Fe^{3+}/Fe^{2+} redox couple in polyanionic framework structures

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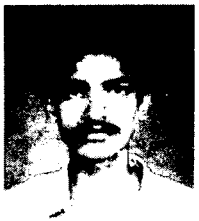
Fe^{3+}/Fe^{2+} redox couple in polyanionic framework structures

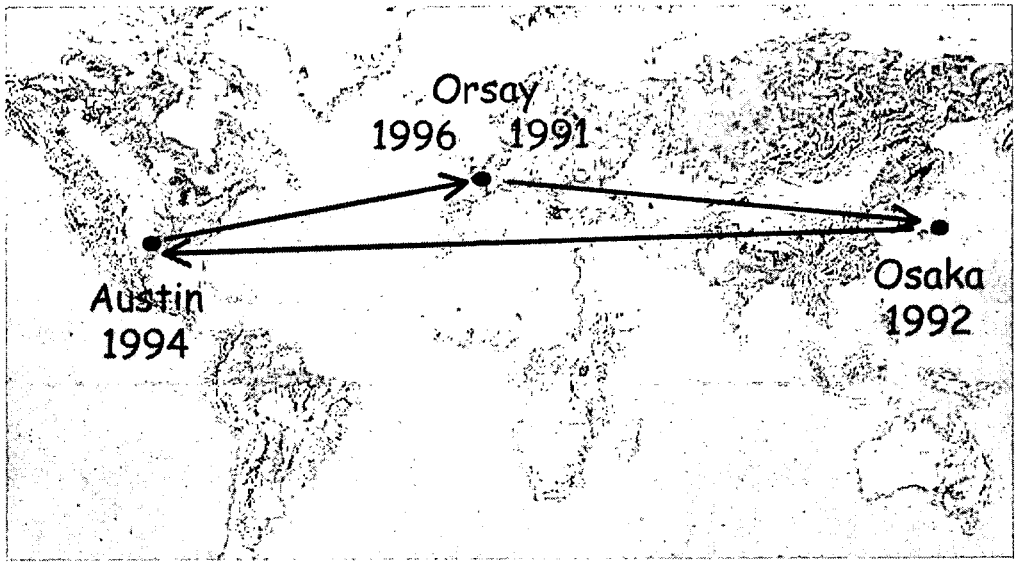
A REVIEW

C. Masquelier

Korean Battery Meeting, Seoul
Nov. 2002

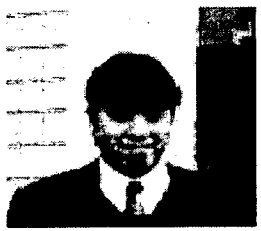


AK Padhi



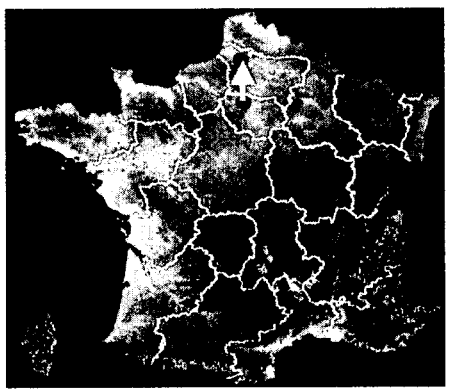
R. Kanno

KS Swamy



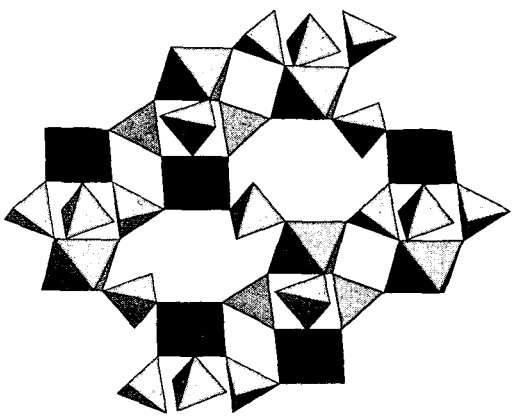
M. Tabuchi

J.B. Goodenough



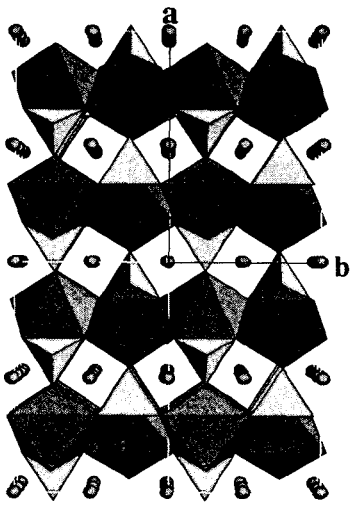
September 2000 : Orsay -> Amiens

High Potential Iron Phosphate compounds
Fe^{3+}/Fe^{2+} redox couple



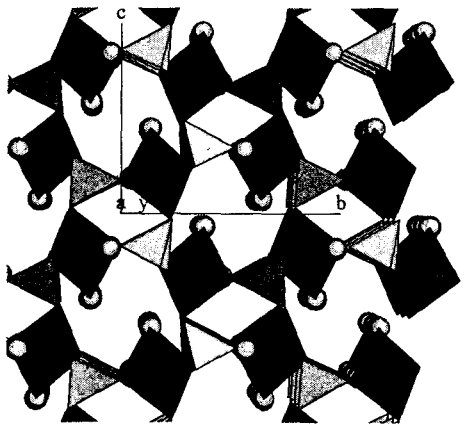
$Li_3Fe_2(PO_4)_3$

$LiFeP_2O_7$



(001)

Olivine $LiFePO_4$



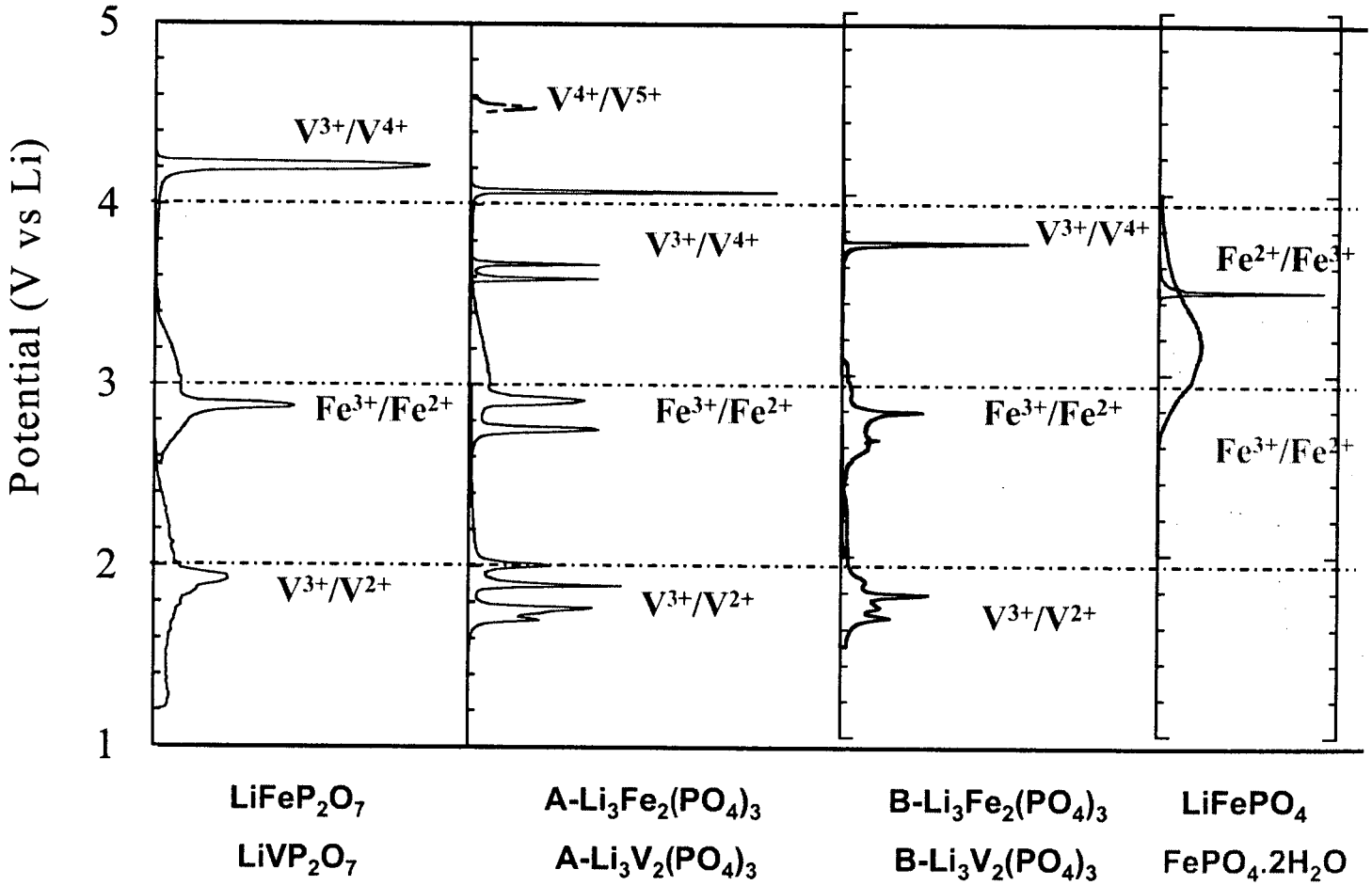
$FePO_4 \cdot 2H_2O$

$Fe_4(P_2O_7)_3 \cdot 4H_2O$

Stable Framework Structures : 1 lithium exchanged per 3d metal

Inductive effect (JBG) : redox potentials at ~3V for Fe^{3+}/Fe^{2+}, at ~4V for V^{4+}/V^{3+}

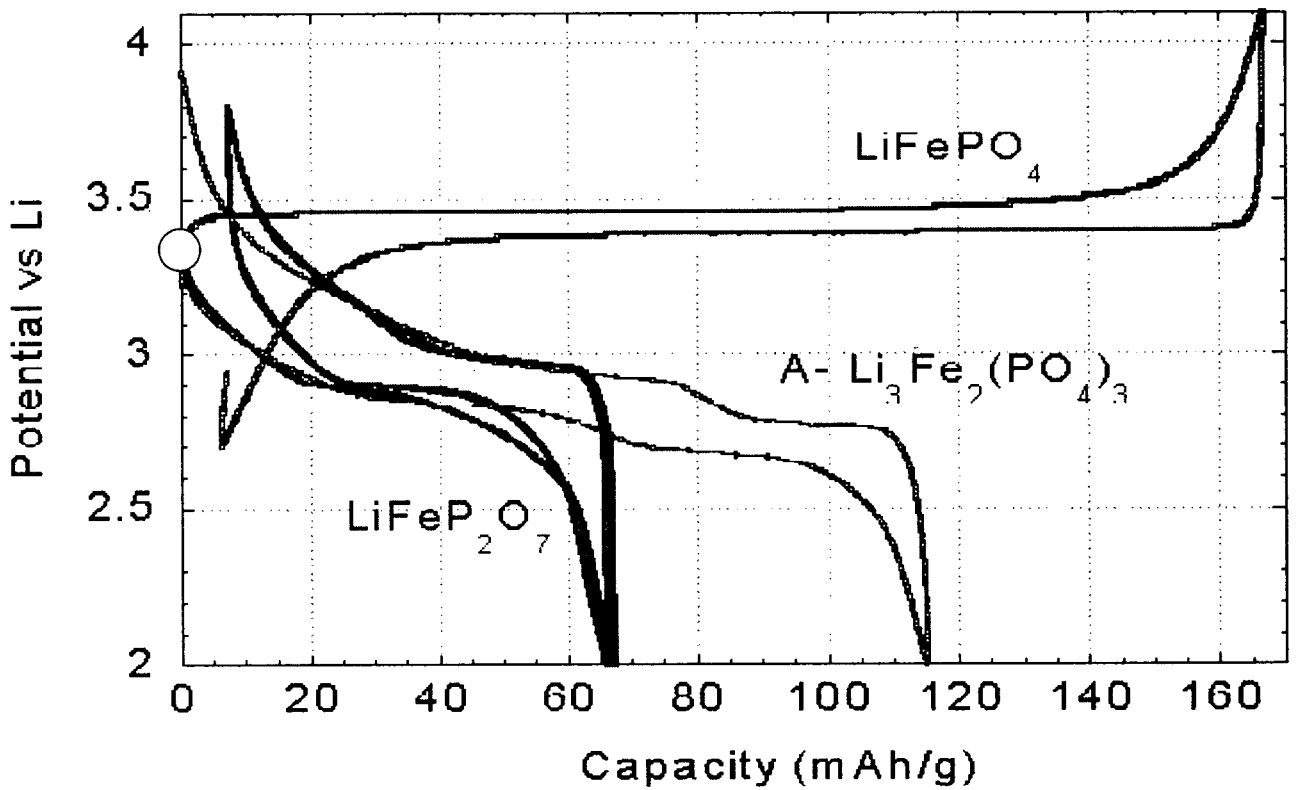
Fe^{3+}/Fe^{2+}, V^{3+}/V^{2+} and V^{4+}/V^{3+} couples



Today's topic : $Fe^{3+/2+}$ phosphates

	Formula	M ($g.mol^{-1}$)	Theor. Capacity (mAh/g)	Operating Voltage vs. Li^+/Li
M/P = 1	$LiFePO_4$	157.8	170	$Fe^{3+/2+}$: 3.45 V
M/P = 1	$FePO_4 . 2H_2O$	186.8	147	$Fe^{3+/2+}$: 3.00 V
M/P = 2/3	$Fe_4(P_2O_7)_3 . 4H_2O$	745.2	144	$Fe^{3+/2+}$: 3.20 V
M/P = 2/3	$Li_3Fe_2(PO_4)_3$	417.4	128	$Fe^{3+/2+}$: 2.80 V
M/P = 1/2	$LiFeP_2O_7$	231.7	116	$Fe^{3+/2+}$: 2.90 V

Potential vs. structure - Capacity vs. Fe/P ratio



$LiFe^{II}PO_4$: discharged state, $Li_3Fe^{III}_2(PO_4)_3$, $LiFe^{III}P_2O_7$: charged state

Problem !!

