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Low Cost SiO_x-Graphite and Olivine Materials

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DOE-BATT Review Meeting
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Project ID: ES048

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: March 2009
- End date: December 2012
- 40% completed

Barriers

- Low energy
- Poor cycle/calendar life

Budget

- Total Project Funding: $730K
- FY10 funding $365K
- FY09 funding $365K

Partners

- V. Battaglia, V. Srinivasan (LBNL)
- J. Goodenough (U. Texas)
- P. Roth (SNL)
- C. Julien-A. Mauger (U. Paris 6)
- D. Wu (Phet)
- C. Sotowa (Showa-Denko)

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Objective

Synthesize and evaluate doped manganese phosphate as low cost cathode material

Replace graphite anode with an alternative material that meets the requirement for low cost and high energy.

Develop *in-situ* and *ex-situ* SEM and TEM techniques to analyze the SEI layer properties.

Approach

- **HQ efforts in the BATT program to investigate and improve SEI layers on alternative anodes include several tasks:**
  - **prepare laminate anode films and powders, and supply them to investigators in Topic 3a involved with SEI analysis using different techniques (*in-situ*, *ex-situ*).**
  - **Identify benefits of binder (SBR, Polyimide, EPDM) compared to PVDF in new anode and cathode materials.**

- **Investigate performance of alternative high-capacity anode and Mn-based olivine materials in laboratory cells**
  - **prepare laminate cathode films and powders and supply them to BATT investigators for evaluation.**

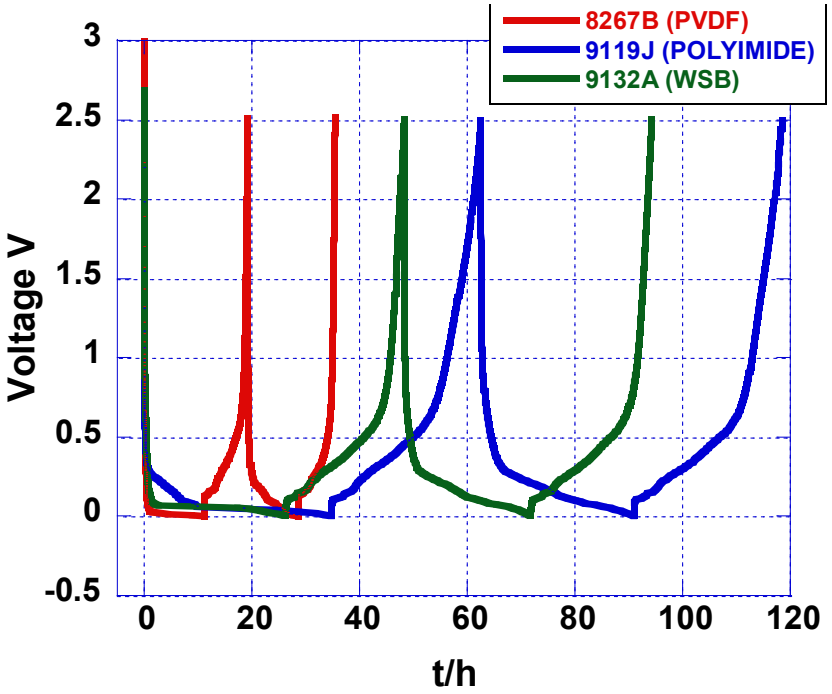
- **Utilize *in-situ*, *ex-situ* SEM and TEM to investigate the SEI layer on the anode and phase transformation in $LiFePO_4$.**

Technical Accomplishments

- **Completed evaluation of the effect of the binder on the SiOx anode performance.**

- **Developed process to improve the performance of Mn-based olivine materials.**
- **Developed *in-situ* and *ex –situ* SEM and TEM techniques to investigate the SEI layer on the anode and phase transformation in olivines and oxides.**

(SiO_x+ Graphite (1:1)) Anode: Binder Effect



Li coin type cell
1M $LiPF_6$-EC-DEC+2%VC

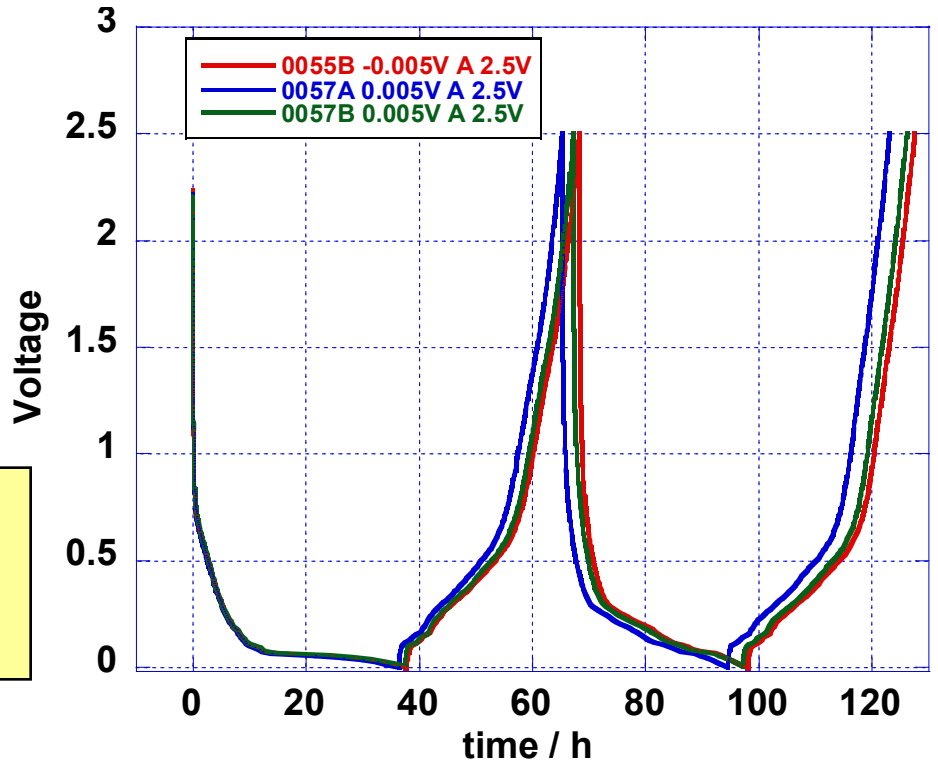
Discharge/Charge: C/24
T=25°C

	PVDF			SBR			Polyimide		
	Capacity (mAh/g)			Capacity (mAh/g)			Capacity (mAh/g)		
	Discharge	Charge	Eff. (%)	Discharge	Charge	Eff. (%)	Discharge	Charge	Eff. (%)
Cycle 1	642	472	73,5	995	843	85	1332	1067	80,1
Cycle 2	541	394	72,8	904	861	95	1085	1058	97,5

- **The highest reversible capacity of the (SiOx +Gr) was observed with the polyimide:**
  Capacity: Polyimide > SBR > PVDF
- **The cell with SBR had the highest 1st cycle coulombic efficiency (CE):**
  1st CE: SBR > Polyimide > PVDF

(SiO_x+ Graphite (1:1)) Anode: Cut-off Voltage

Binder: Polyimide
Discharge/Charge: C/24
1M $LiPF_6$-EC-DEC+2%VC



- **Reversible capacity and coulombic efficiency of (SiO_x + graphite) anode were affected by the discharge cut-off voltage.**

	V cut off (mV)	1st Ah. Eff. (%)	2ed Ah. Eff. (%)	Rev.Cap. (mAh/g)
0057A	**0.0**	**79.1**	**97.3**	**1098**
0057B	**5.0**	**80.1**	**98.4**	**1128**
0055B	**-5.0**	**79.3**	**96.9**	**1111**

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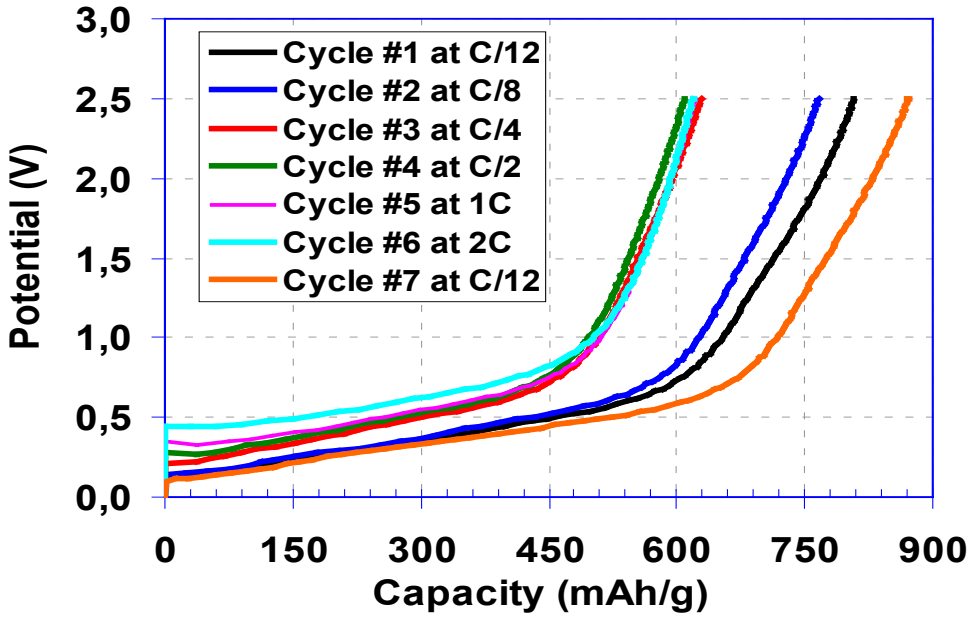
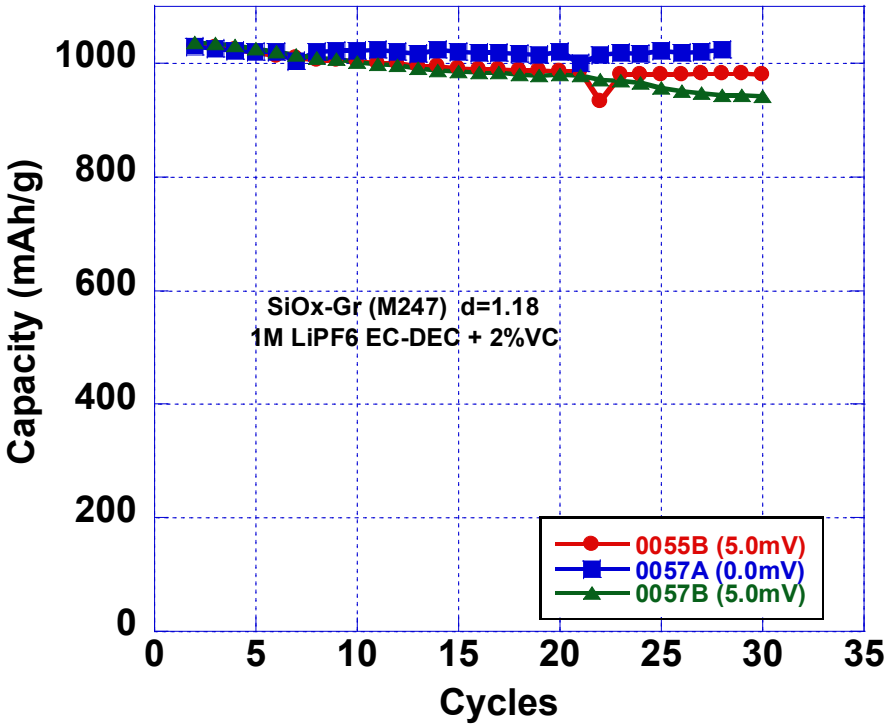
Technical Accomplishments

