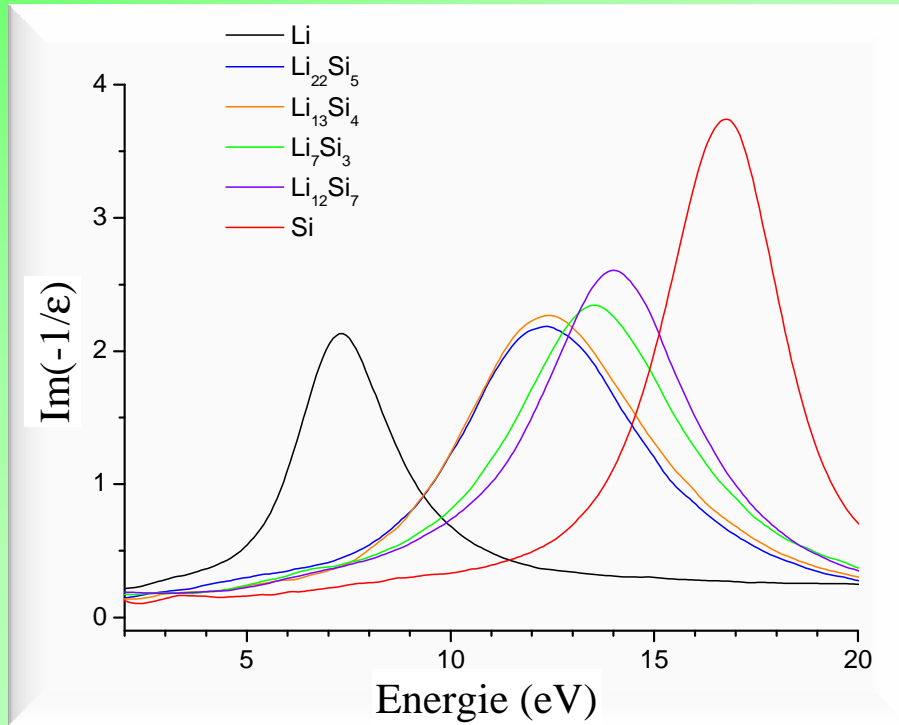


Etudes d'électrodes négatives au silicium



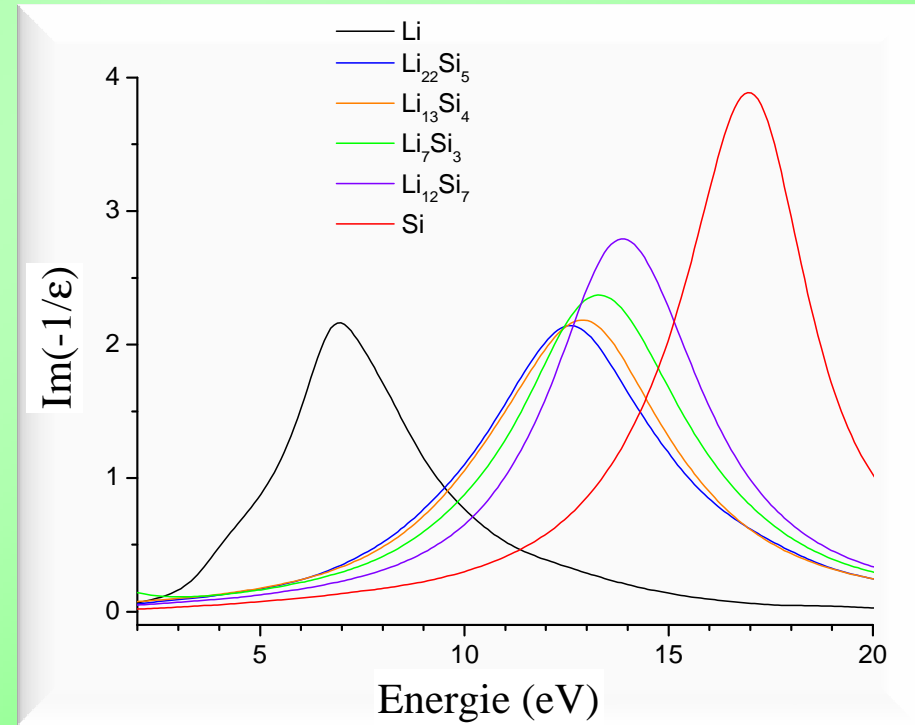
Expériences

(ELF règle de somme)