Low Electronic Conductivity => Slow kinetics

<u>Trying to overpass this handicap :</u>

- Low Temperature preparation
- Ball milling of Csp / Active material mixture
- Chemical Carbon coating

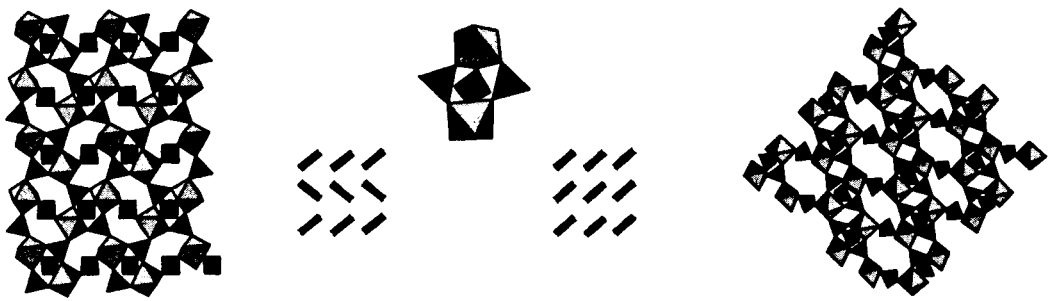
A : $Li_3Fe_2(PO_4)_3$ B : $LiFeP_2O_7$ C : $LiFePO_4$ D : $FePO_4.nH_2O$

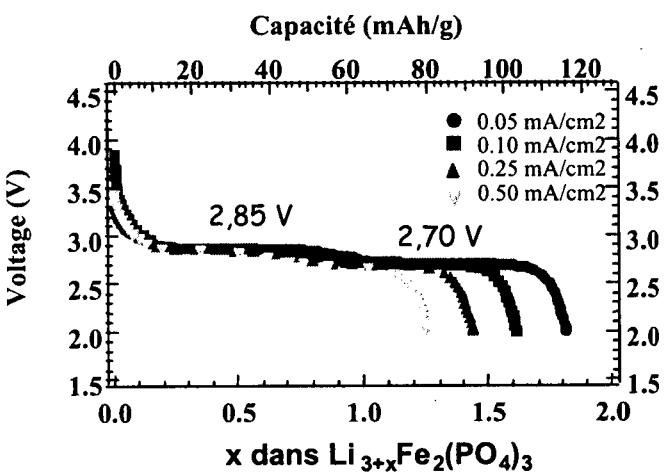
A : $Li_{3+x}Fe_2(PO_4)_3$

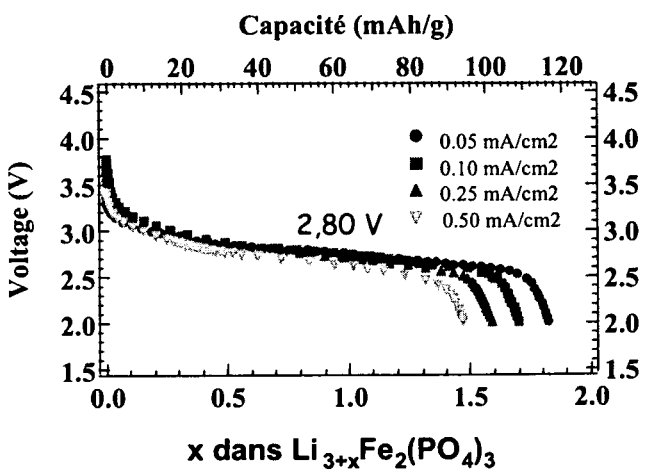
Monoclinic ($P2_1/n$)
ceramic

$Li_3Fe_2(PO_4)_3$

Rhombohedral (R-3)
flux, ion exchange

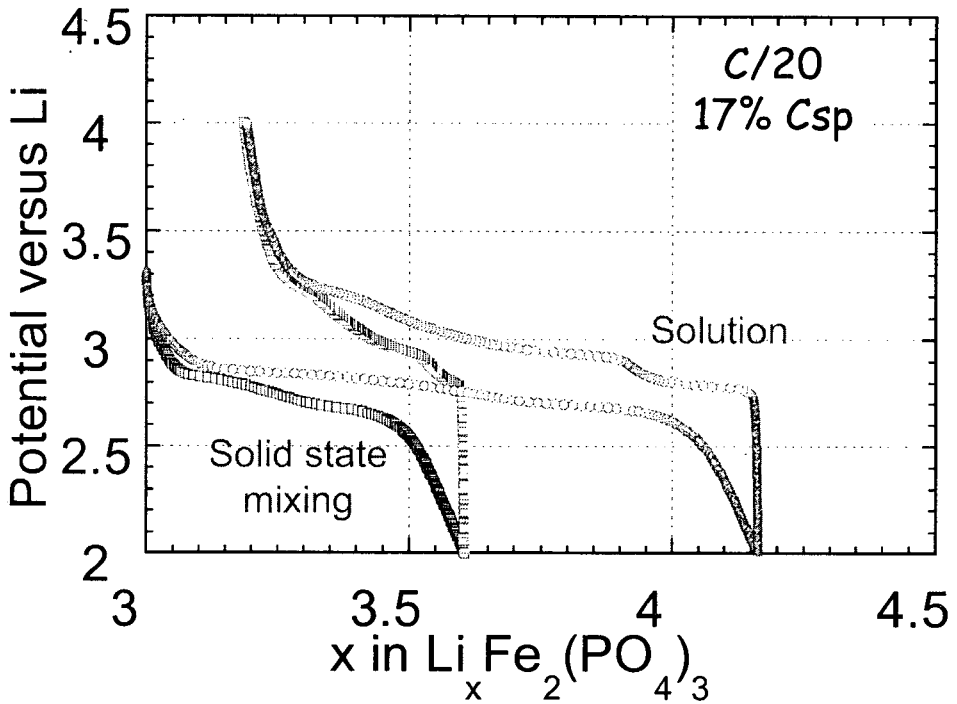




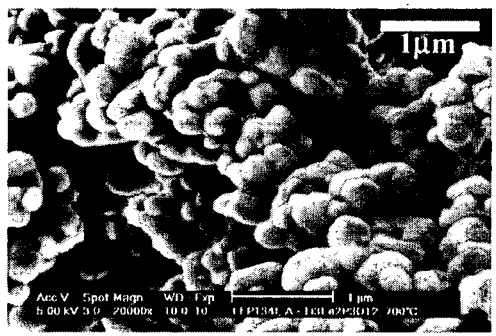


C. Masquelier, A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Solid State Chem., 135, 228 (1998)*
C. Masquelier, Calin Wurm, J. Rodríguez-Carvajal, J. Gaubicher, and L. Nazar, *Chem. Mater. 12(2), 525-532 (2000).*

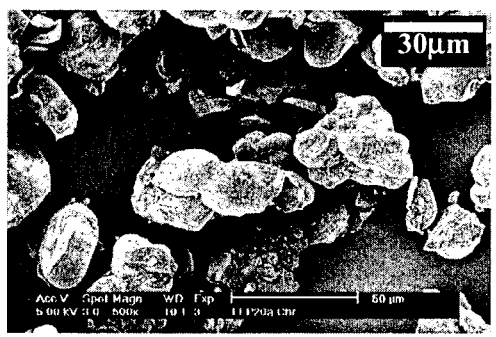
A : $Li_{3+x}Fe_2(PO_4)_3$



Low T, ~500°C, from solution route



High T (800-900°C) solid state reaction



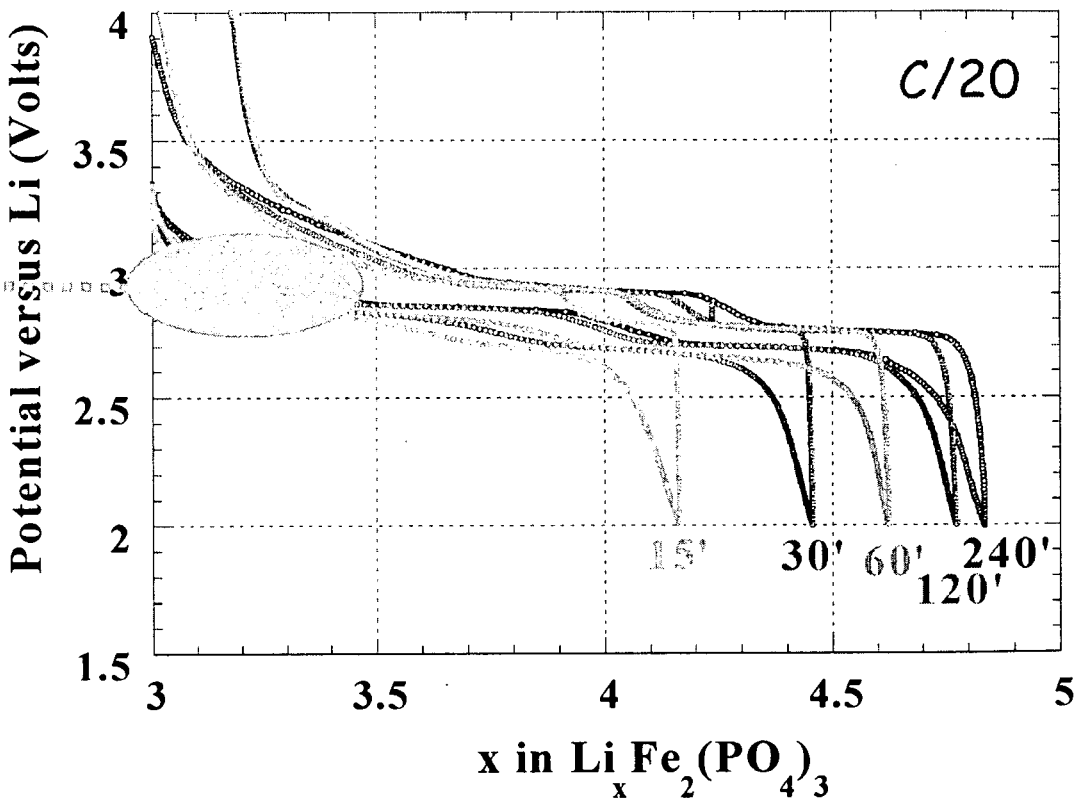
By solution route : lower particle size

⇩

Increase of capacity when in domain of stability of the electrolyte

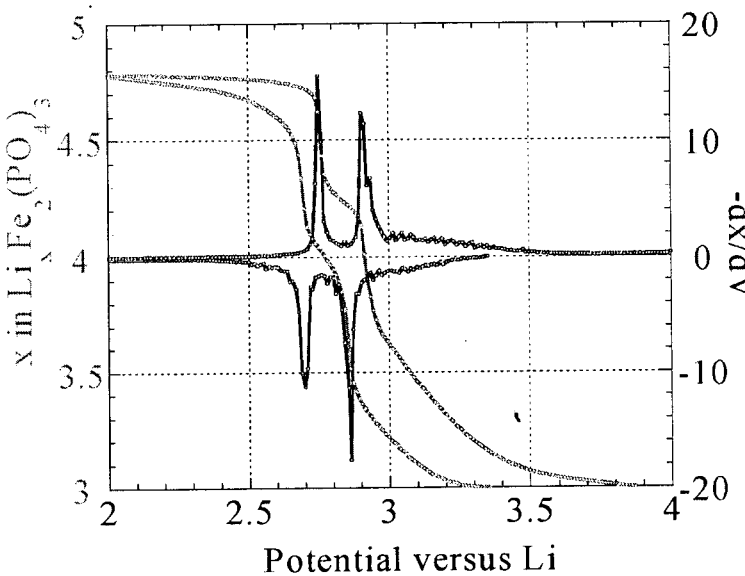
A : $Li_{3+x}Fe_2(PO_4)_3$: Ball-milling with 17% of C-SP

% of amorphous (Li-Fe-P-O) increases with Ball-milling time



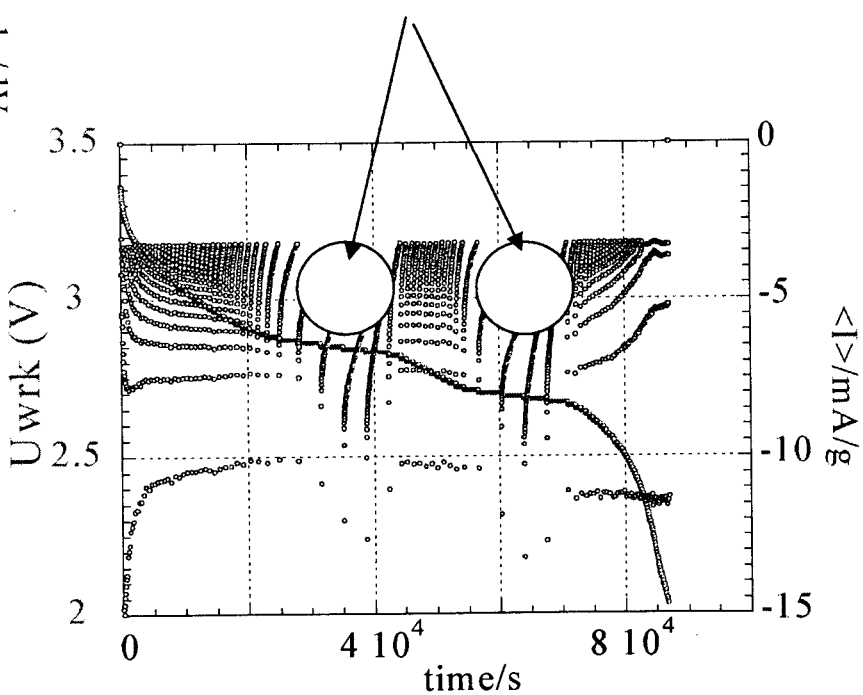
M. Morcrette, C. Wurm and C. Masquelier, *Solid State Sciences, 4, 239-246 (2002).*