(SiO_x+ Graphite (1:1)) Anode

Binder: Polyimide
Discharge/Charge: C/12
1M $LiPF_6$-EC-DEC+ 2%VC

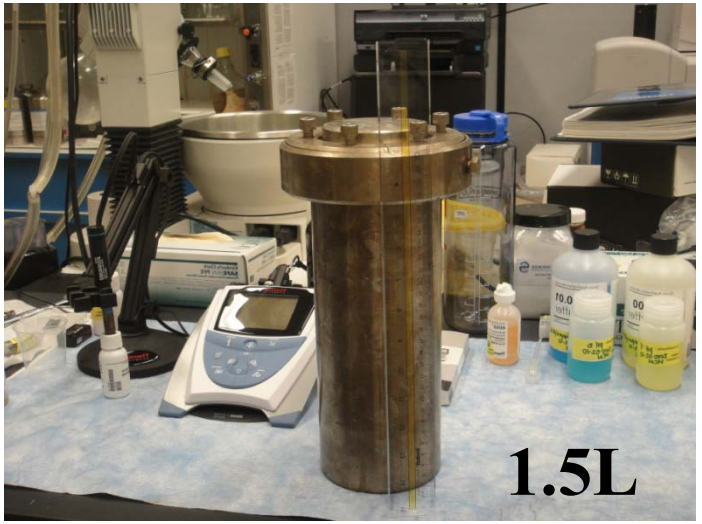




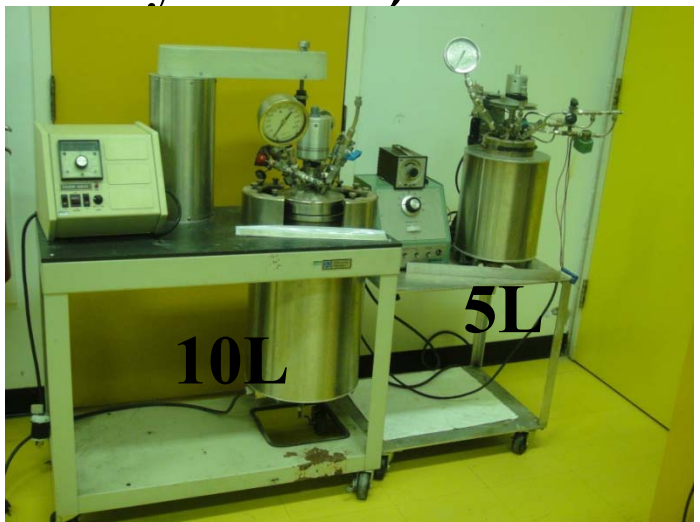
- **The cut-off voltage had a small effect on the capacity fade with cycling at C/12**
- **A stable capacity (600mAh/g) was observed from C/4 to 2C, and still the cell delivered > 800 mAh/g in the following cycle at C/12 rate.**

$LiMn_{(1-x)}M_xPO_4$ Cathode Material Scale-Up

- $LiMn_{(1-x)}M_xPO_4$ material synthesis techniques:
  - Hydrothermal process
    - Wet milling
      - carbon coating ~ 2%



- Electrode:
  - $LiMn_{(1-x)}M_xPO_4$ (from hydrothermal synthesis)
  - Composition:
    5% VGCF, 10% carbon black,
    10% PVDF



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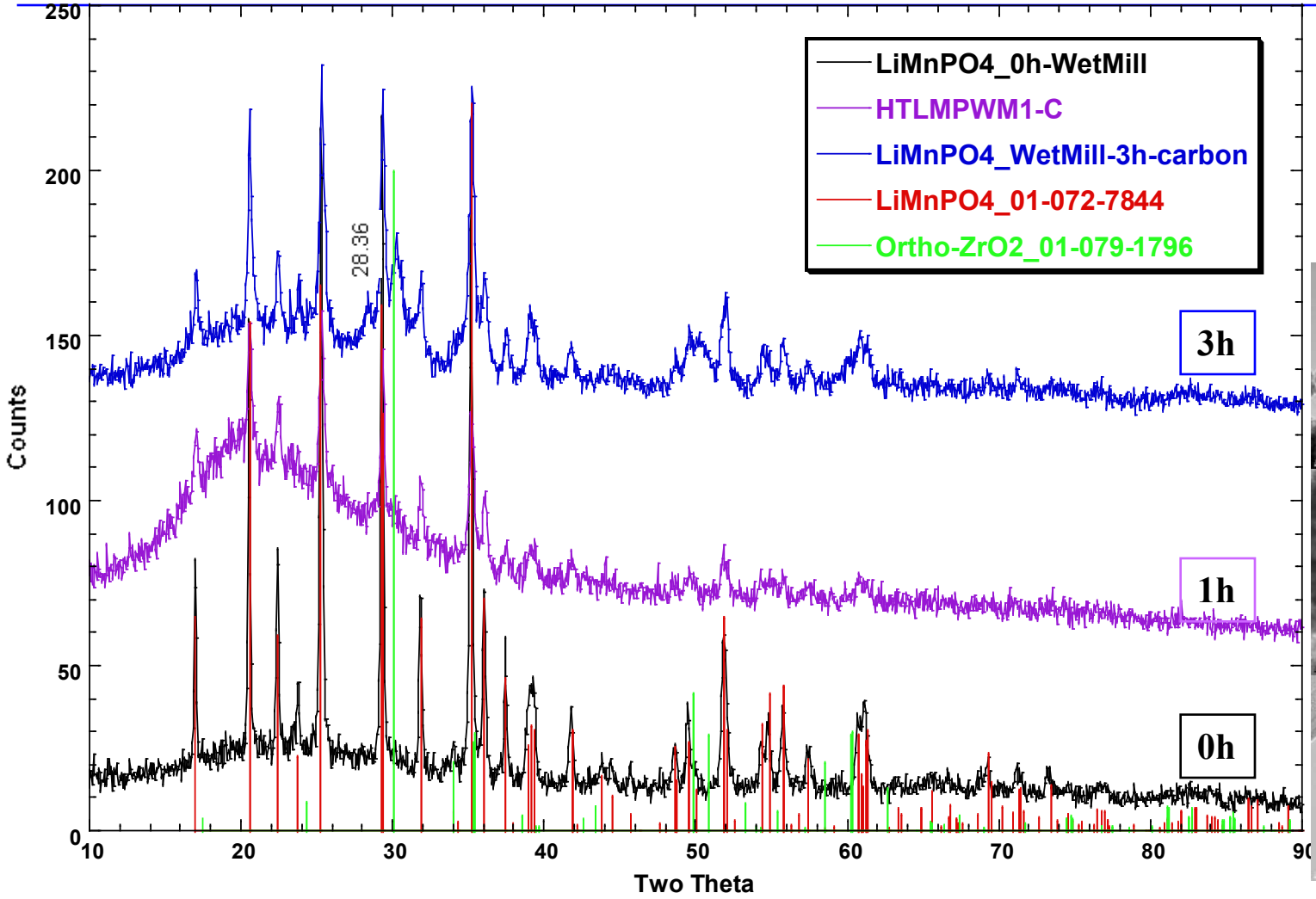
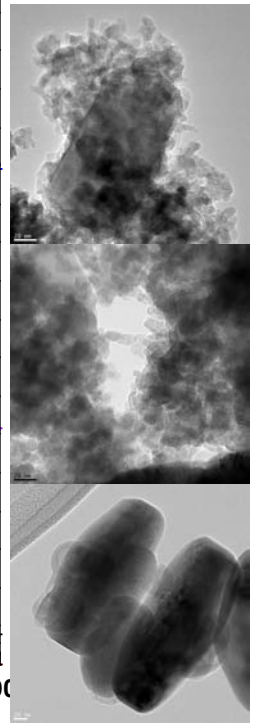
XRD of $LiMnPO_4$: wet milled and C-coated





-The crystallinity of the olivine structure was reduced by wet milling.

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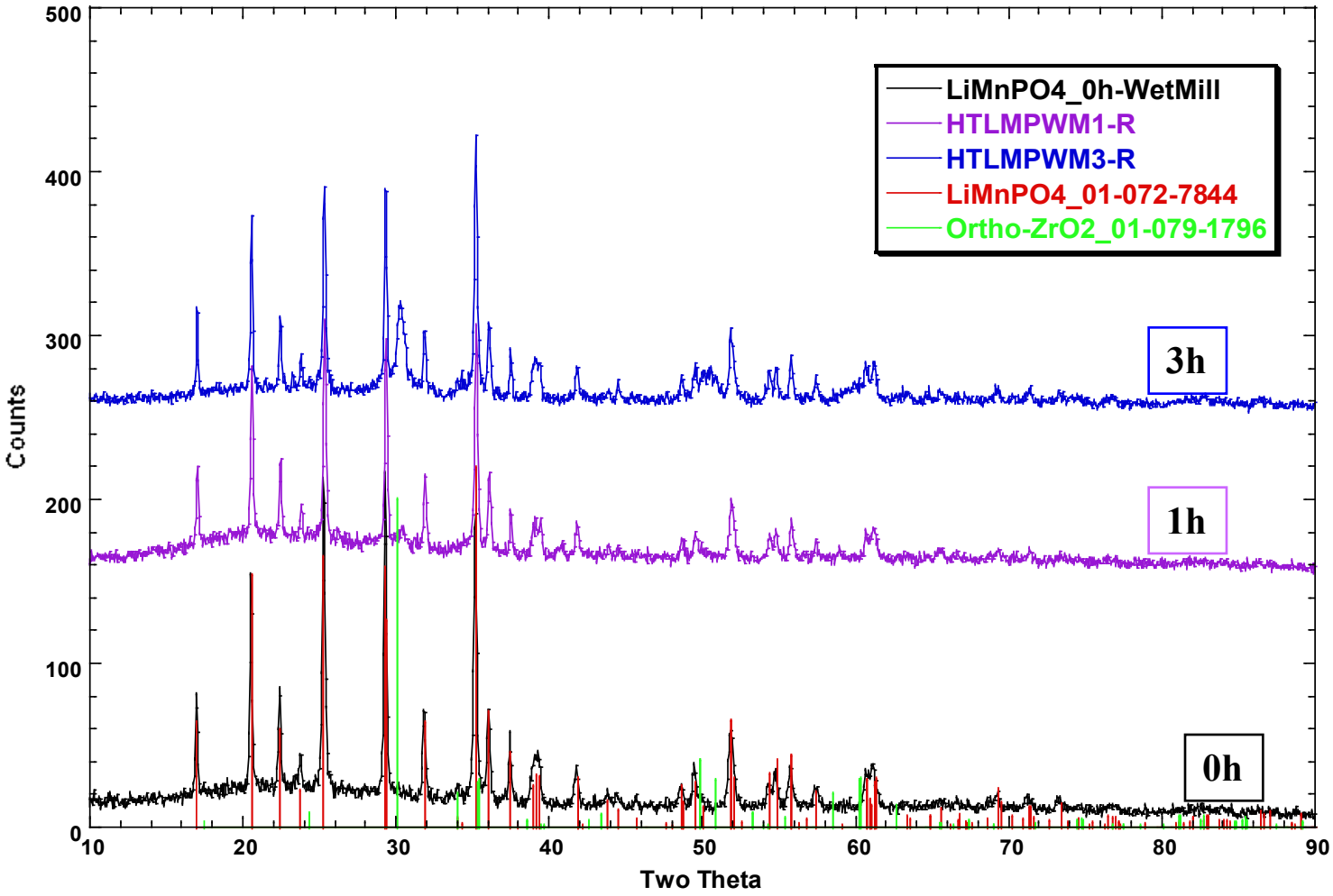
XRD of $LiMnPO_4$: wet milled and C-coated



- The crystallinity of the carbon-coated samples increased after re-heating at 700°C.