Calculs

(WIEN2k, FWHM)



Temps d'acquisition = 10 ms

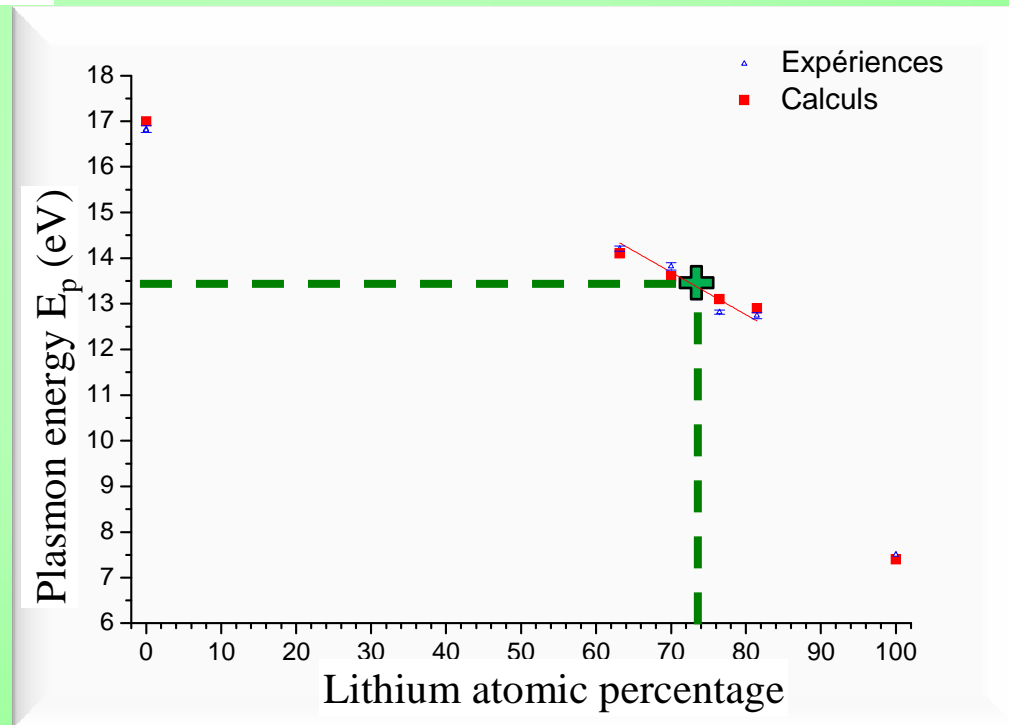
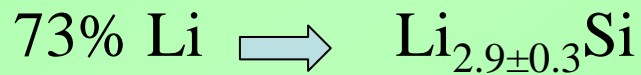
$t/\lambda = 0.3$ to 2.5

Etudes d'électrodes négatives au silicium

Compound (Li _x Si)	x from core losses	E _p (eV) <i>Drude</i>	E _p (eV) <i>WIEN2k</i>	E _p (eV) <i>Exp.</i>
Si (x=0)	0	16.6	17.0	16.83 (0.05)
Li ₁₂ Si ₇ (x=1.7)	1.5	13.5	14.1	14.21 (0.03)
Li ₇ Si ₃ (x=2.3)	2.5	13.0	13.6	13.82 (0.04)
Li ₁₃ Si ₄ (x=3.3)	3.1	12.2	13.1	12.83 (0.02)
Li ₂₂ Si ₅ (x=4.4)	4.2	11.9	12.9	12.74 (0.03)
Li	-	8.0	7.4	7.5 (0.1)

Fit par le modèle de
Drude (ou Jelium)

$$E_p = \sqrt{\frac{ne^2\hbar^2}{\epsilon_0 m}}$$



Les batteries au lithium ont besoin
de la microscopie électronique

Merci de votre attention

Merci à tous les contributeurs :

L'Institut des Matériaux Jean Rouxel
Université de Nantes

Partenaires financiers (ANR, Ministère, industriels...)