A : $Li_{3+x}Fe_2(PO_4)_3$, Slow Potentiodynamic cycling

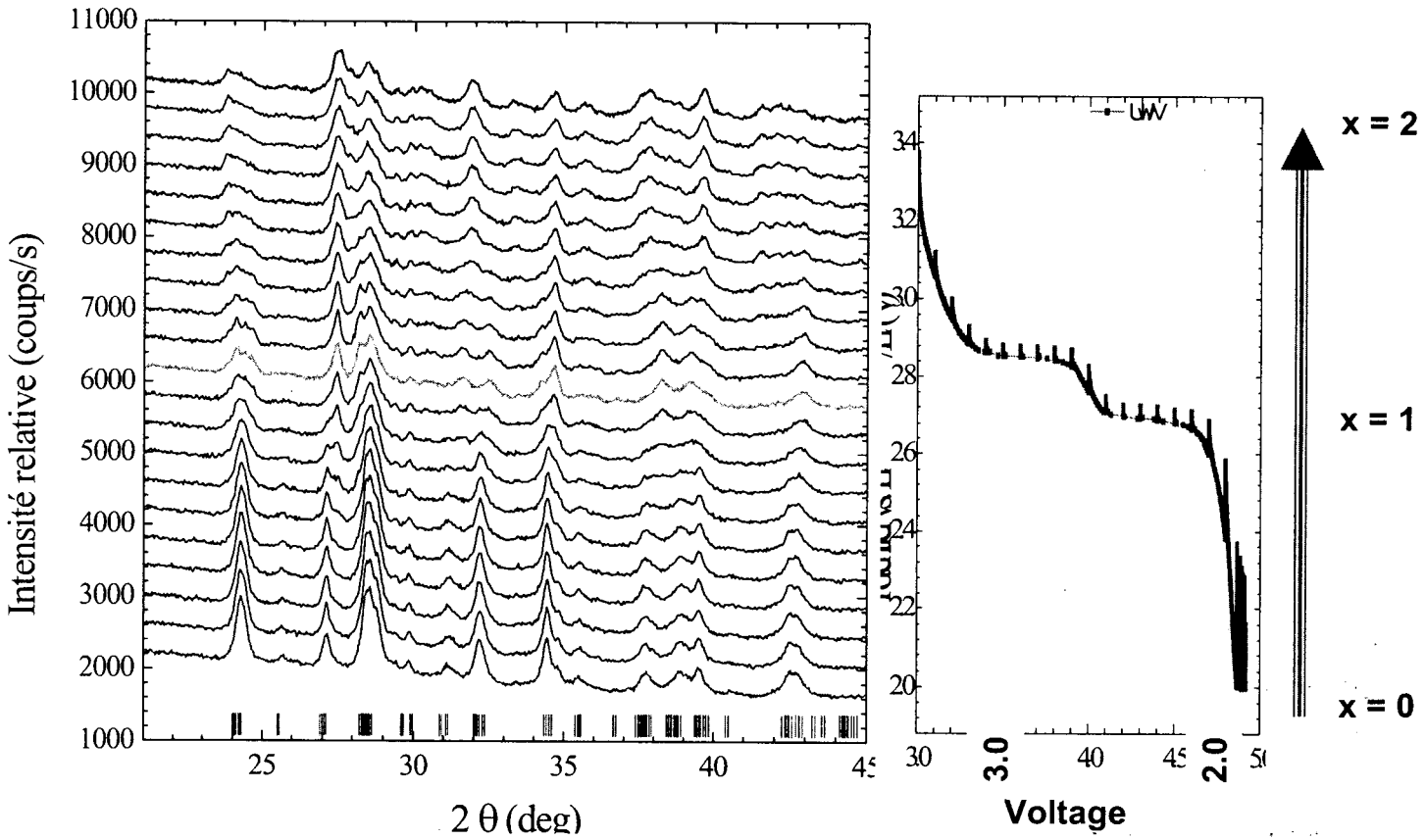


2 phase transitions still exist, at 2.93 V and 2.78 V vs. Li

Kinetics at phase transitions slowed down by poor intrinsic electronic transport within each phase

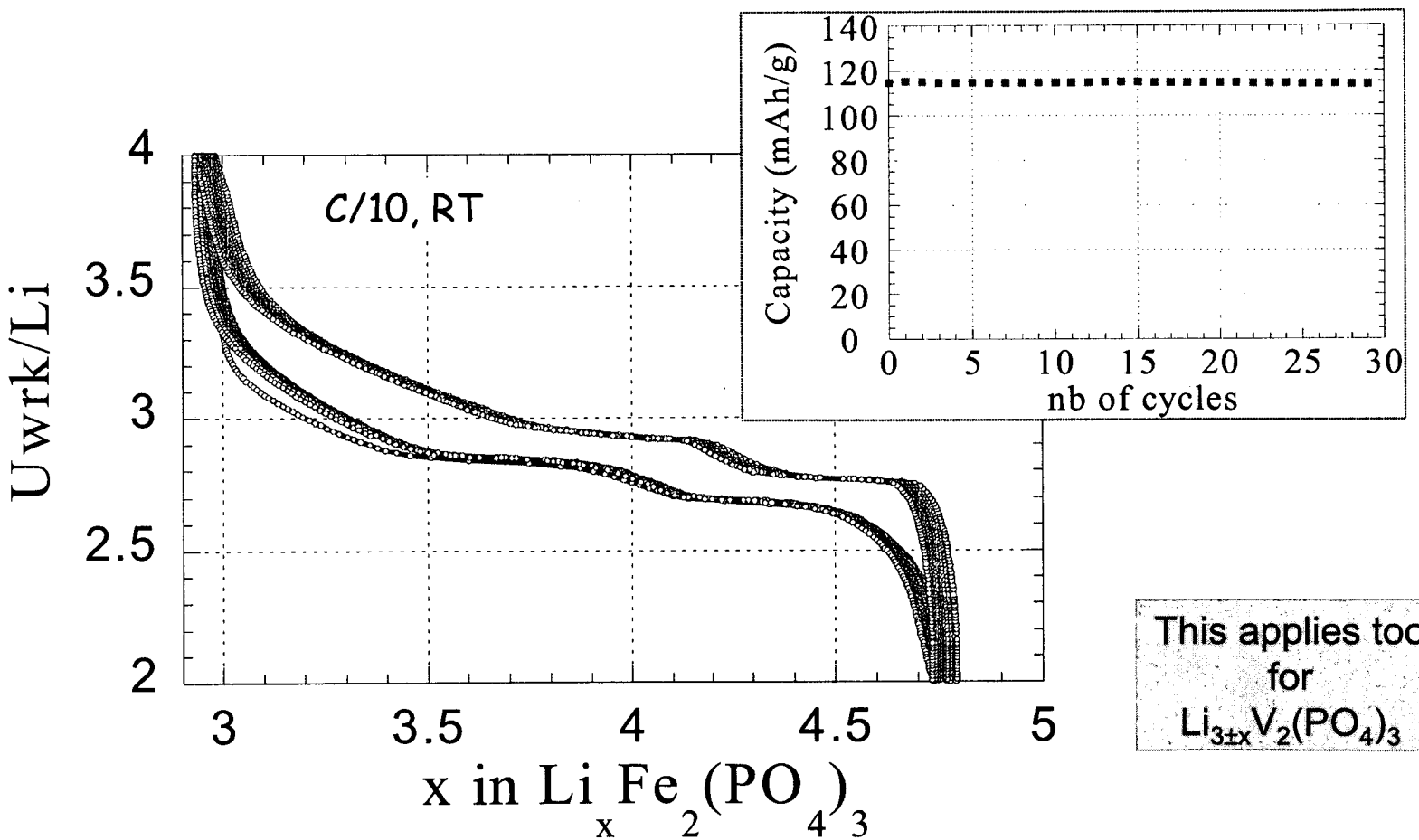


A : $Li_{3+x}Fe_2(PO_4)_3$, in situ X-Ray diffraction



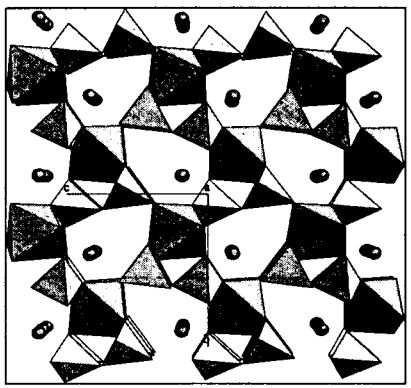
Very subttle 2-phase transitions, intermediate Li^+ ordering at x = 1 ??

A : Optimized $Li_{3+x}Fe_2(PO_4)_3$: cycling at C/10, RT

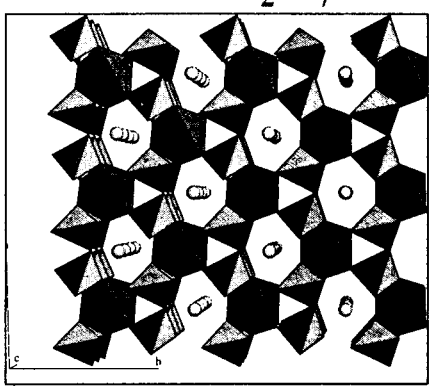


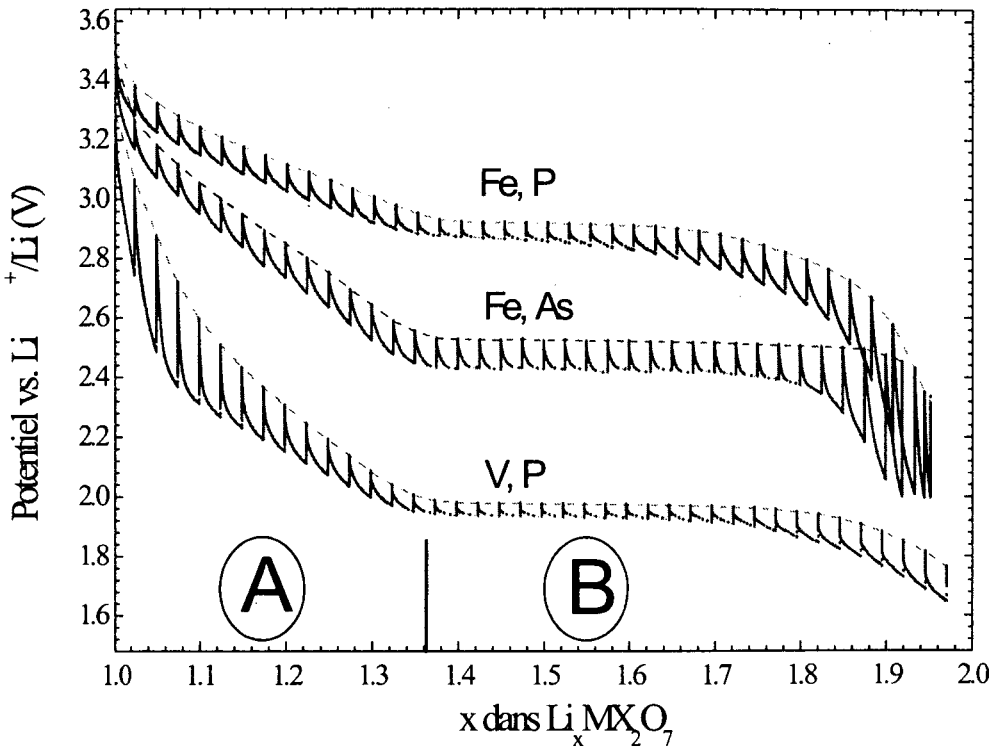
B : $Li_{1+x}MX_2O_7$ (M = Fe, V ; X = P, As)

$LiFeP_2O_7$, $LiVP_2O_7$



$LiFeAs_2O_7$

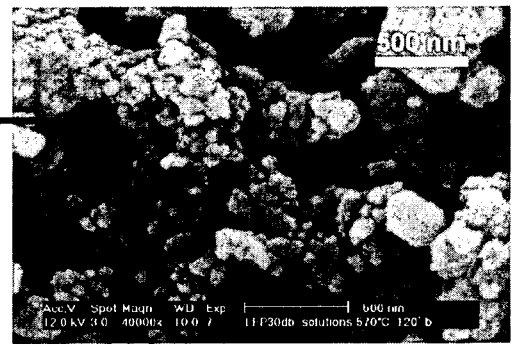




G. Rousse, C. Wurm, C. Masquelier and J. Rodríguez-Carvajal, *Solid State Sciences, 4, 973-978 (2002).*

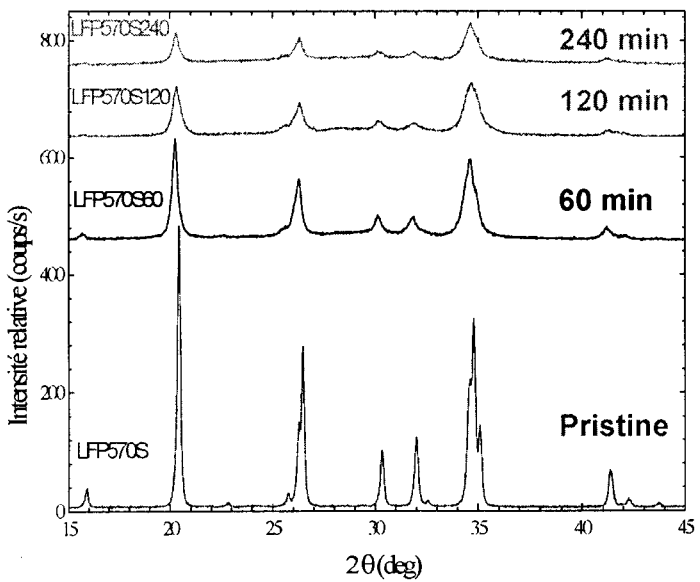
G. Rousse, C. Wurm, M. Morcrette, J. Rodriguez-Carvajal3, J. Gaubicher and C. Masquelier, *Int. J. Inorg. Mater. 3, 881 (2001)*