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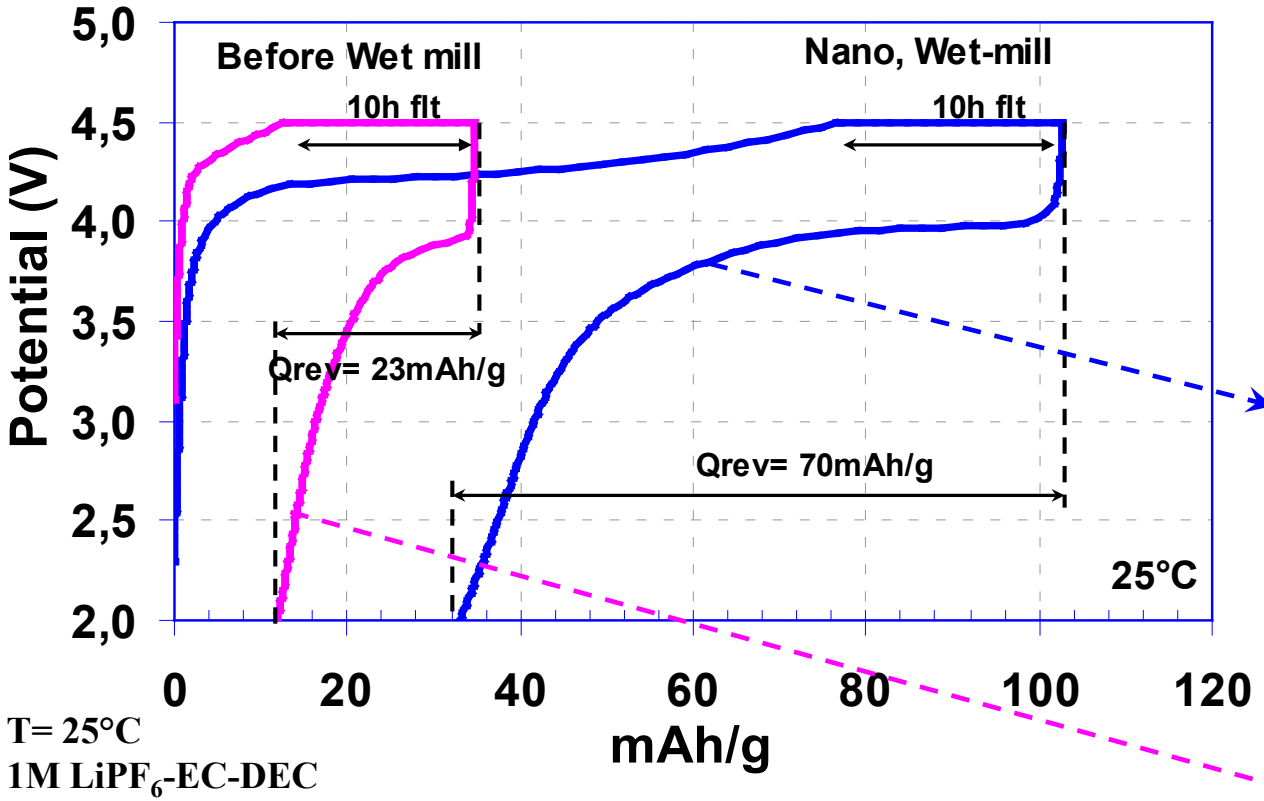
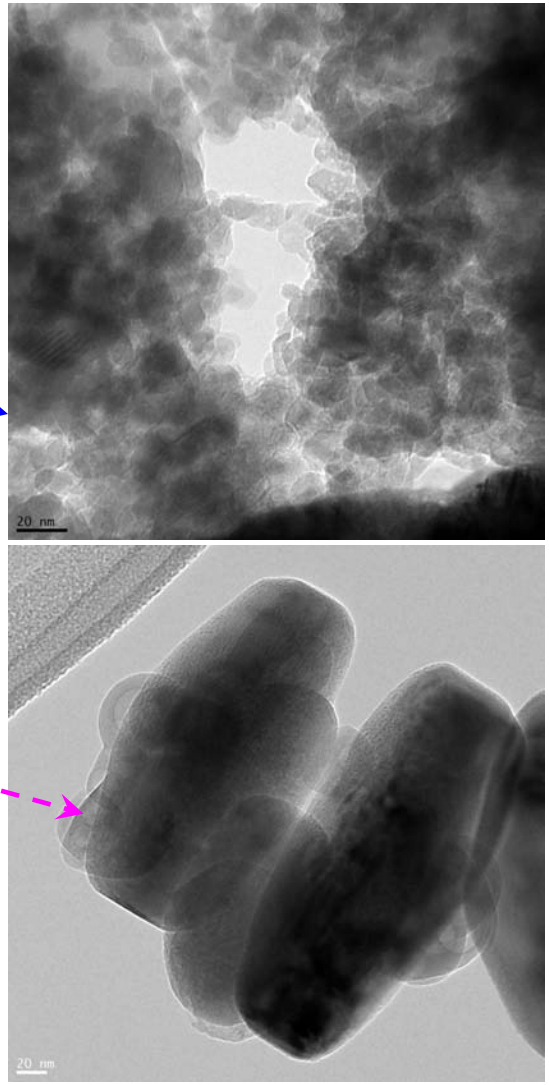
Nano-$LiMnPO_4$ Cathode Material

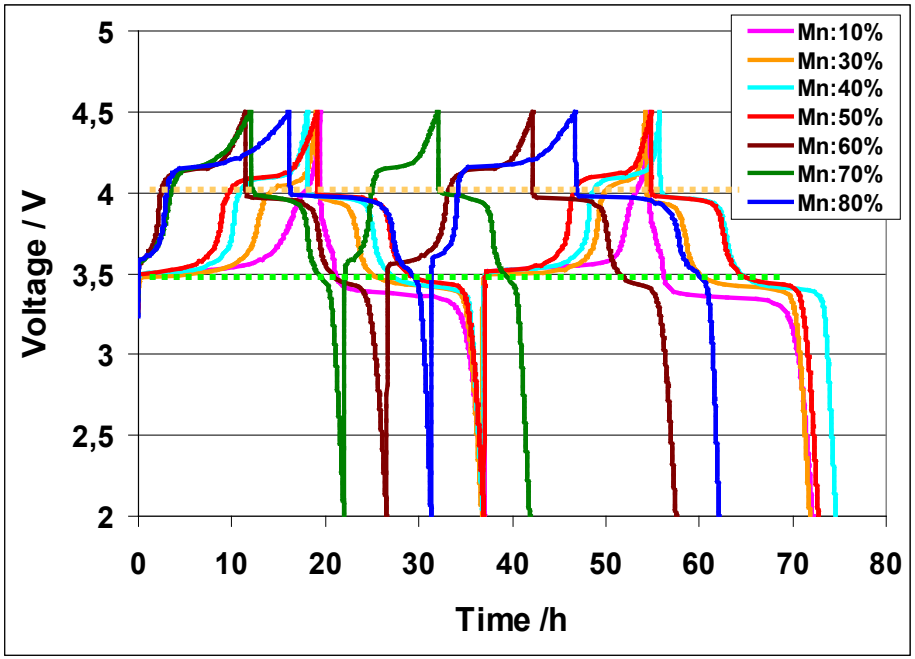


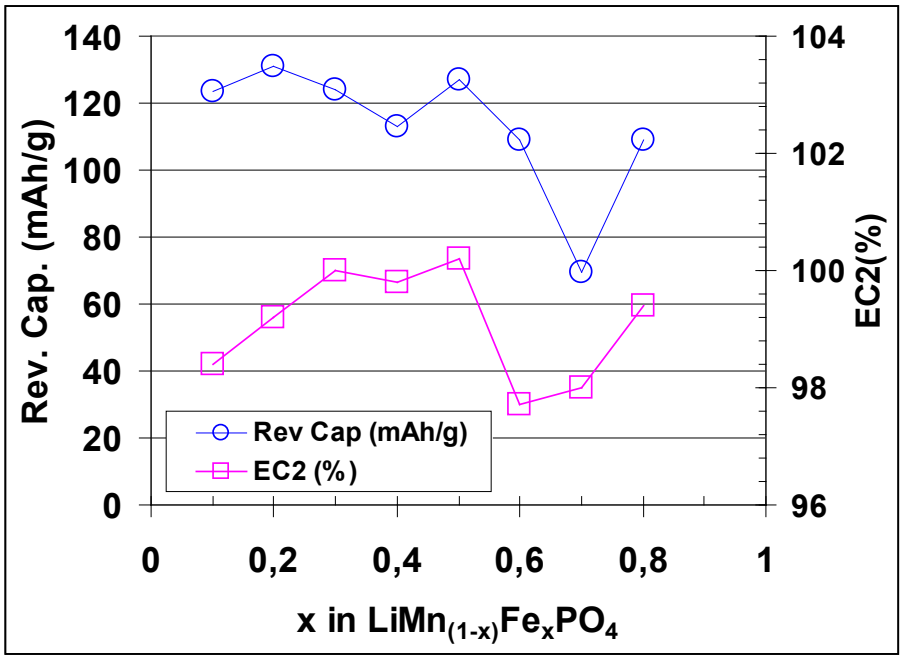
T= 25°C
1M $LiPF_6$-EC-DEC



- The 1st cycle capacity of C-LiMnPO4 increased from 23 mAh/g to 70mAh/g after nano wet-mill.

$LiMn_{(1-x)}Fe_xPO_4$ Cathode Material





Rate: C/24, T= 25°C
1M $LiPF_6$-EC-DEC

-The reversible capacity of Fe-doped LiMnPO4 at RT increased.
-A stable 4V plateau was observed even with 80% Mn.

Technical Accomplishments

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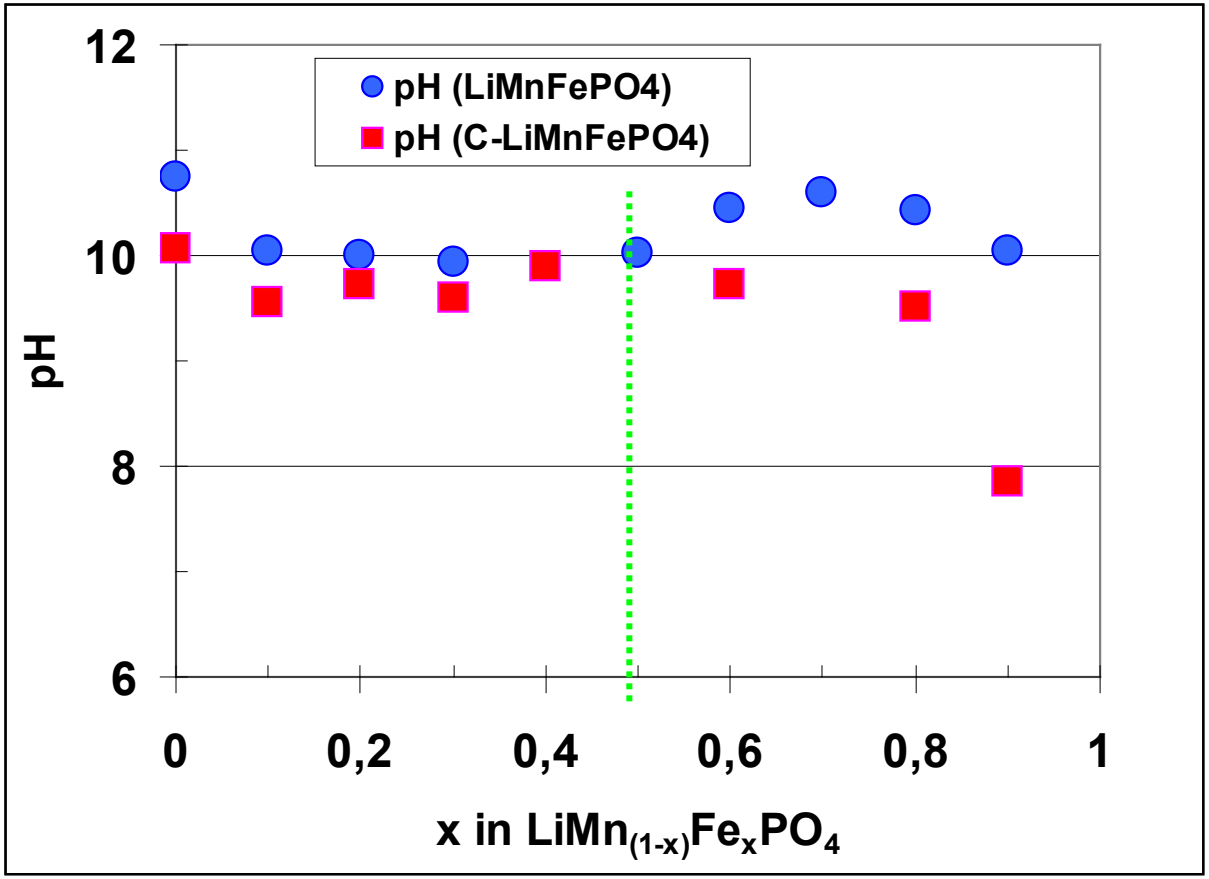
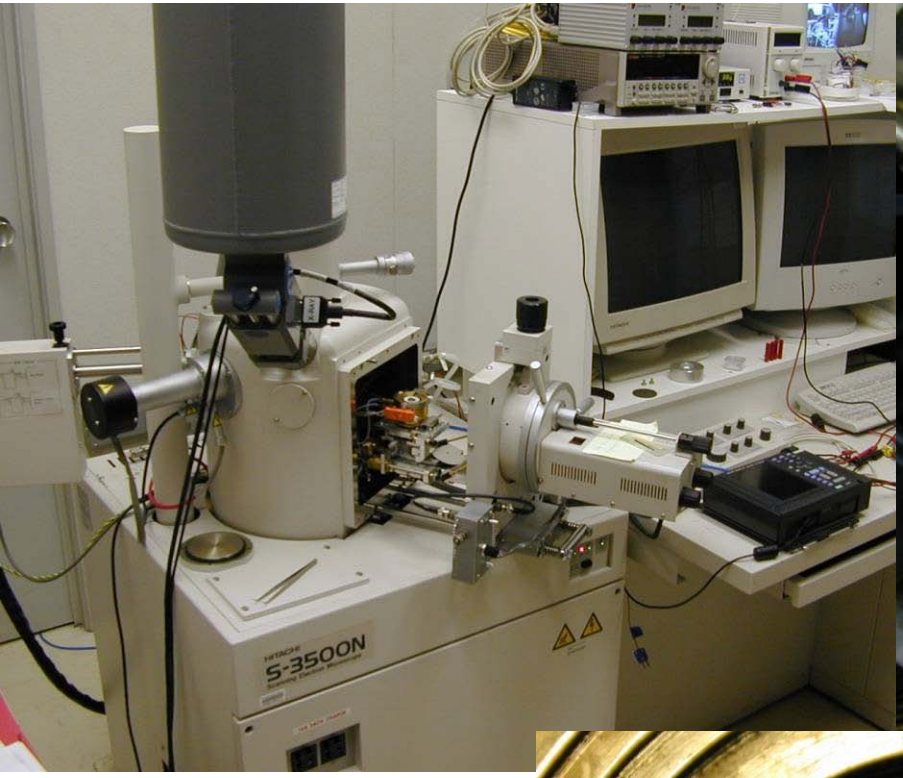
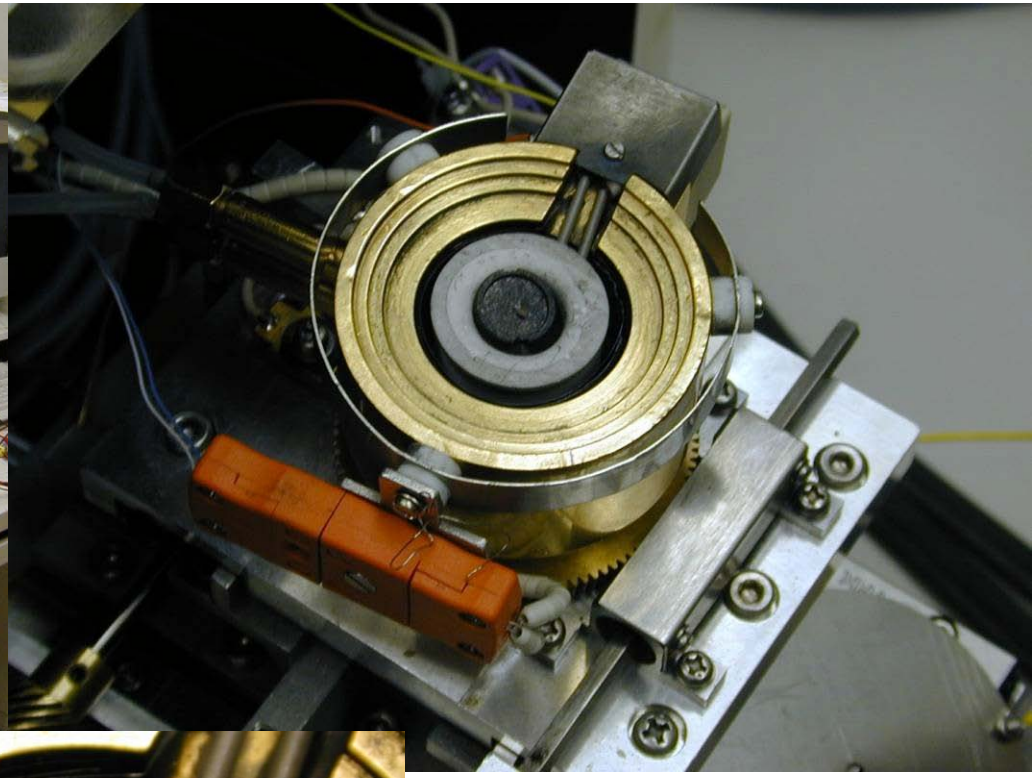
$LiMn_{(1-x)}Fe_xPO_4$ Cathode Material

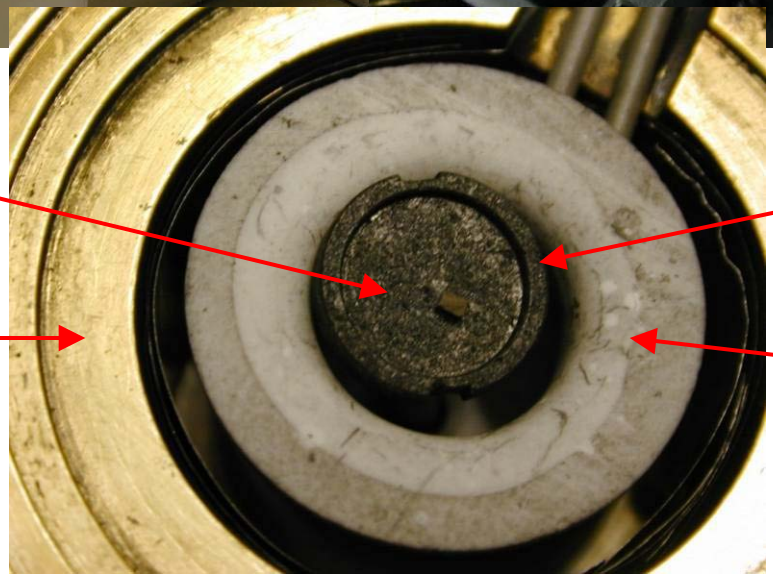


- The pH of the C-coated material decreased when Mn is > 0.5.

In situ SEM studies of $Li(Fe,Mn)PO_4$ melts (low cost)







material

graphite crucible

insulating ceramics

furnace

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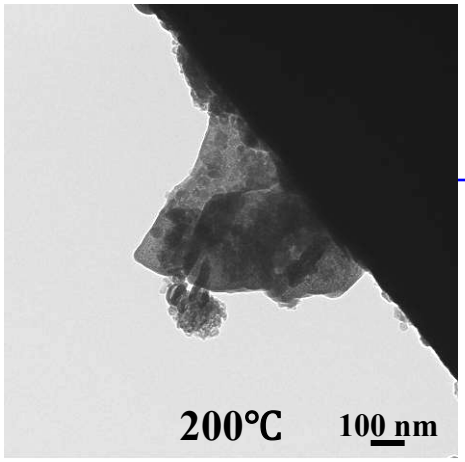
In-Situ Studies by TEM

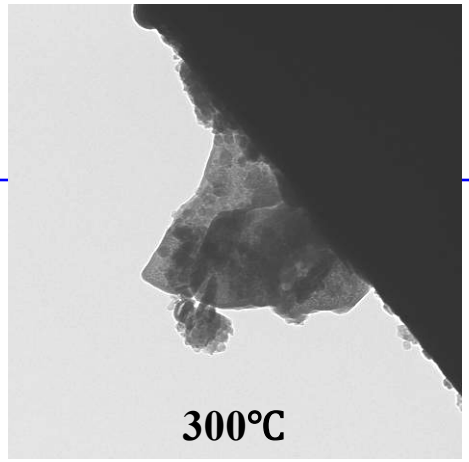
I) Starting material : Fe, Li-precursor, Phosphor-precursor + polymer

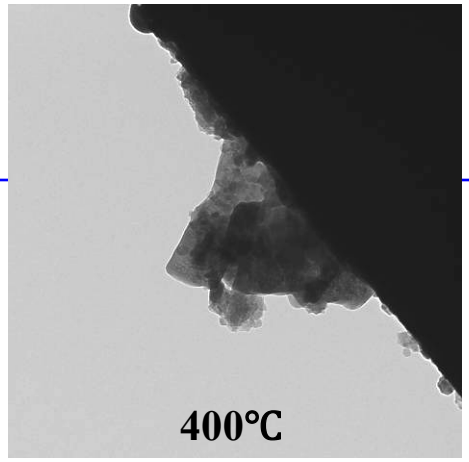
heat at 700 °C in N_2 gas

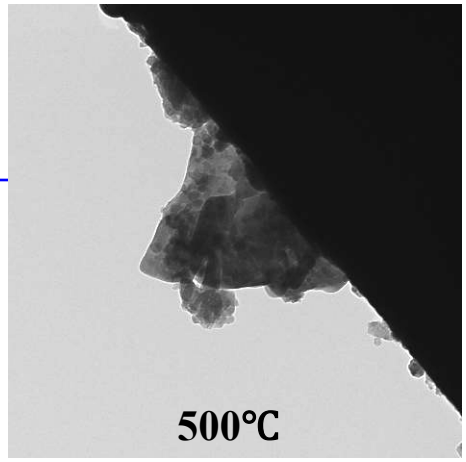
II) C- LiFePO4 : heat 300- 900 °C

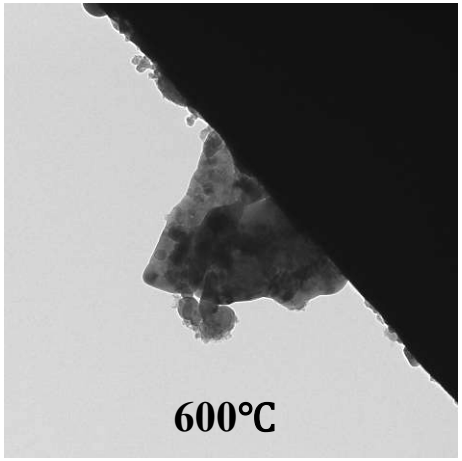
III) Doping effect ? : Mg, V, Mn, Nb, Zr etc…