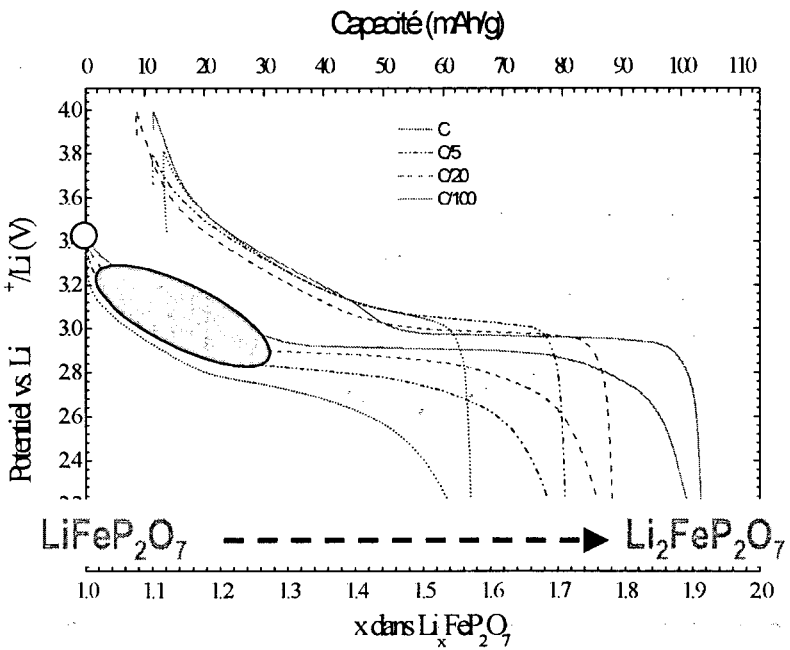
B : $Li_{1+x}FeP_2O_7$



Obtained pure at 570°C from a solution method

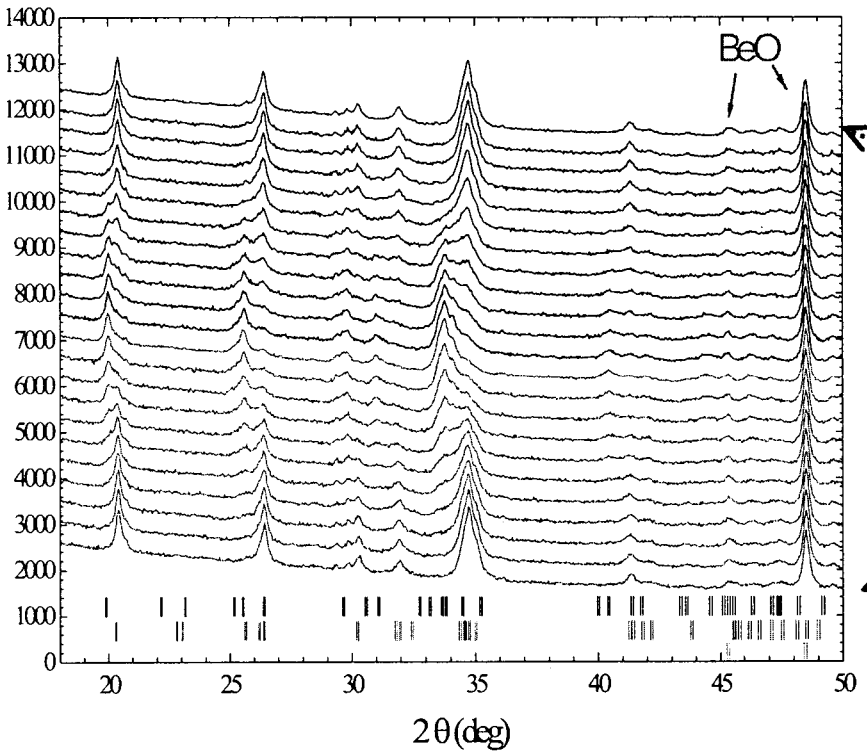
Ball-milling the AM/C composite

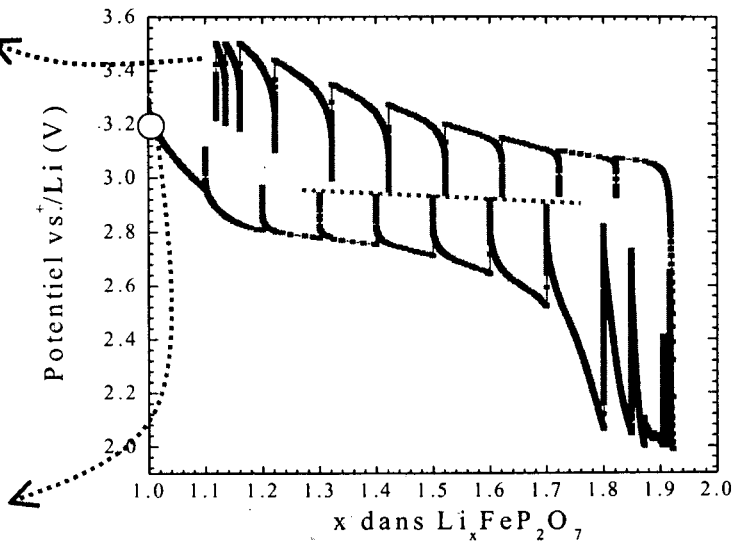




C. Wurm, M. Morcrette, G. Rousse, L. Dupont and C. Masquelier, Chem. Mater. 14(7), 2701 (2002).

B : $Li_{1+x}FeP_2O_7$, in situ X-Ray diffraction





Solid solution process (amorphous part), …, then, 2-phase reaction, highly reversible

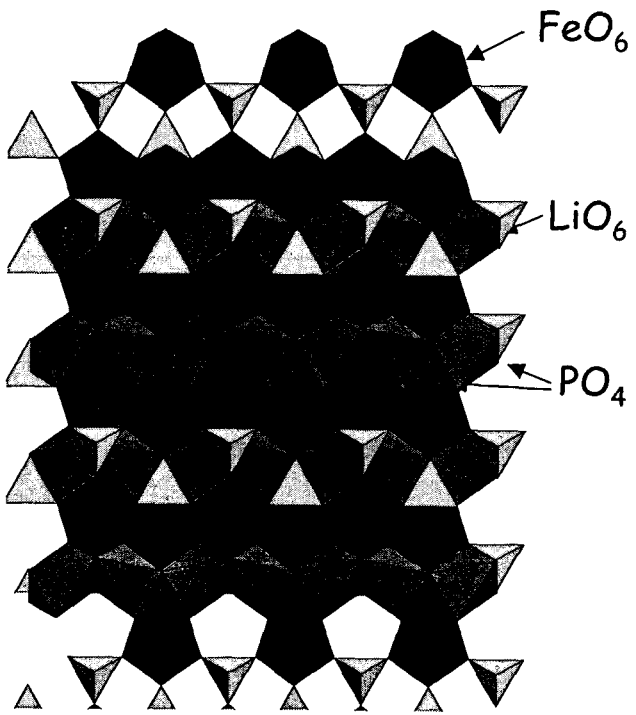
$Li_2FeP_2O_7$ indexed in same space group, $\Delta V/V = +5\%$

C : Triphyllite $LiFe^{II}PO_4$

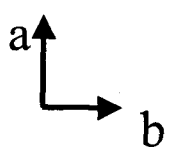
$[TeOc_2]$ Layer : $\tau_{octa} = \frac{1}{2}$, $\tau_{tétra} = 1/8$

LiO_6 share edges along [010]

FeO_6 isolated from each other within each $TeOc_2$ layer

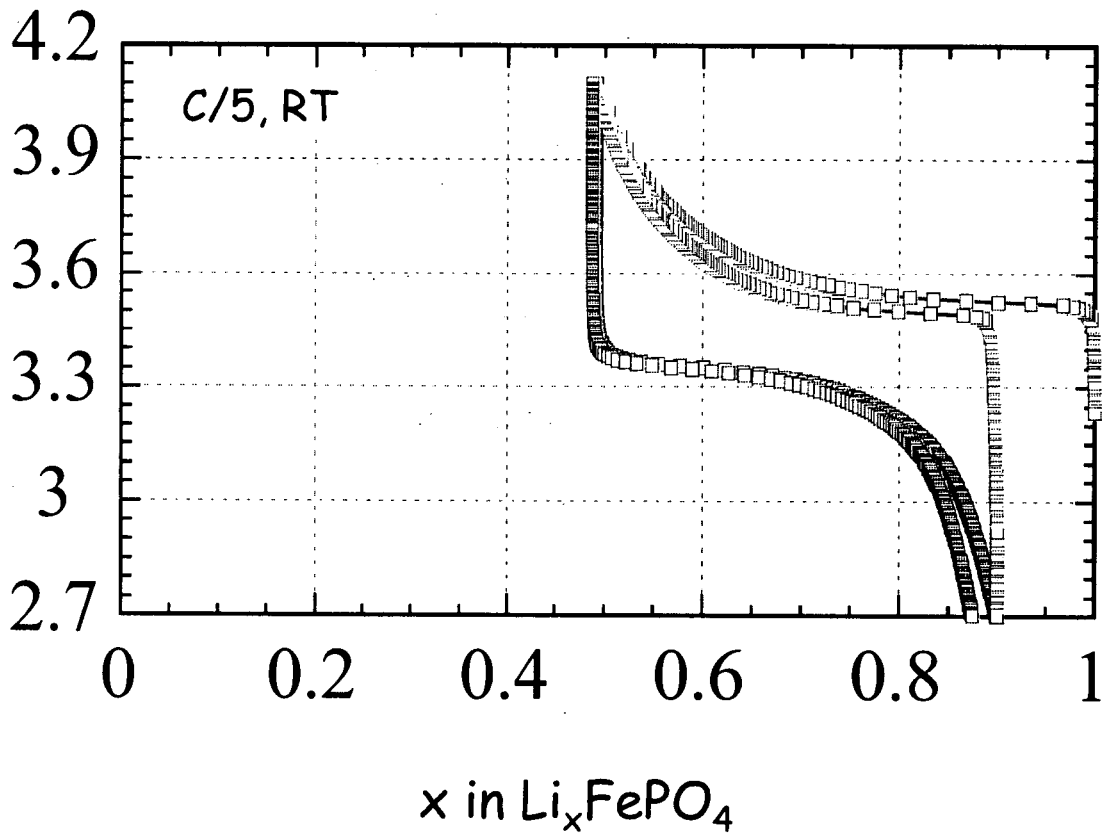


FeO_6 share corners within (100)

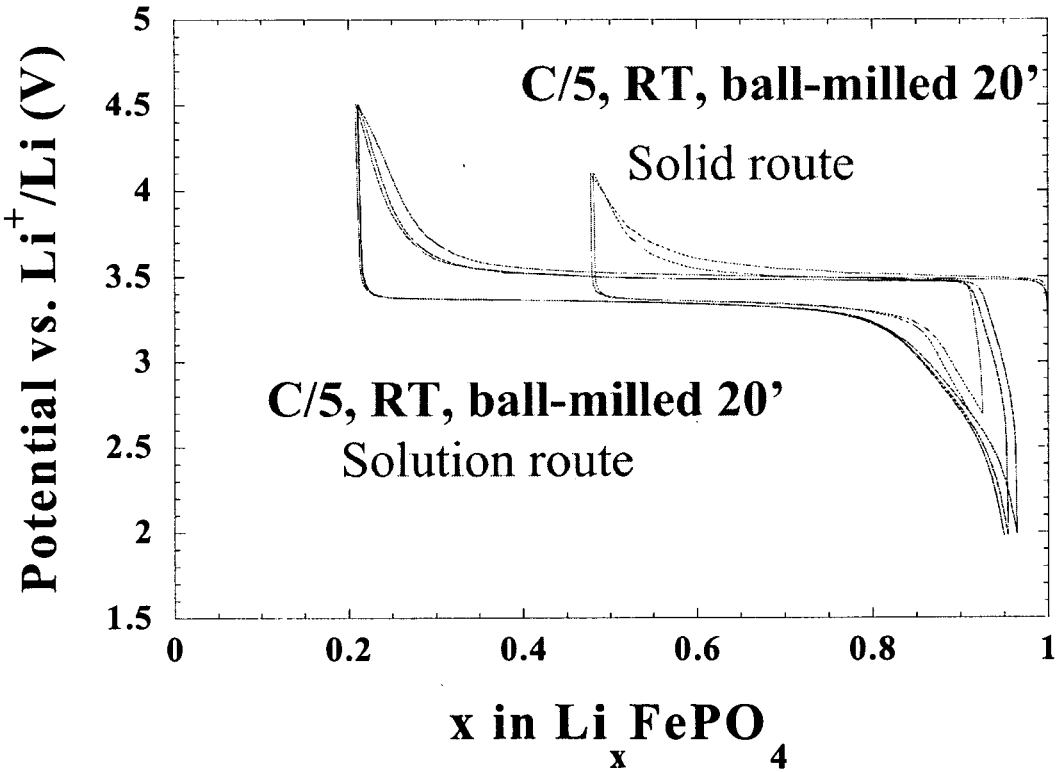


C : $LiFePO_4$, « standard » electrode preparation

$LiFePO_4$ obtained at 500°C, mixed with 17% of C-SP, mortar

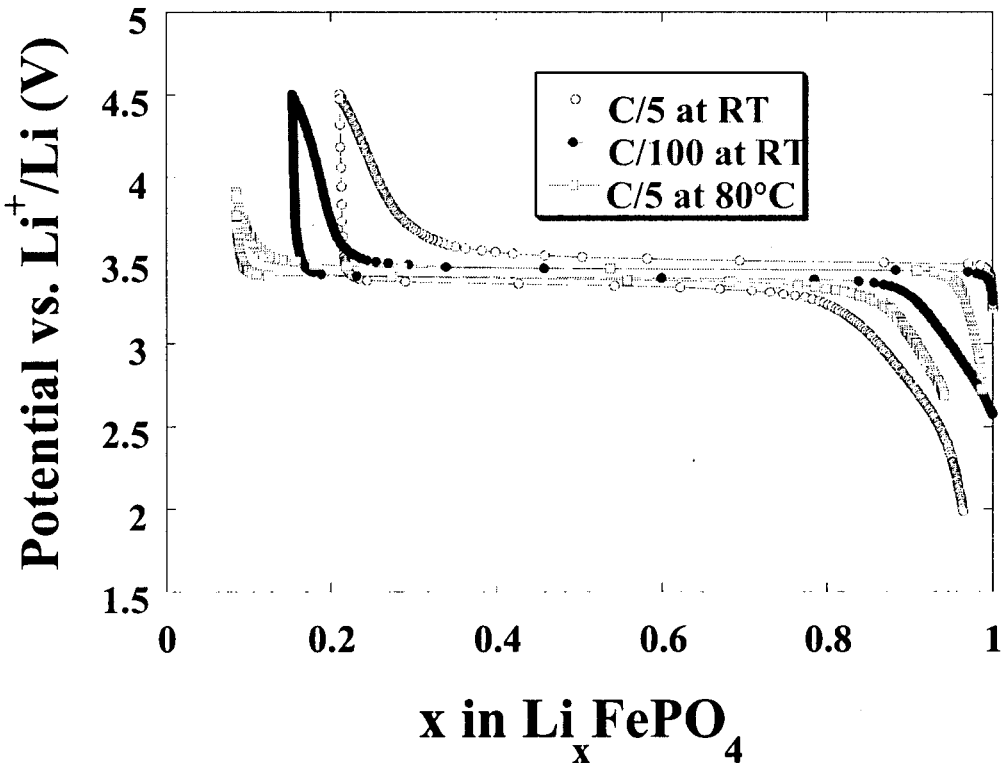


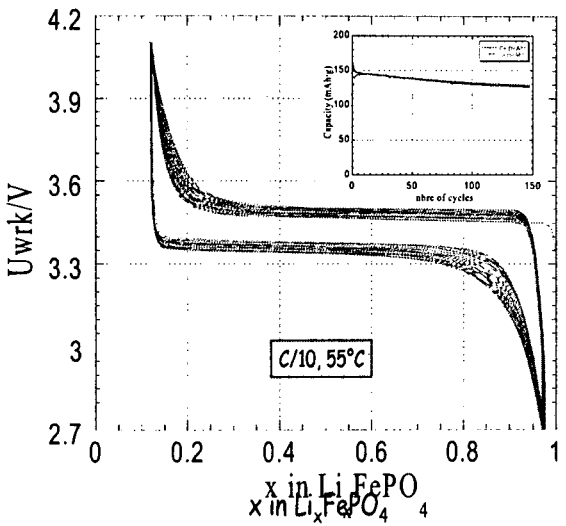
C : $LiFePO_4$, Ball-milling with 17% C-SP for 20'



Control of extrinsic parameters : Ball-milling favours « physical » Carbon coating

C : $LiFePO_4$ ball-milled with Carbon : effect of regime and T

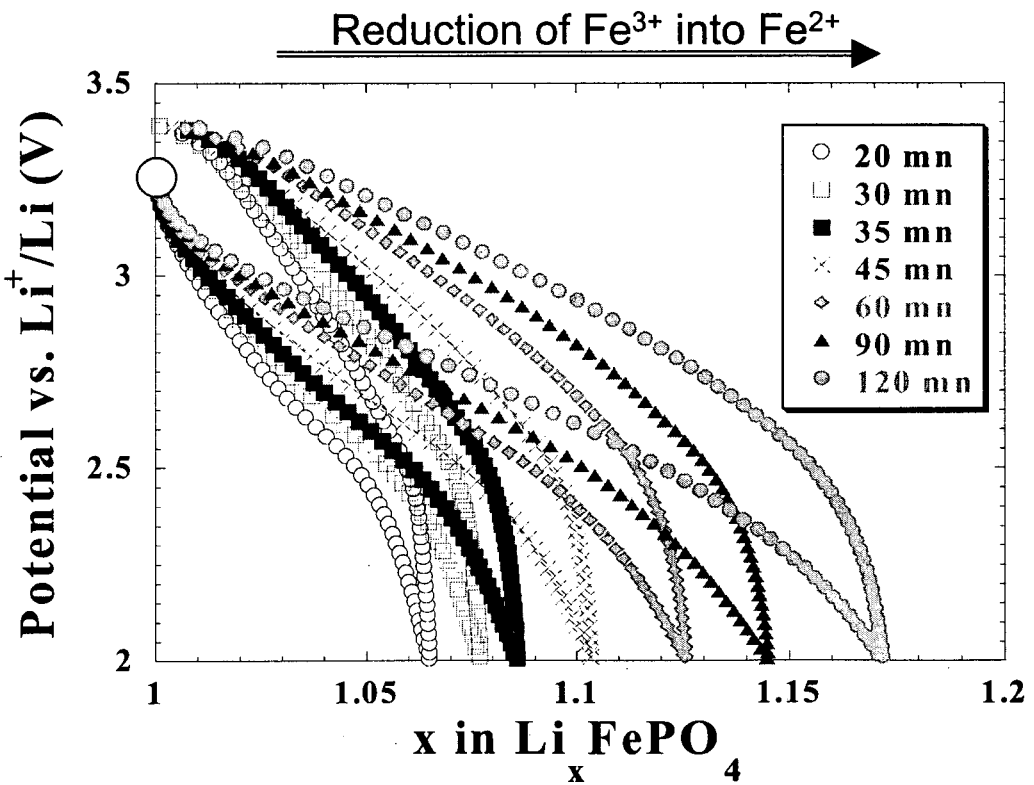




M. Morcrette, C. Wurm, J. Gaubicher, C. Masquelier, *Lithium Battery Discussions, Arcachon, May 2001*

C : $LiFePO_4$, Ball-milling with 17% C-SP : effect of time…

Caution : ball-milling may result in partial amorphisation
and oxidation of the active material : it can be reduced electrochemically then !!