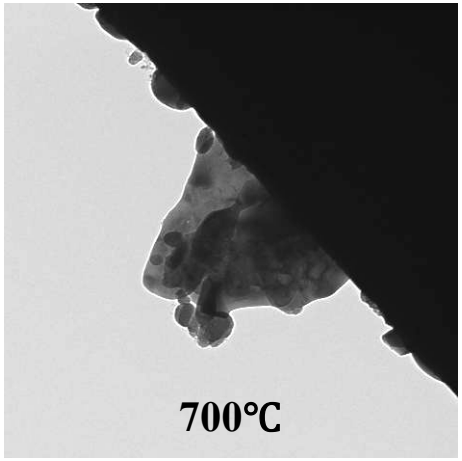


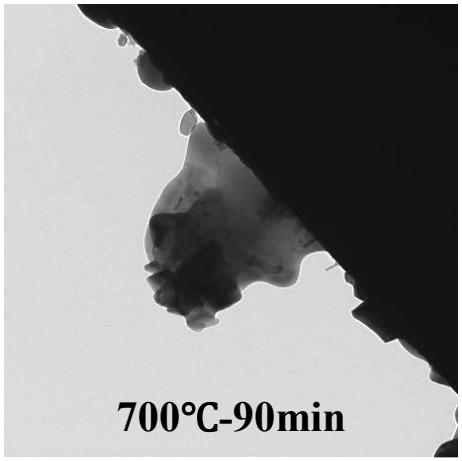


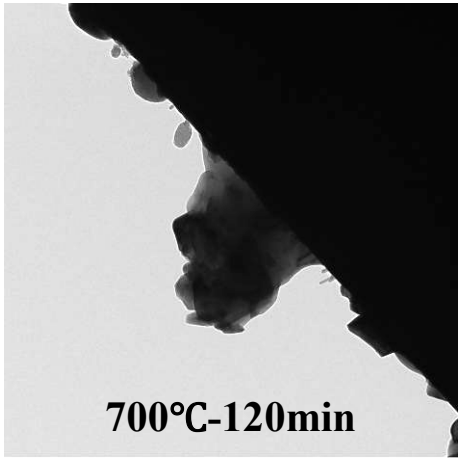


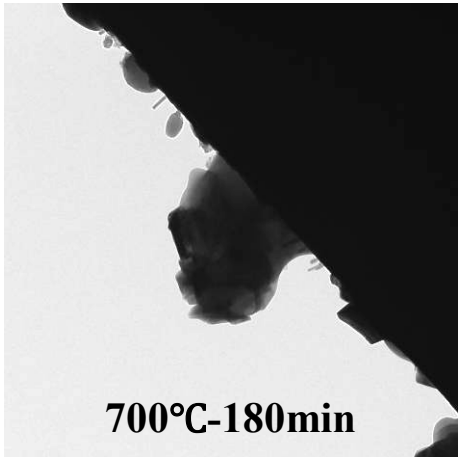




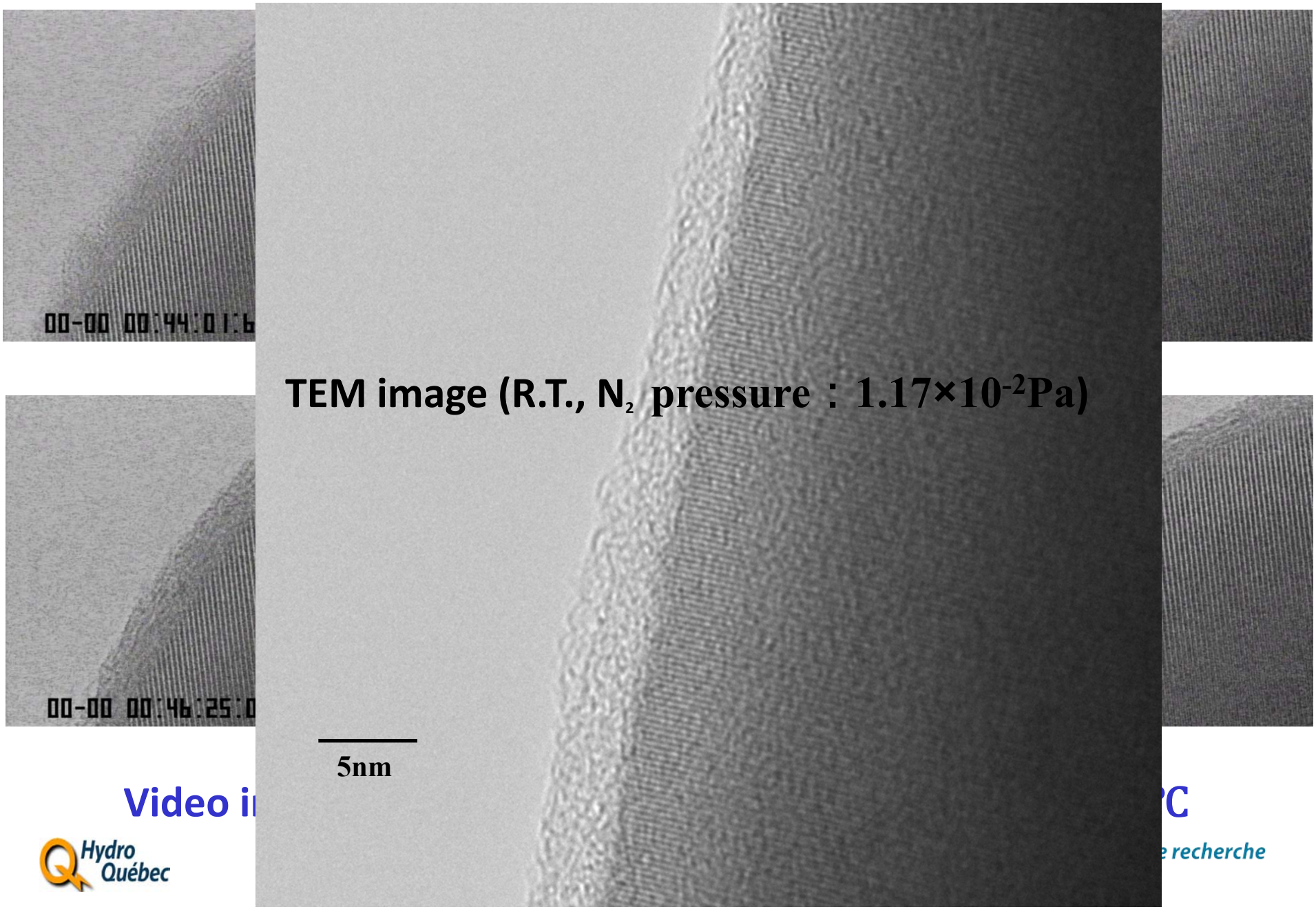








N_2 pressure（Pa）：1.2×10^{-2}



Video i C

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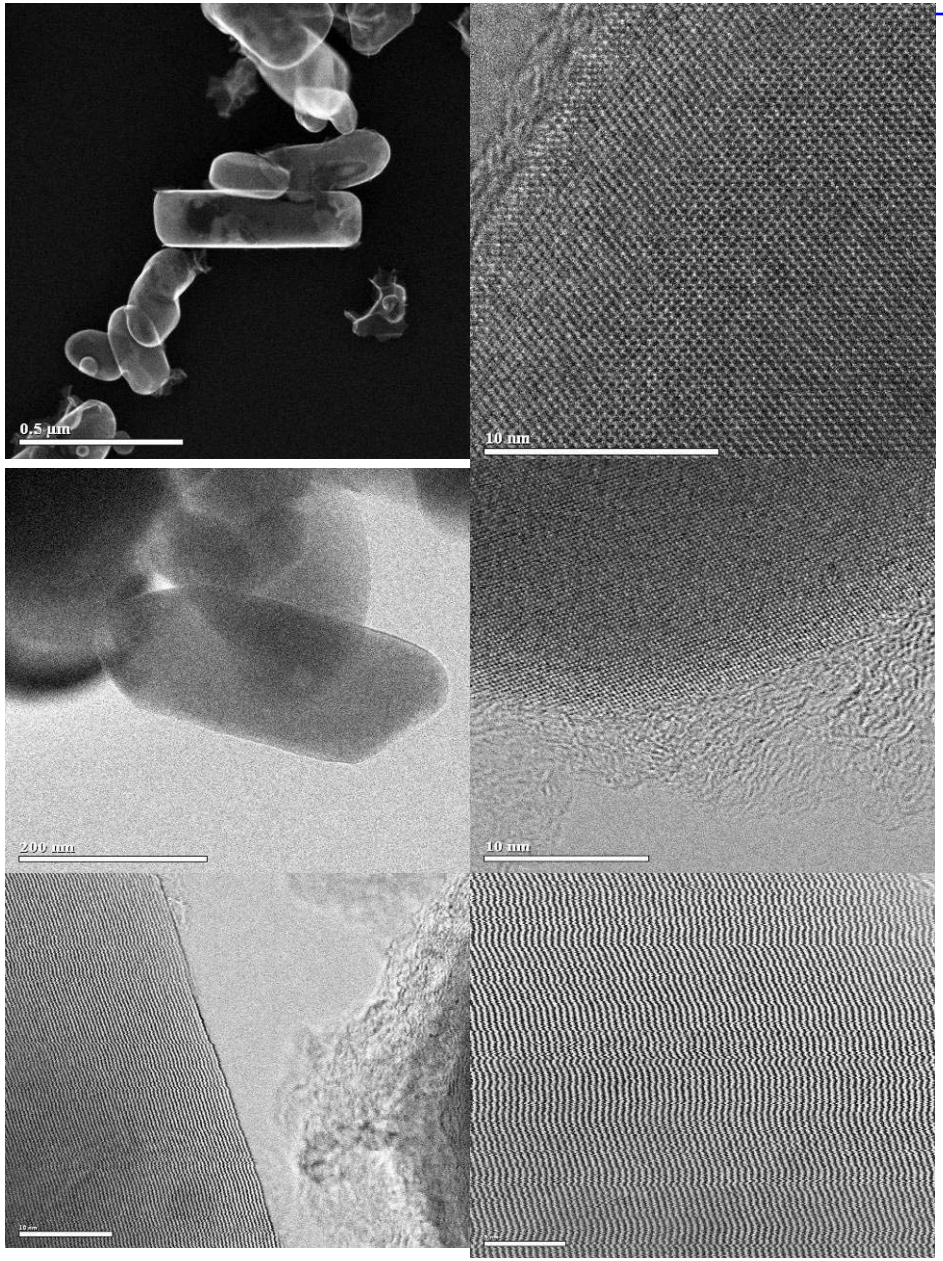
In situ HRTEM of Nanostructured C-$LiFePO_4$ During Heat Treatment



BF-TEM image and (b) HRTEM image of the carbon-coated $LiFePO_4$ particles at room temperature.

BF-TEM image and HRTEM image of the carbon-coated $LiFePO_4$ particles heated at 450 C.

BF-TEM image and HRTEM of the image carbon-coated $LiFePO_4$ particles heated at 900 C.

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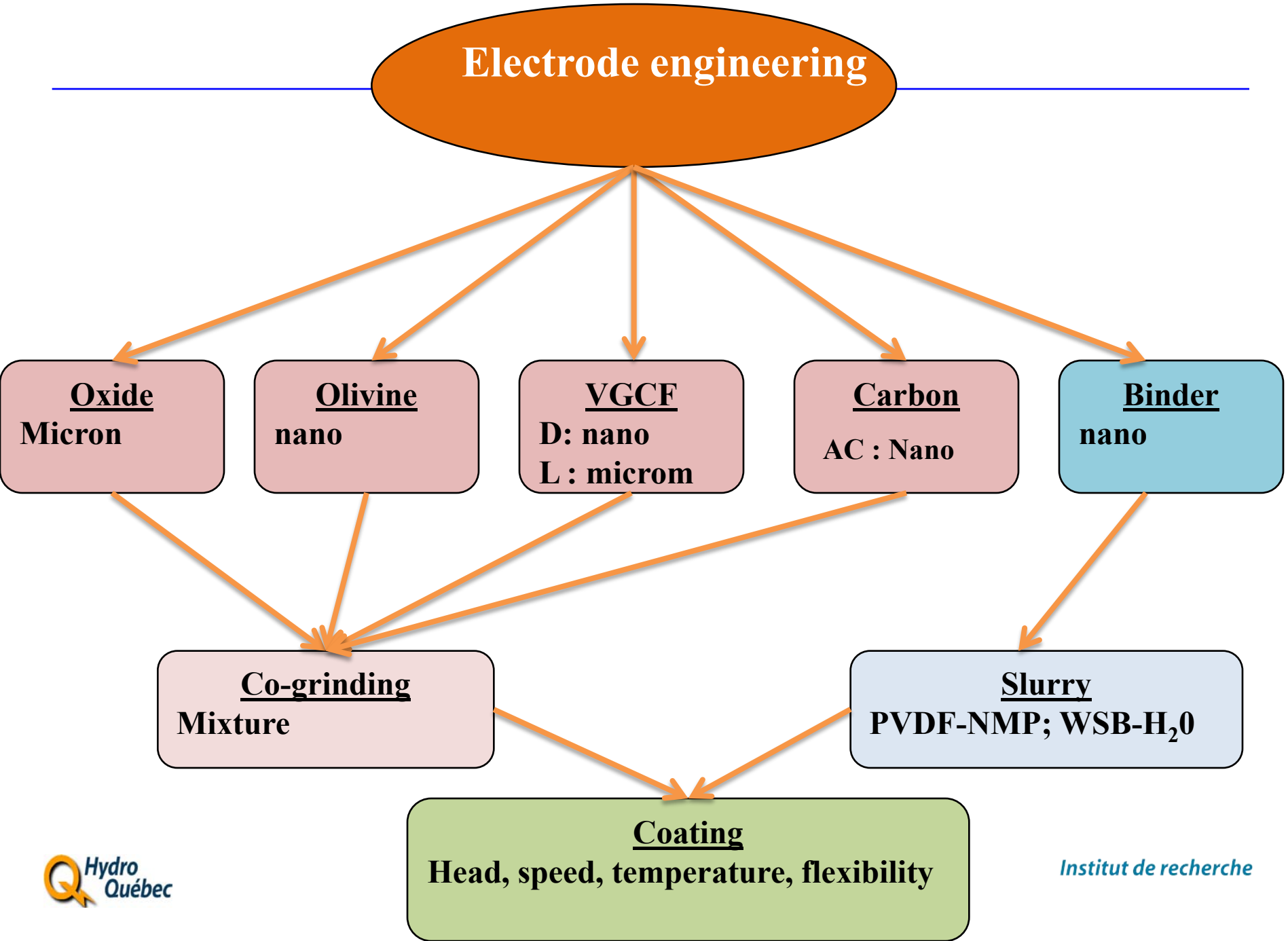
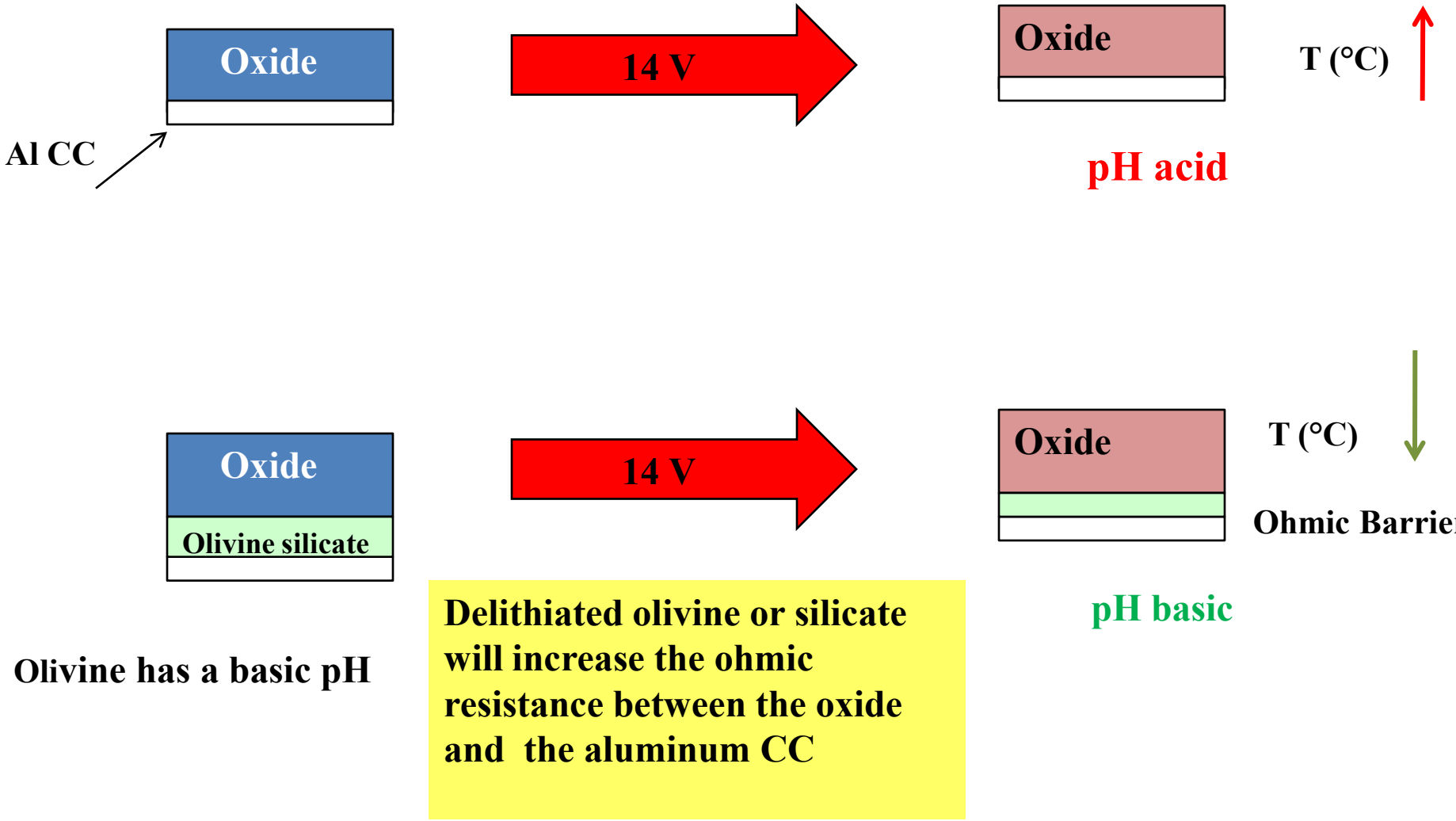
$$2LiFePO_4 + 9/2C \Rightarrow 1/2Li_4P_2O_7 + Fe_2P + 9/2CO$$


Electrode engineering
Oxide
Micron
Olivine
nano
VGCF
D: nano
L : microm
Carbon
AC : Nano
Binder
nano
Co-grinding
Mixture
Slurry
PVDF-NMP; WSB-H20
Coating
Head, speed, temperature, flexibility

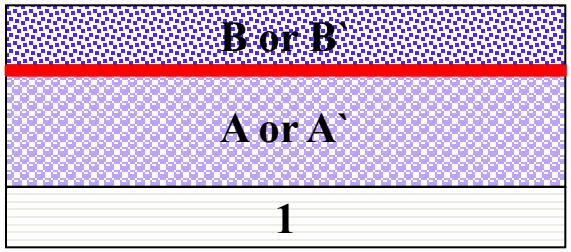
Multilayer : Oxide-Olivine, Overcharge



Olivine has a basic pH

Delithiated olivine or silicate will increase the ohmic resistance between the oxide and the aluminum CC

HQ Multilayers technologies



Multilayer CATHODE:

A: $LiFePO_4$, LiMnPO4, LiFeSiO4

B: $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

Multi layer ANODE:

A: Graphite , carbon

B: $Li_4Ti_5O_{12}$, Sn, Al, Ag, , SiO, Si

Combination I:

1- Current collector

A- Layer with WSB (H_2O)

B- Layer with PVDF (solvent)

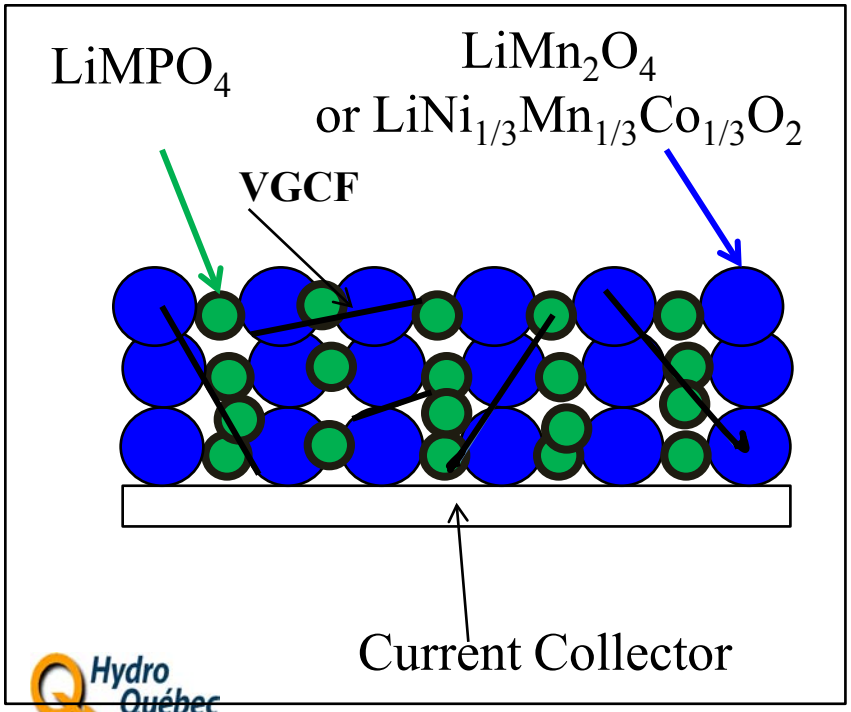
Combination II:

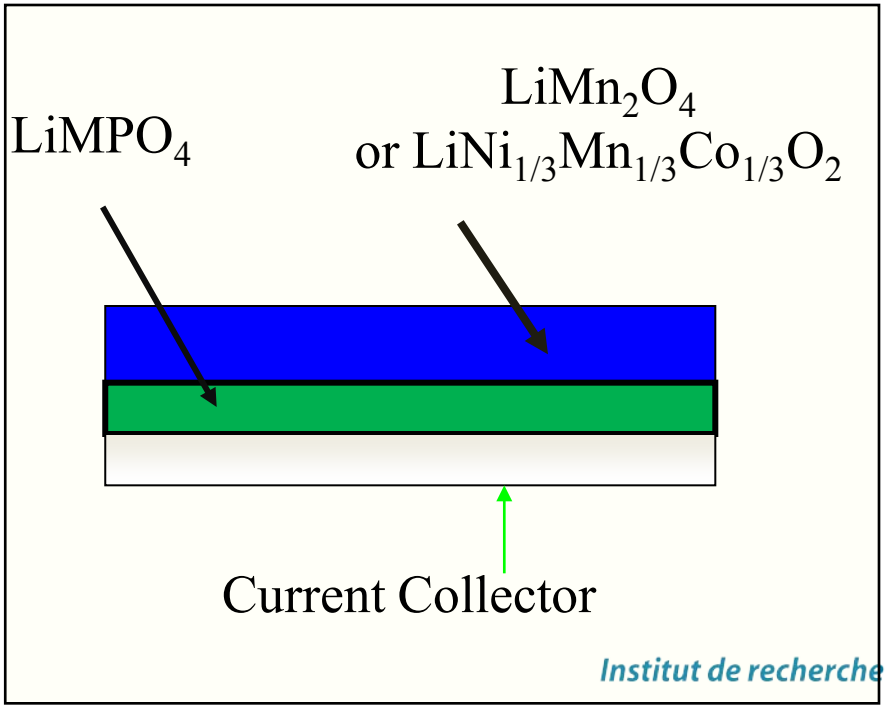
A`- Layer with PVDF (solvent)

B`- Layer with WSB (H_2O)

Dual Materials and Multilayer Electrodes

- **Low-cost mixed powders:**
  - **$LiMnPO_4$-$LiMn_2O_4$ (20%/80%)**
- **Multilayer electrodes:**
  - **$LiMnPO_4$ –$LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$**
    - **Overcharge protection**
    - **Improved stability from decreased oxygen generation**