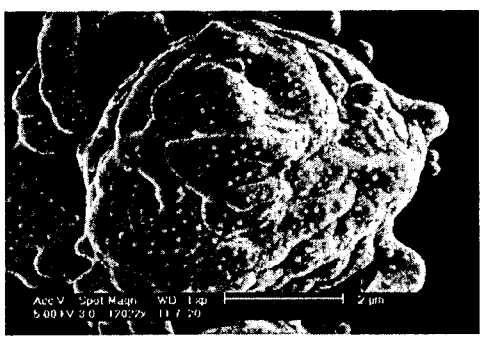


C : $LiFePO_4$: *in situ* carbon coating from polyacrylonitrile

1) Mixing of precursors in H_2O : LiH_2PO_4, $Fe(NO_3)_3 . 9H_2O$
   Acrylonitrile (distilled monomer)
   H_2O_2 (initiator of polymerisation)
   Stearic Acid (tensio-actif)

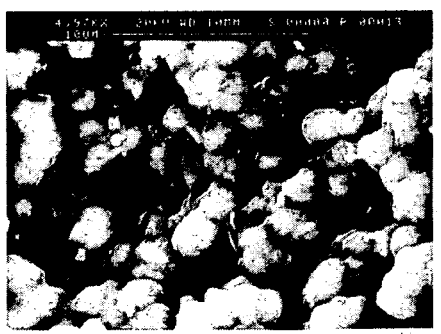
2) Slow evaporation under <u>air</u> of volatile species

3) Annealing between 150°C and 800°C under N_2/H_2



C ratio < 1%

The amount of coated carbon is <u>controlled</u> by the amount of acrylonitrile in the initial liquid mixture,

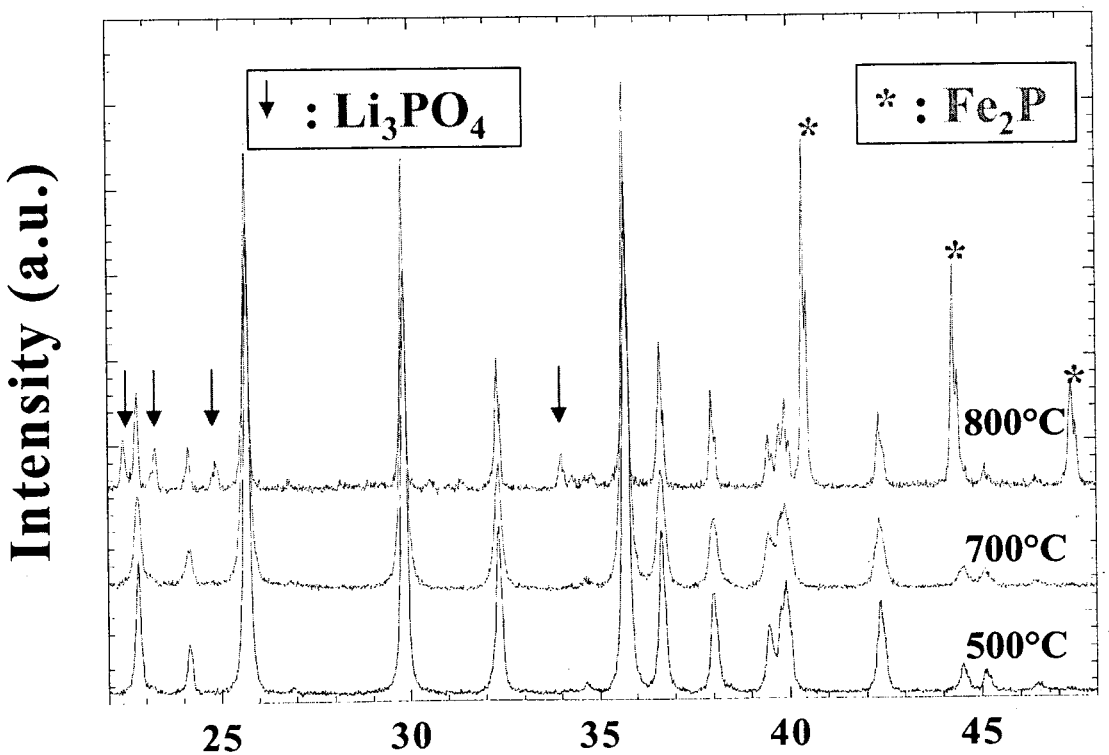


C ratio = 5%

C : $LiFePO_4$: *in situ* carbon coating from polyacrylonitrile

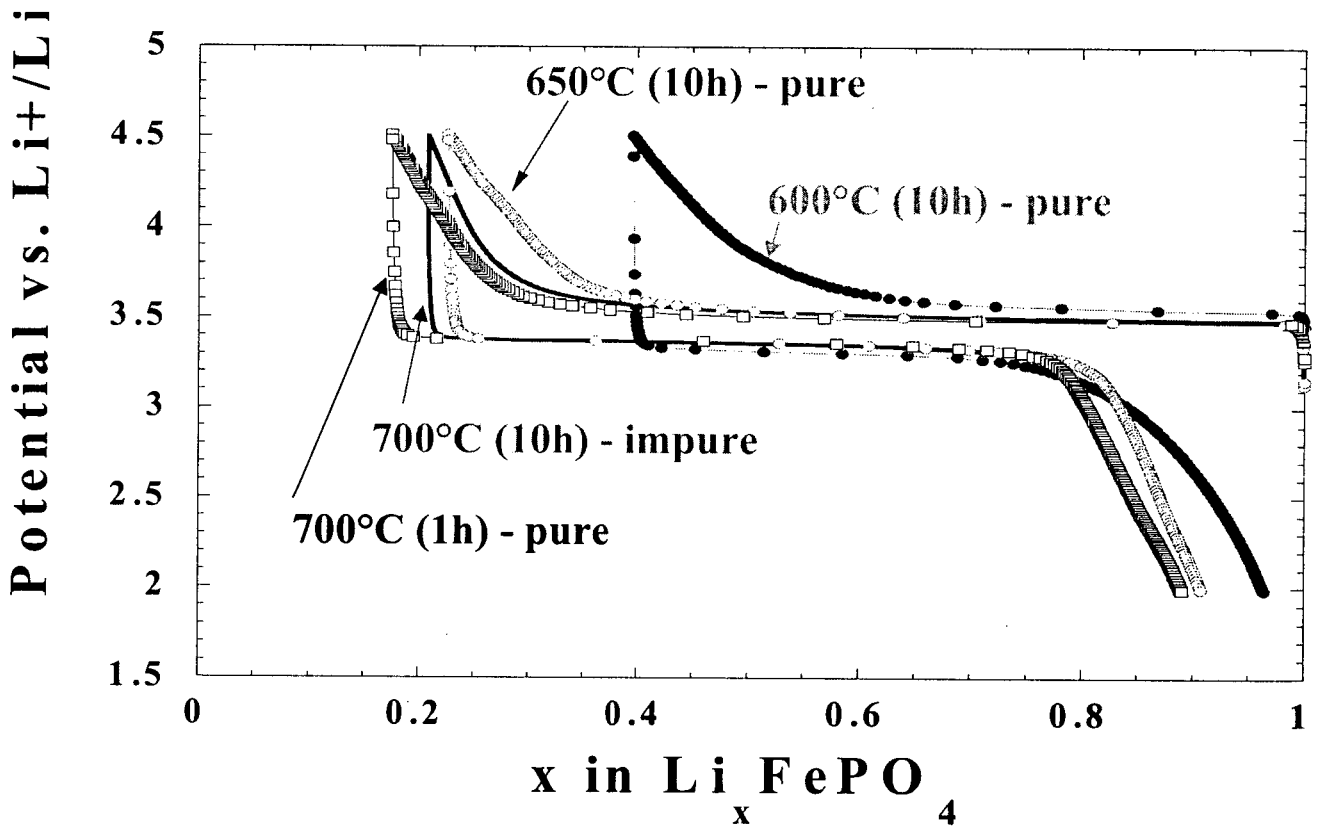
The annealing temperature (under N_2/H_2) of the composite is very important

: formation of Fe_2P and Li_3PO_4 if too reducing !!!



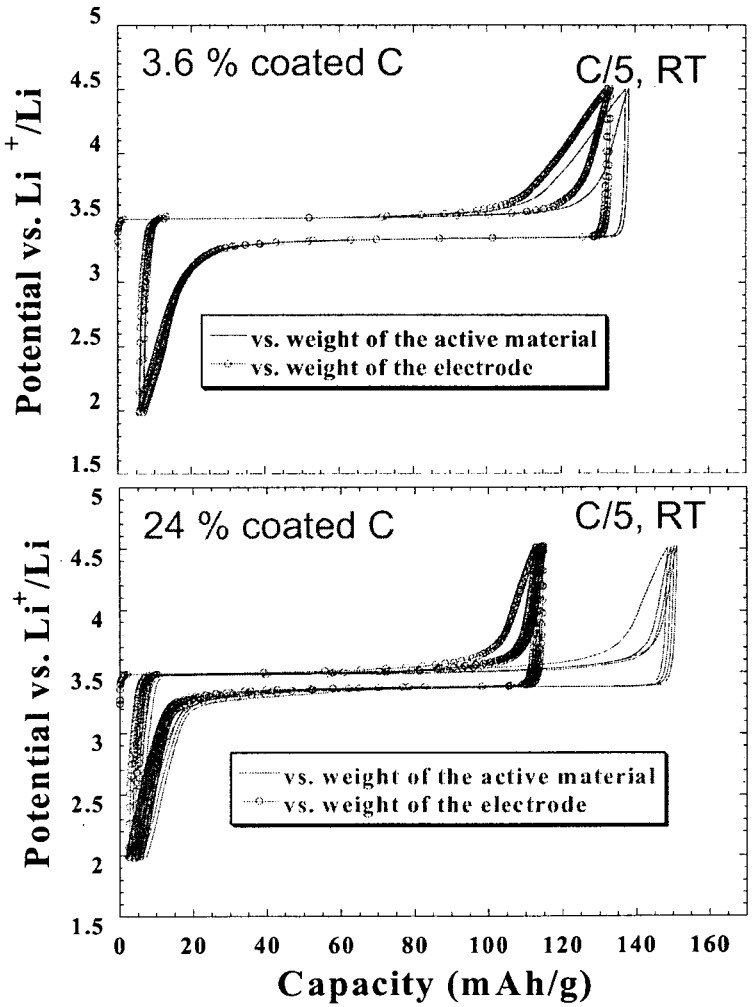
C : $LiFePO_4$: *in situ* carbon coating from polyacrylonitrile

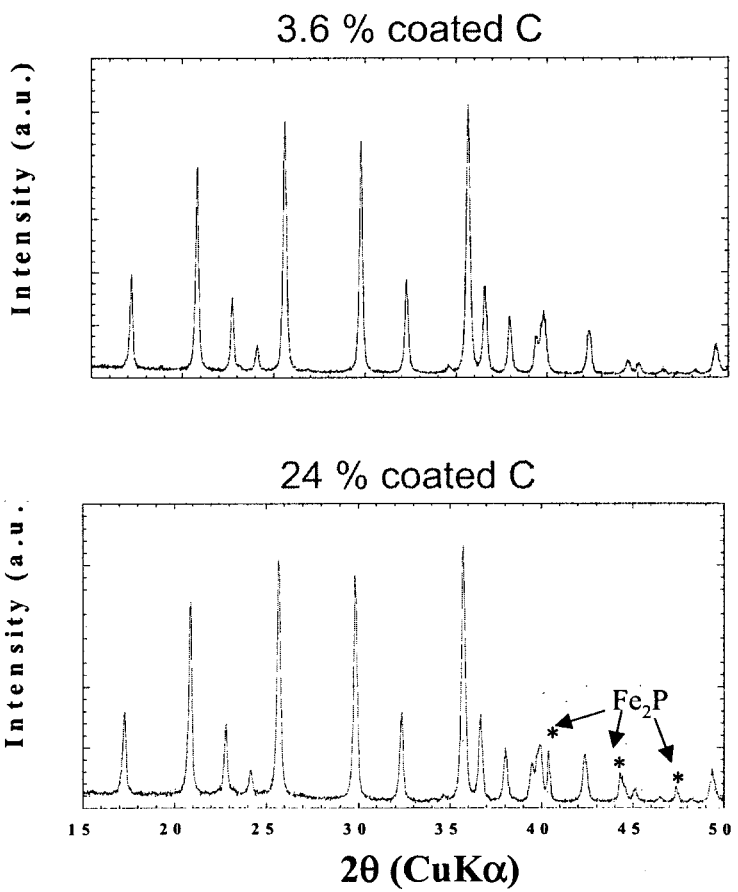
The <u>as-made composite</u> (18% of C) solid may be used <u>directly</u> as a positive electrode : the capacity depends on the amount of carbon coated and on impurities !!



The <u>as-made</u> composite may be used <u>directly</u> as a positive electrode :

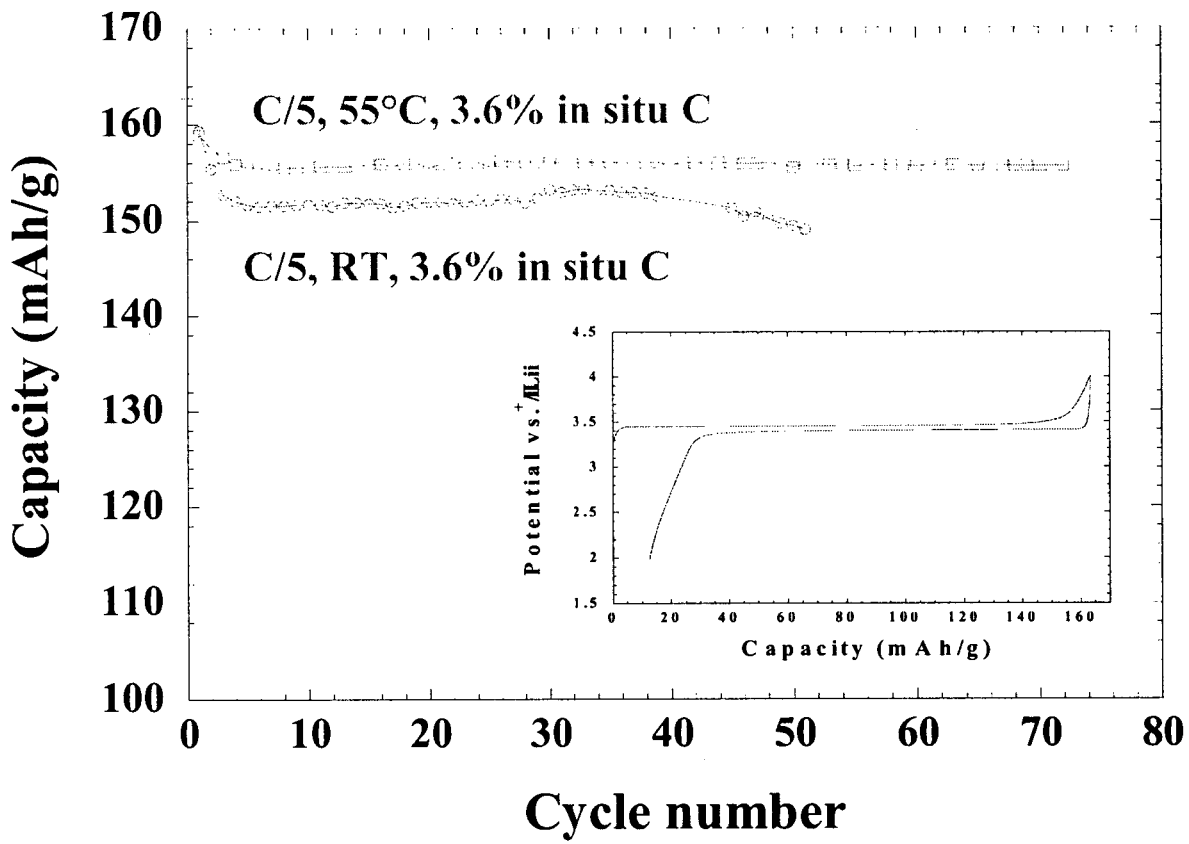
mAh/g of ELECTRODE ≠ mAh/g of ACTIVE MATERIAL



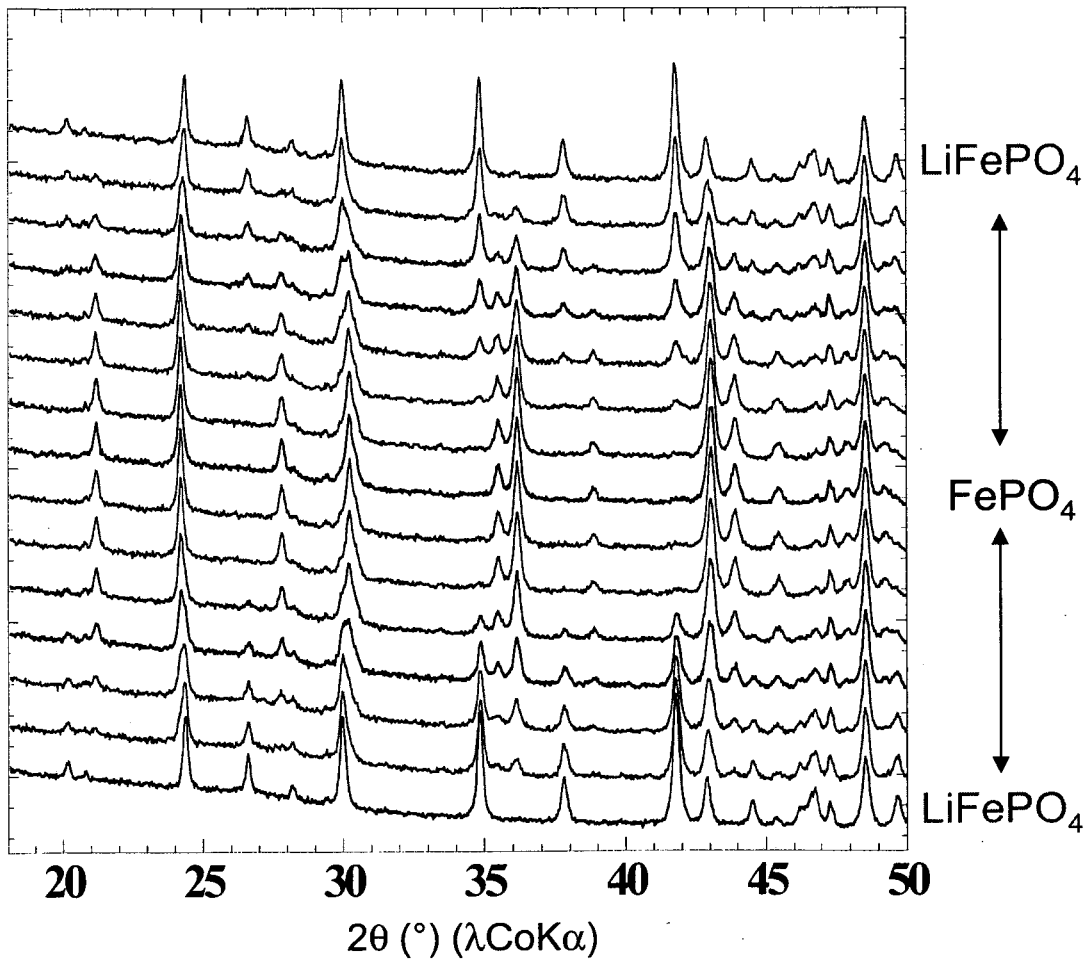


C : $LiFePO_4$, electrode configuration important too !!

The composite material is embedded in a Bellcore plastic film, coin-cells were fabricated for prolongated cycling, thick electrodes (~30 mg) were used……



C : $LiFePO_4$ / $FePO_4$: full, reversible, reaction achieved



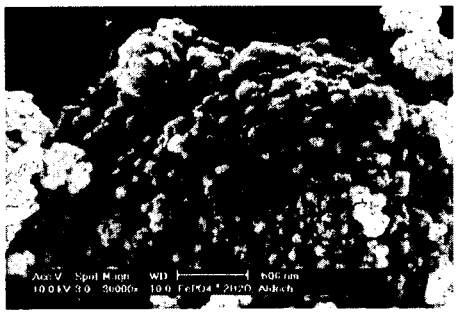
In situ XRD

CoKα,
PSD counter
θ–θ reflection

10 hours !!

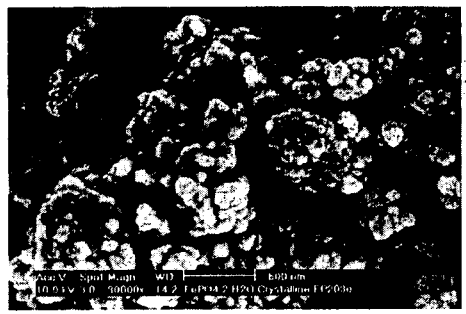
D : $Fe^{III}PO_4 . nH_2O$

Amorphous $FePO_4.nH_2O$



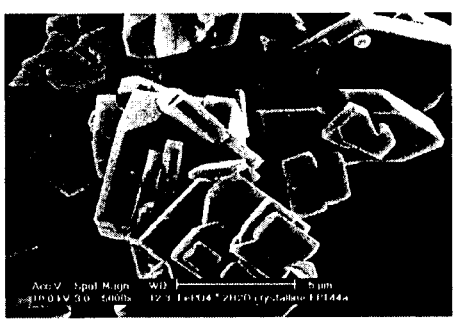
B.E.T = 29 m^2/g, < 100 nm

Amorphous $FePO_4$



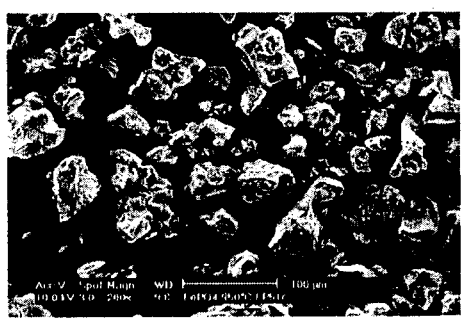
B.E.T = 28 m^2/g, < 100 nm

Crystalline $FePO_4.2H_2O$
Metastrengite



B.E.T = 2 m^2/g, ~10 µm

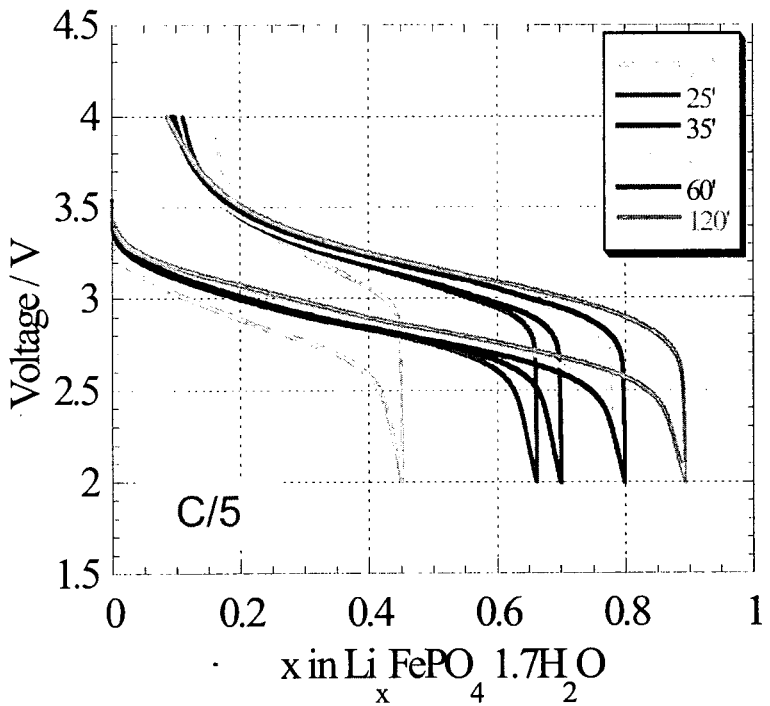
Crystalline α-$FePO_4$
Low quartz



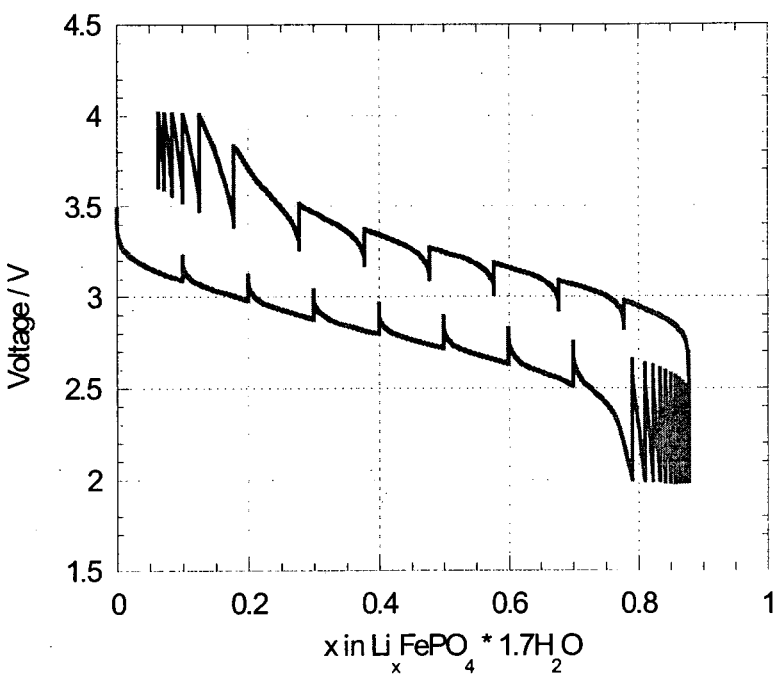
B.E.T < 1 m^2/g, ~50µm

D : amorphous $FePO_4 . 1.7H_2O$ (Aldrich)

Ball-milling !!