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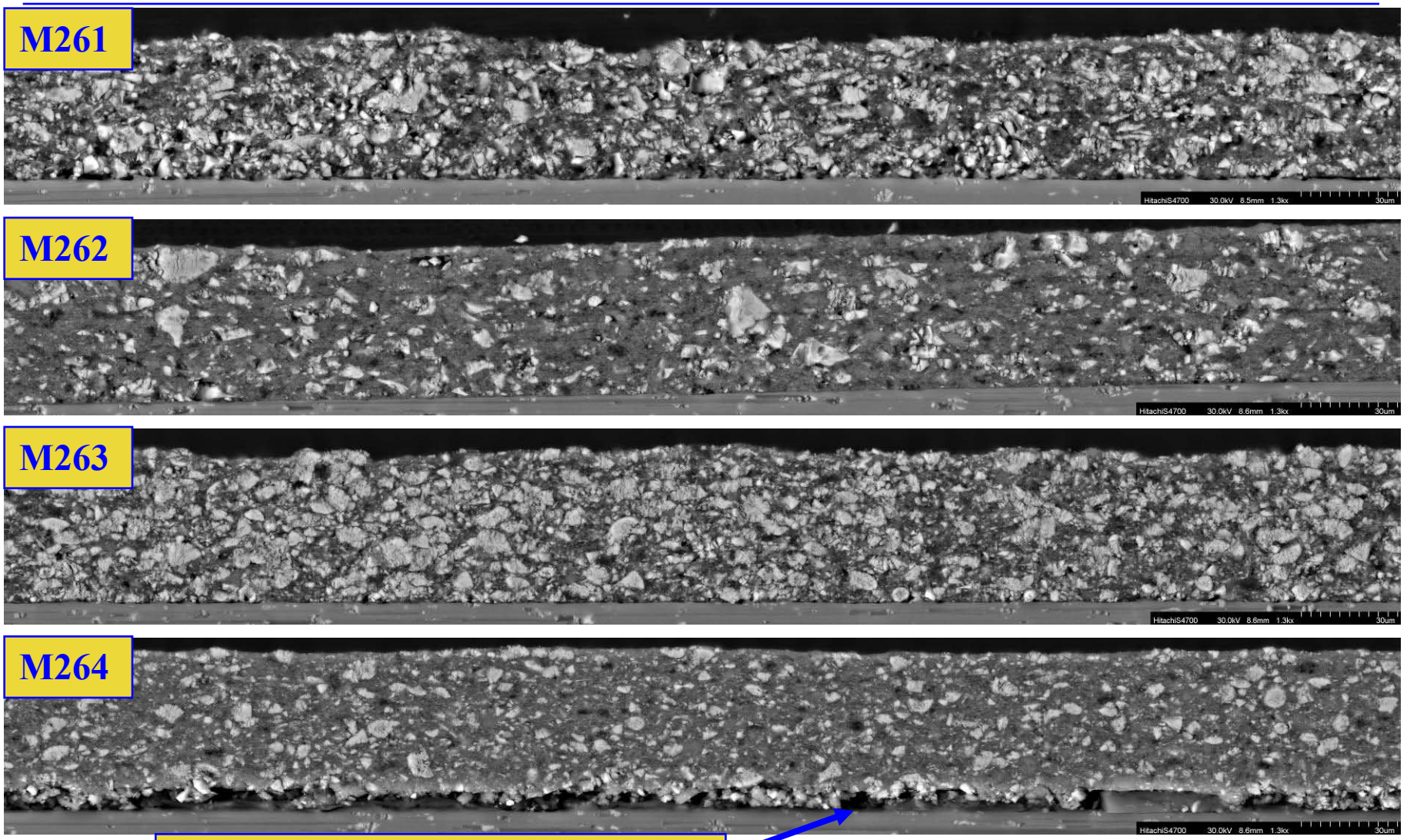
Dispersion Quality : Retro-diffusion Mode



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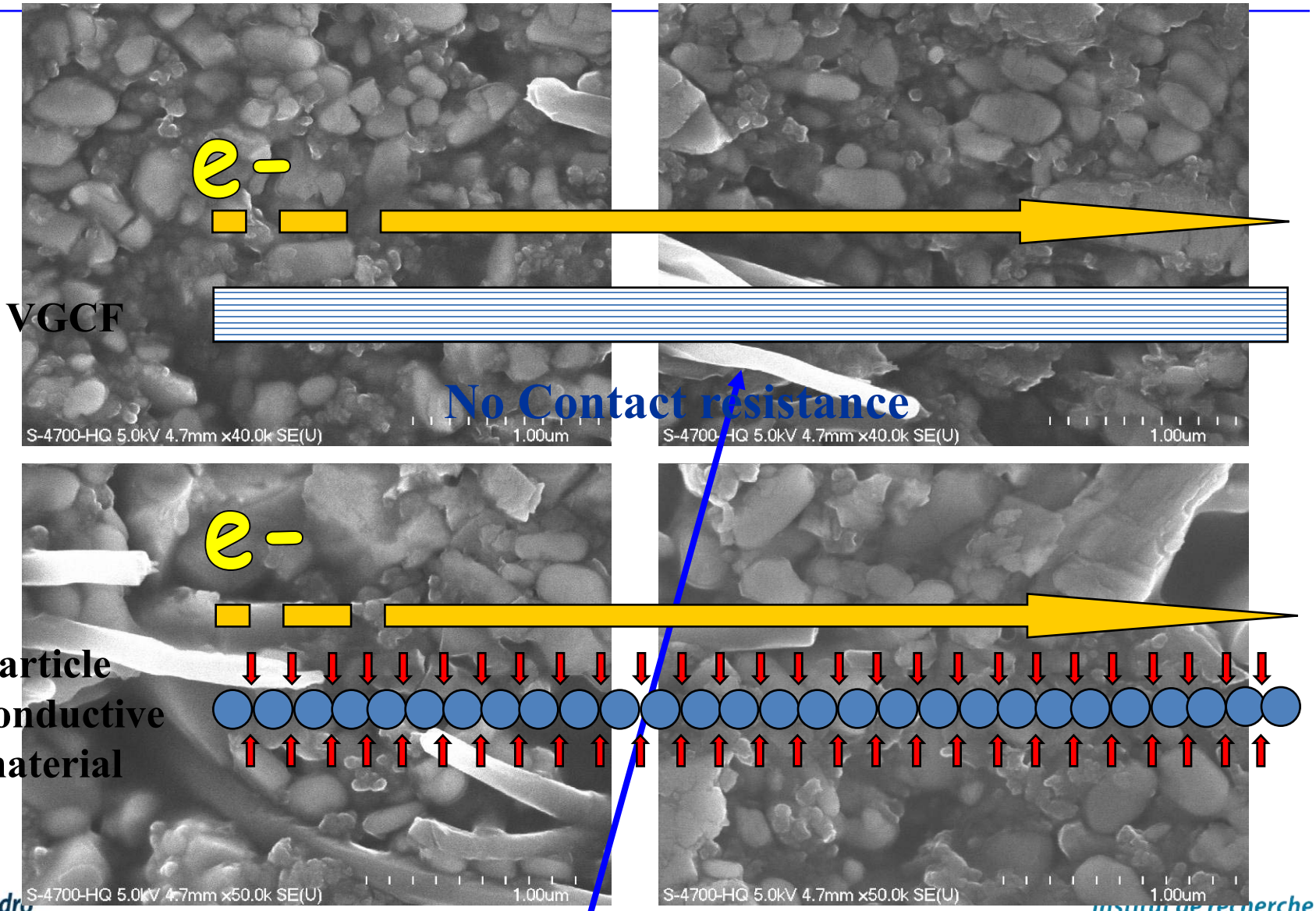
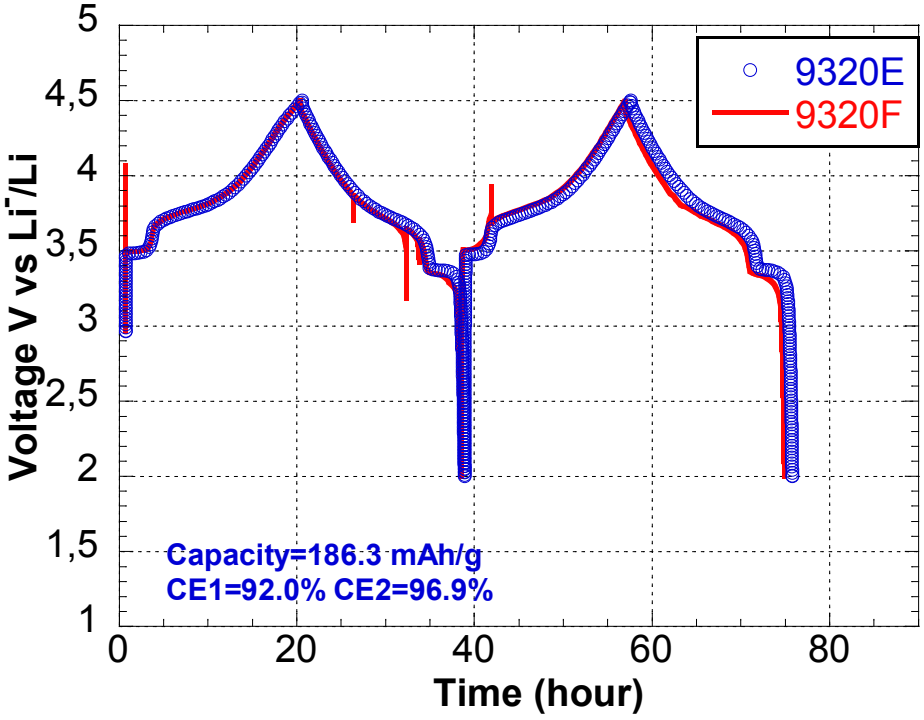
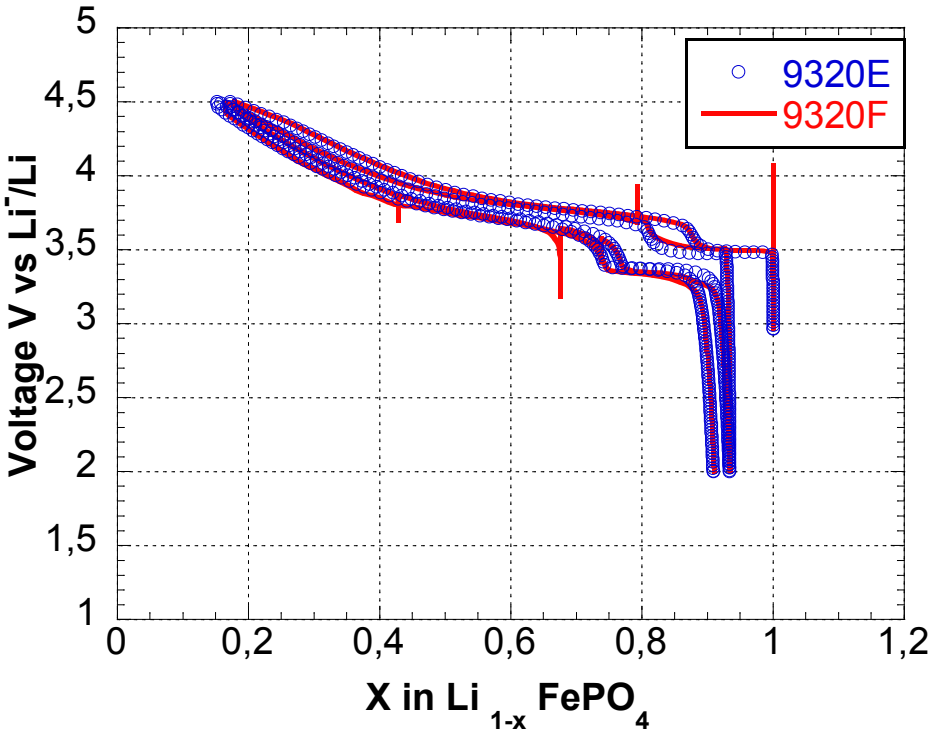

e-
VGCF
No Contact resistance
S-4700-HQ 5.0kV 4.7mm x40.0k SE(U)
1.00um
S-4700-HQ 5.0kV 4.7mm x40.0k SE(U)
1.00um
e-
Particle
conductive
material
S-4700-HQ 5.0kV 4.7mm x50.0k SE(U)
1.00um
S-4700-HQ 5.0kV 4.7mm x50.0k SE(U)
1.00um
Bad mixture with VGCF

20% $LiFePO_4$ + 80% $Li(MnNiCo)_{1/3}O_2$





-No problem for the cut off voltage at 2 V.
-The 1st cycle CE = 93 % with 2 V cut-off voltage.