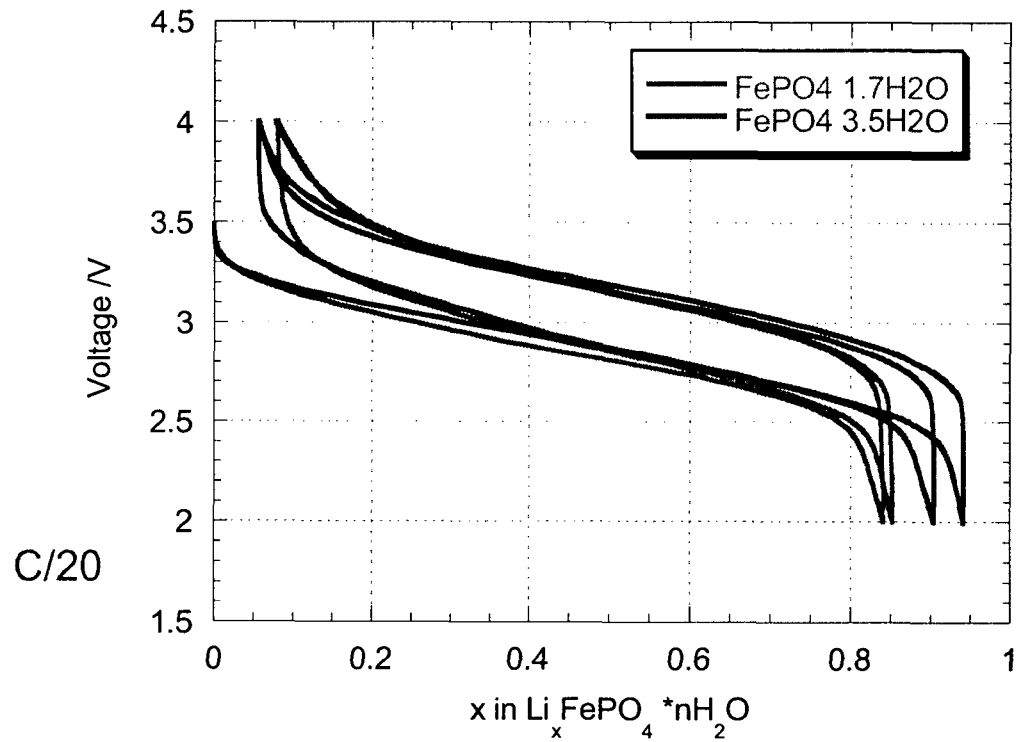


GITT



Average potential = 3.0 V vs. Li^+/Li : <u>local</u> inductive effect

D : amorphous $FePO_4 . nH_2O$ (Aldrich)

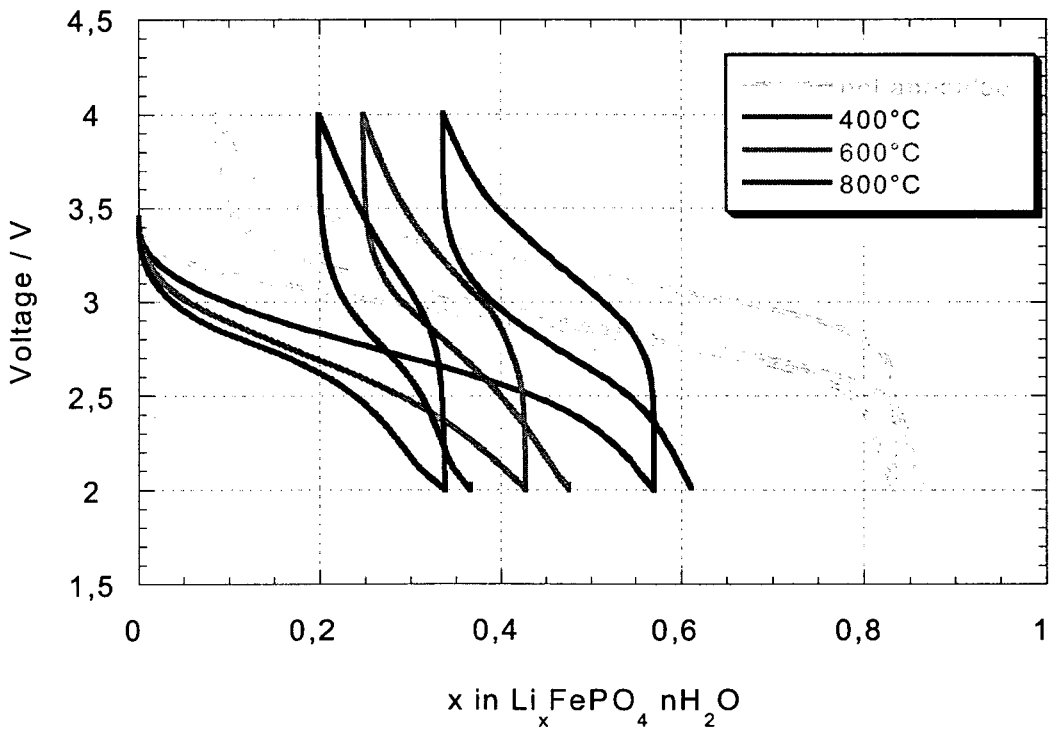


Beneficial role of "H_2O" : promote ion transport ??

D : Annealing $FePO_4 . nH_2O$

800°C ← 600°C ← 400°C ← Pristine

$FePO_4$ $FePO_4$ $FePO_4$ $FePO_4.1.7H_2O$



D : Crystalline $FePO_4 . 2H_2O$ (metastrengite)

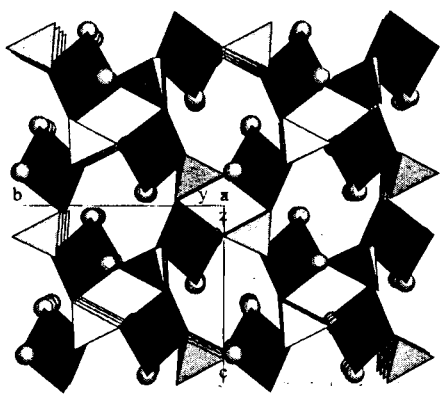
$Fe_2(SO_4)_3*xH_2O$;
$Fe(NO_3)_3*9H_2O$;
$FeCl_3*6H_2O$…

1:1

H_3PO_4;
$NH_4H_2PO_4$;
NaH_2PO_4;
Na_2HPO_4…

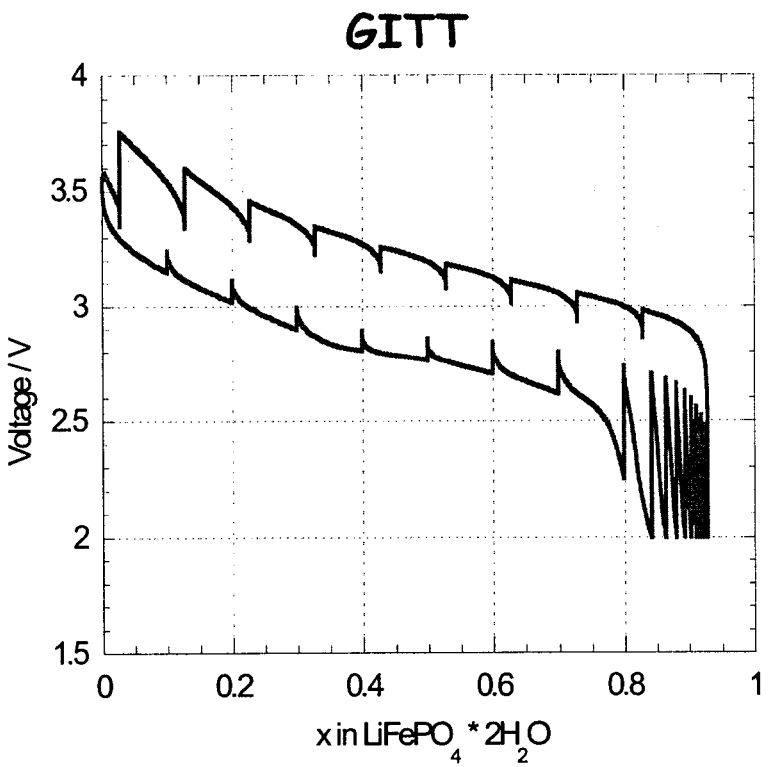
100°C in reflux, acidic pH,
stirring for days

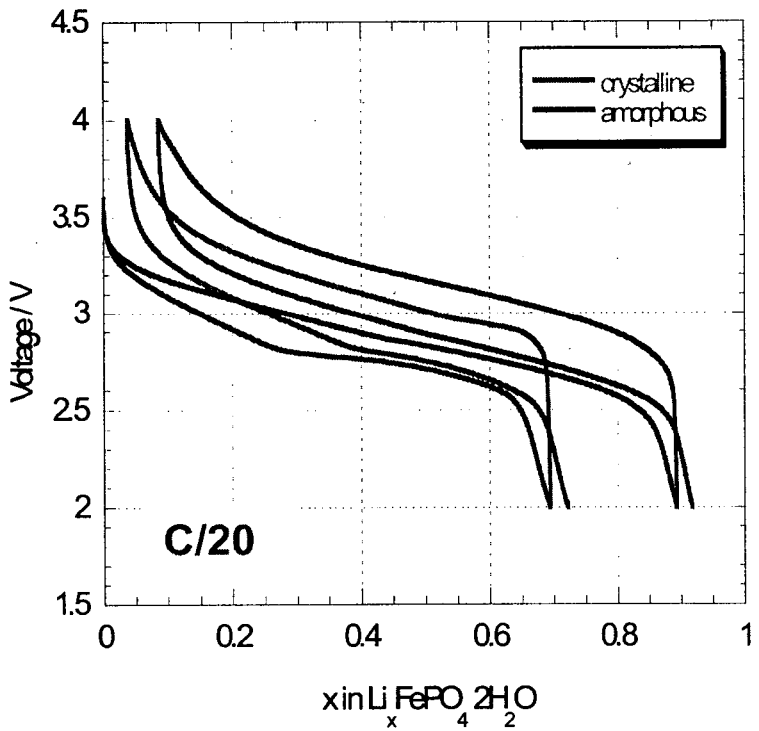
Filtering,
washing with water,
drying (55°C)



$FePO_4 . 2H_2O$ H_4FePO_6

D : Crystalline $FePO_4 . 2H_2O$ (metastrengite)





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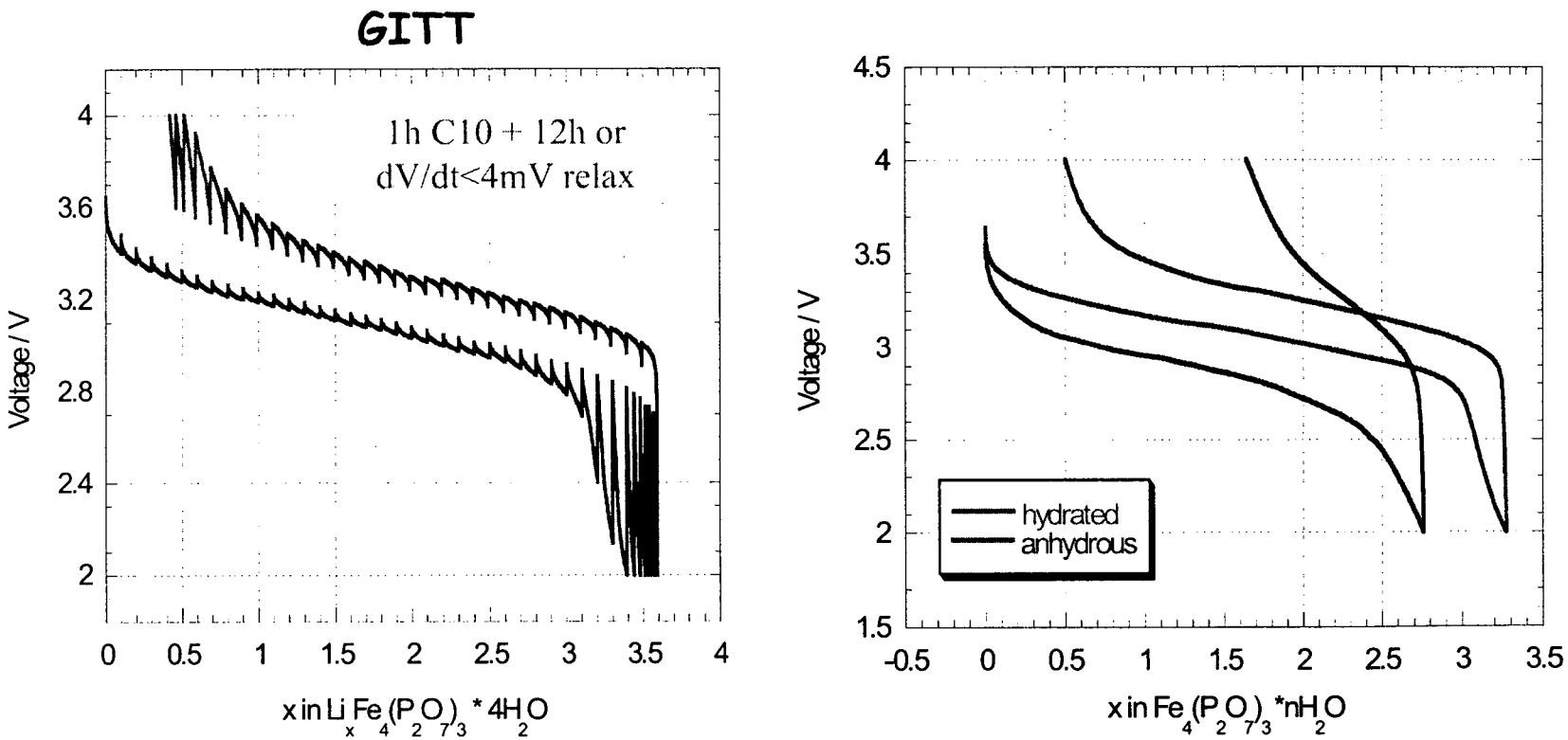
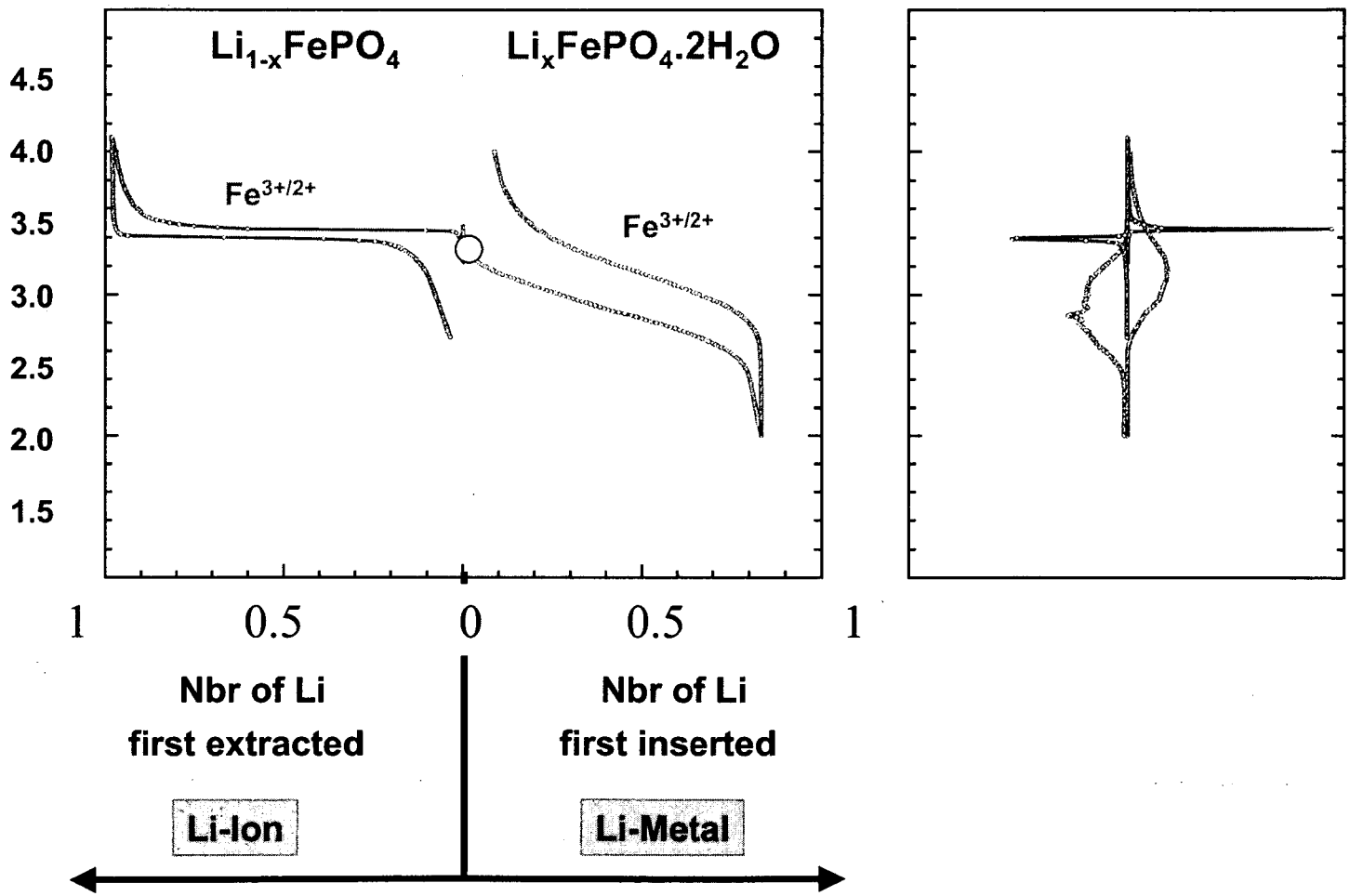
E : amorphous $Fe_4(P_2O_7)_3 . 4H_2O$ (Aldrich)