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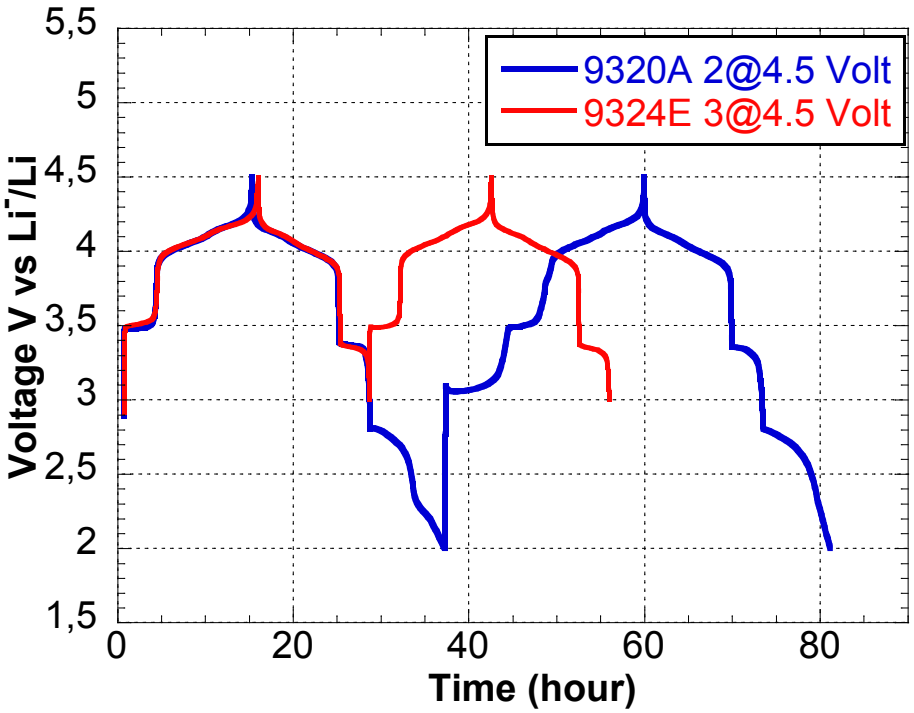
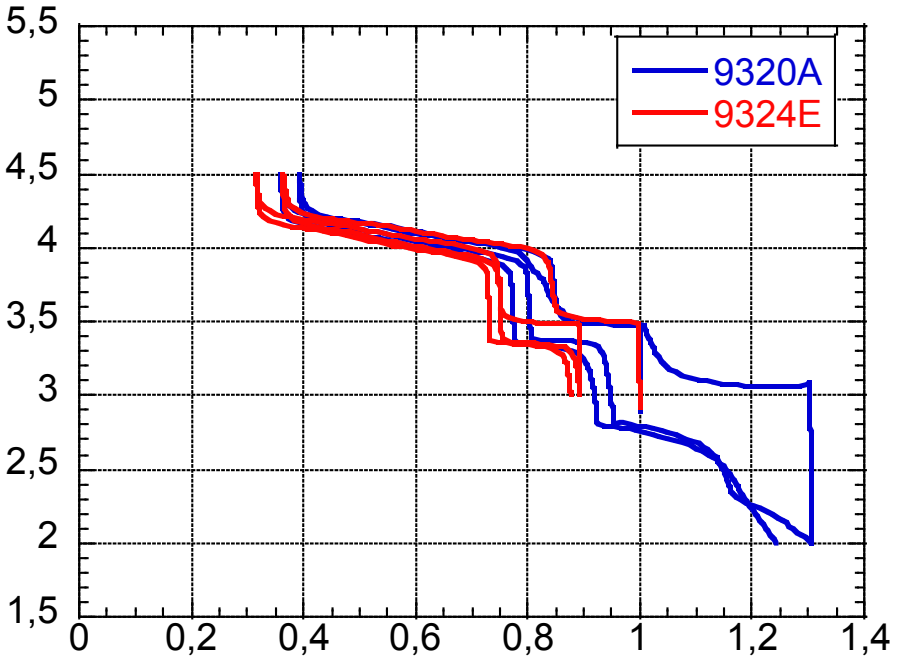
20% $LiFePO_4$ + 80% $LiMn_2O_4$





- For High rate , for LiFePO4, the cut off voltage is 2 V.
- Capacity and cycle life is higher with 2 V cut-off voltage.
- The 1st cycle CE = 85 % with 3 V cut-off voltage.

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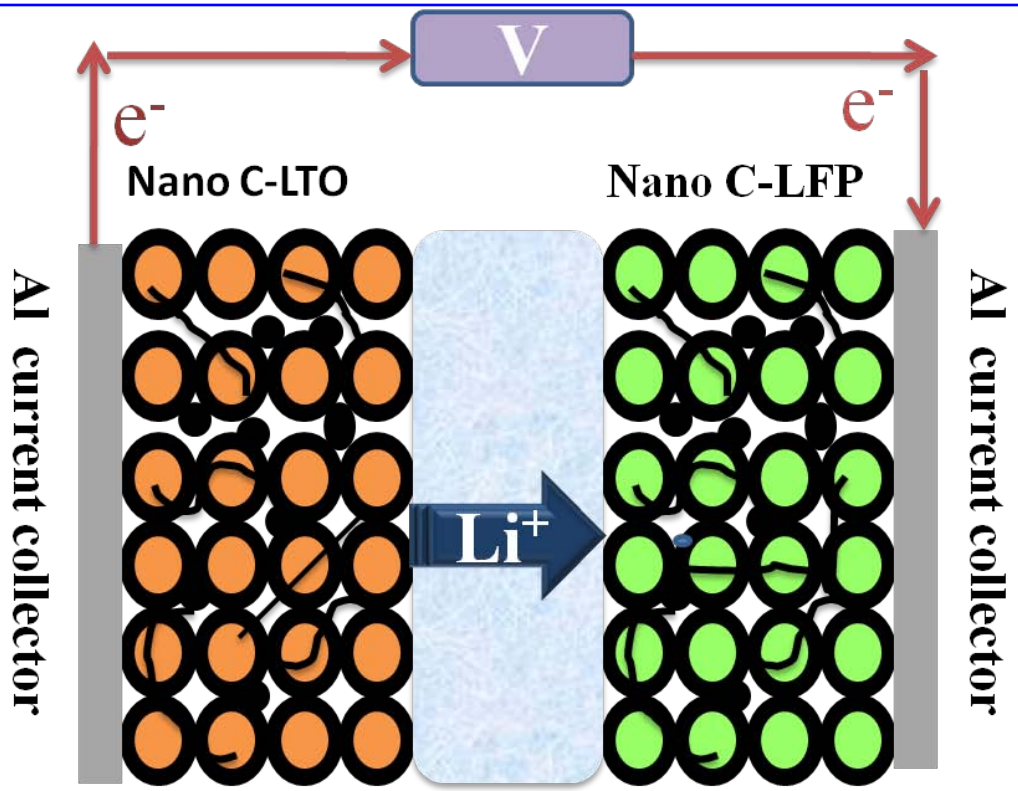
Installation for fabrication of 18650 cylindrical cells

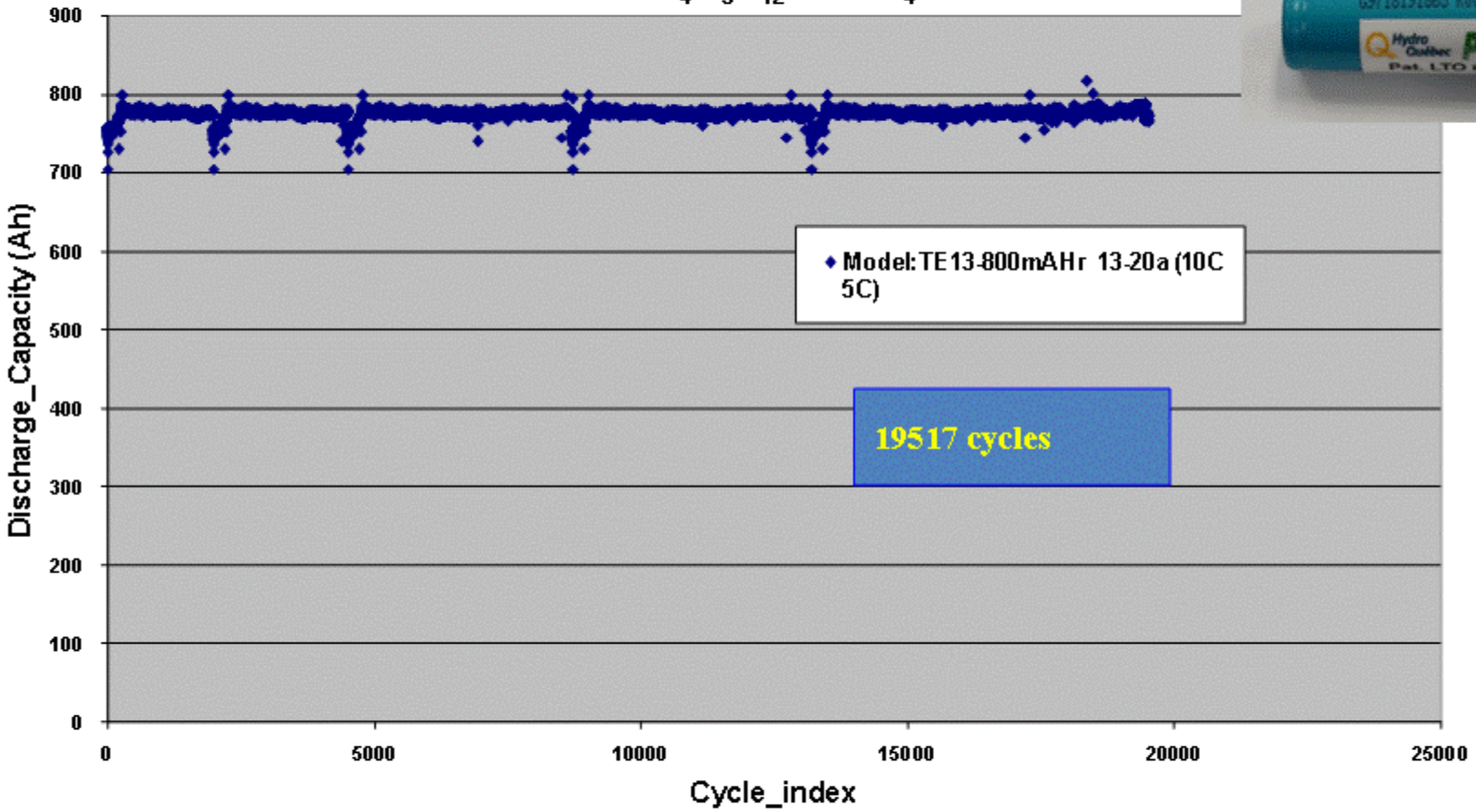
Training on 18650 cell assembly at IREQ

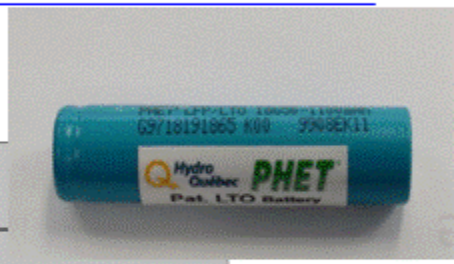
Nano C-LTO/Nano C-LFP



- Anode and cathode consists of nano-size particles
- The absence of passivation films gives rise to low internal resistance and consequently high power and long cycle life in batteries
- Flexibility in the choice of electrolyte
- No cell formation required

C-$Li_4Ti_5O_{12}$ /C-$LiFePO_4$ (100 %DOD)





With one cycle/day, cell cycle life is projected to be >50 years.

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Summary

- With the Polyimide binder (SiO_x: Gr (1:1)) anode shows a reversible capacity of 1026mAh/g and 1st CE of 80%, and stable cycling capacity of at C/12.
- (SiOx: Gr(1:1)) anode shows a reversible capacity of 1026 mAh/g, 1st cycle CE of 80%, and stable cycling capacity of 990mAh/g at C/12 rate with polyimide binder.
- The effect of the binder on the (SiO_x: Gr (1:1)) anode performance is the following:

  Reversible Capacity: Polyimide > SBR > PVDF

  1st CE: SBR > Polyimide > PVDF
- $LiMnPO_4$ was synthesized by hydrothermal method followed by wet-milling process:
  - The particle size was reduce from 0.25µm to less than 50nm
  - 104 mAh/g at 25°C for the 1st charge, and 70mAh/g reversible capacity.
- Doped LiMnFePO4 showed a remarkable improvement of 4V plateau even with 80% Mn.
- *In-situ* studies explored the phase transformation of olivines.
- Training to fabricate 18650 cells started.

Future Activities

- **Rest of this year**
  - **Continue evaluation of mixed graphite-SiO_x as an alternative anode.**
  - **Continue improving the performance doped $LiMnMPO_4$ as low cost cathode for Li-Ion cells.**
  - **Conduct *in-situ* SEM and TEM studies of olivines and oxide-olivines.**
  - **Investigate dual oxide-olivine by coating the oxide (1/3 and $LiMnAlO_2$) with olivine (improve performance at different SOC and energy-power, safety performance).**
  - **Evaluate dual oxide-olivine as mixed powders or multilayer structures in cathodes**
  - **Continue supplying laminated electrode, powders and 18650 cells to investigators in the BATT program.**
  - **Fabricate and test 18650 cells with oxide-$LiM_1M_2PO_4$ cathodes and SiO/graphite anodes, and provide cells to investigators in the BATT program for evaluation.**
- **All milestones completed**