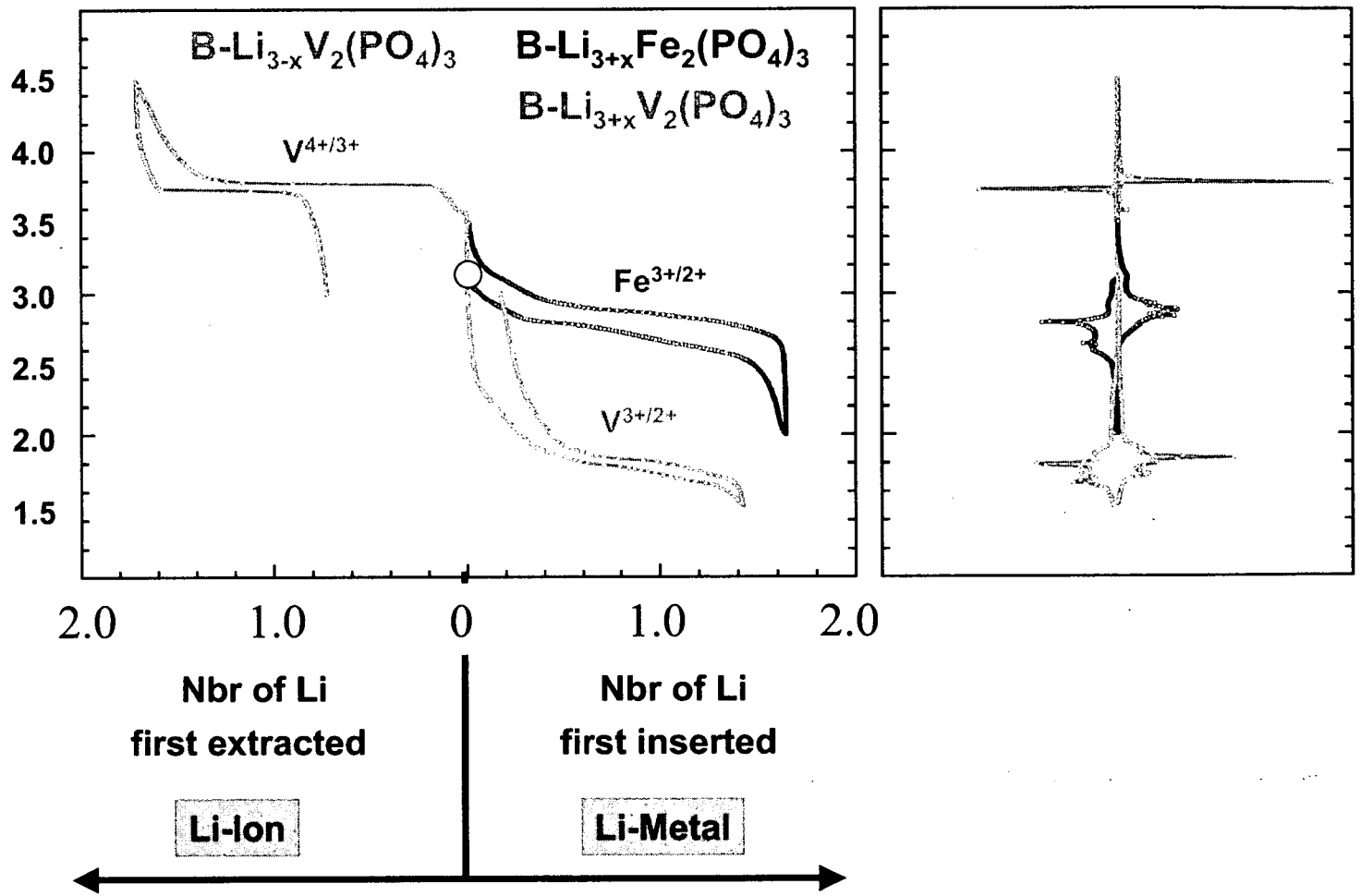


Average potential = 3.2 V vs. Li^+/Li : <u>local</u> inductive effect stronger for Fe/P = 2/3

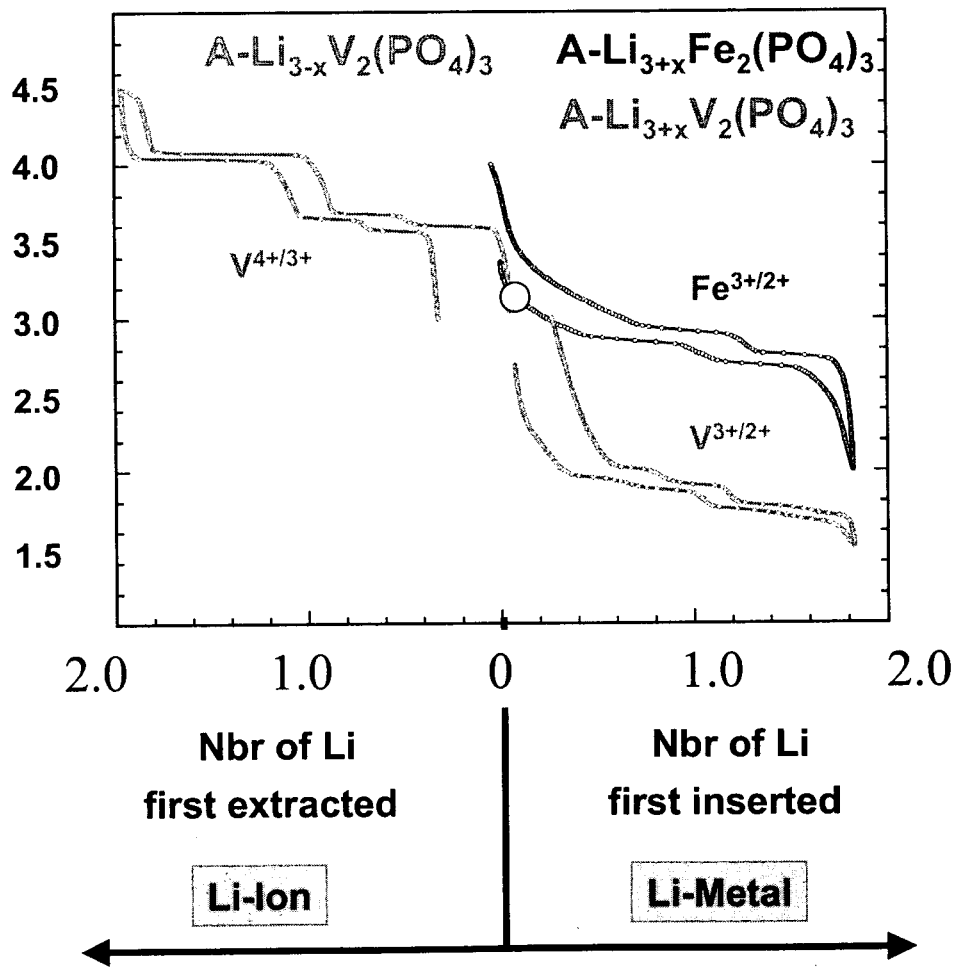
SUMMARY : Fe/P = 1

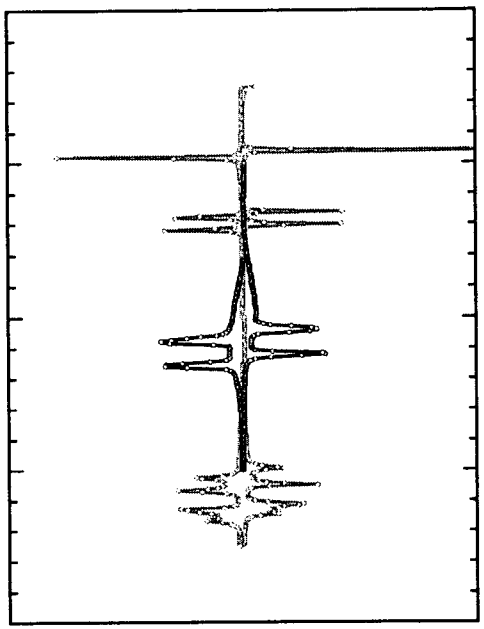


SUMMARY : M/P = 2/3

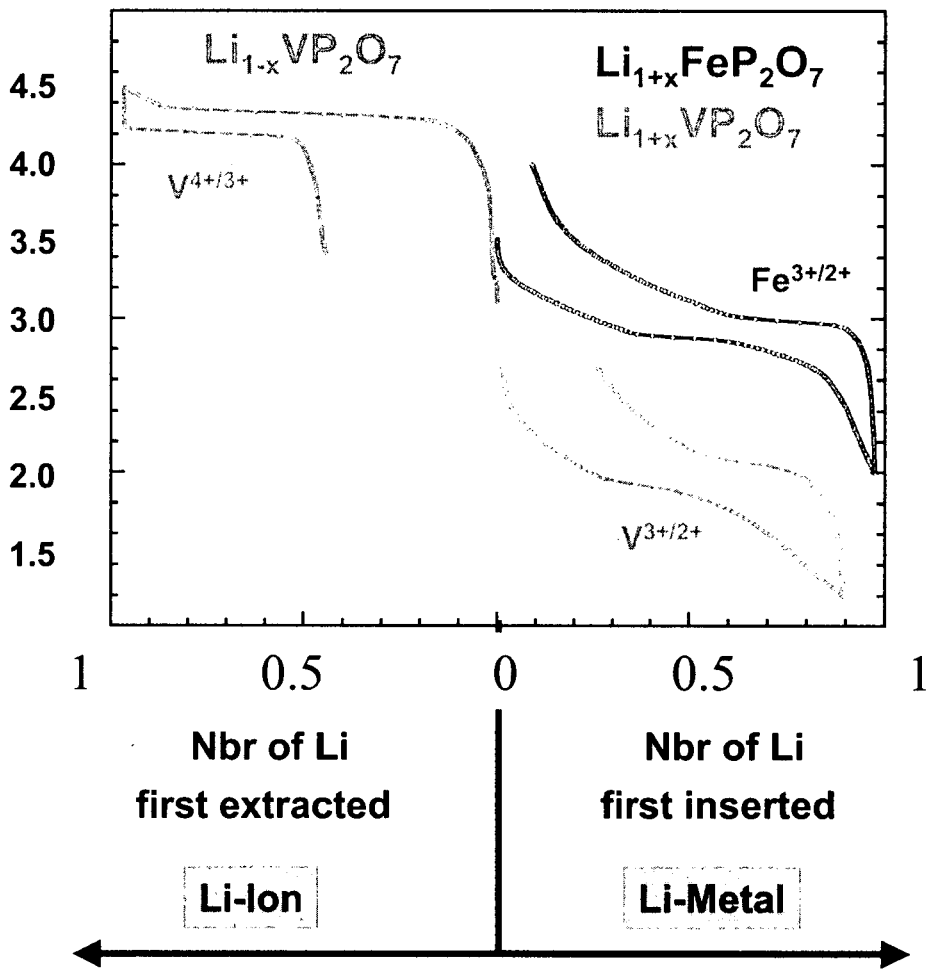


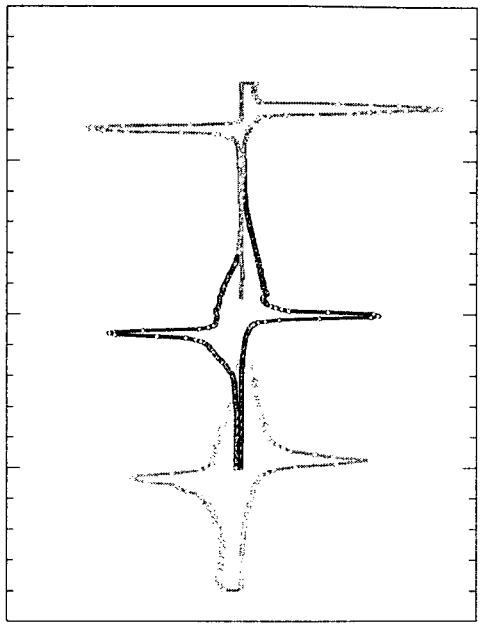
SUMMARY : M/P = 2/3



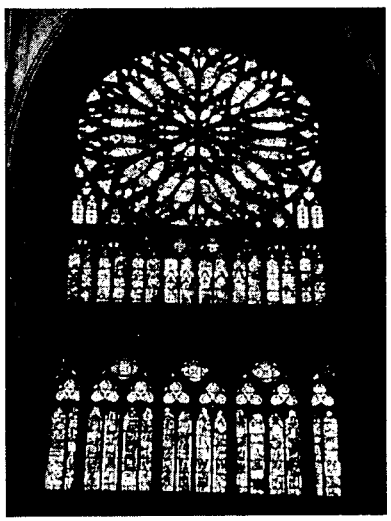


SUMMARY : M/P = 1/2





Thanks ….



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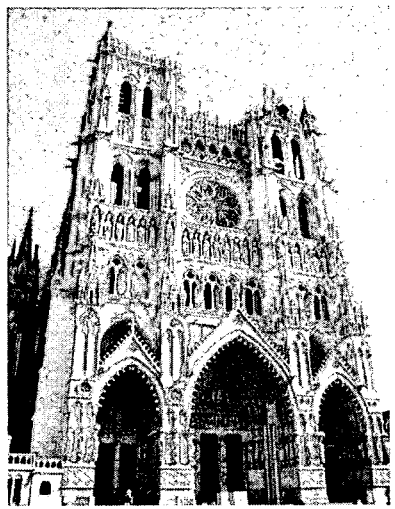
Mathieu Morcrette

Jean-Marie Tarascon



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