

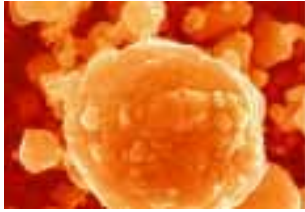


# Key elements on $\text{LiFePO}_4$ :

## Performances, Stability and availability

Guoxian Liang and Michel Gauthier, Phostech Lithium Inc  
Nathalie Ravet and Christophe Michot, Université de Montréal  
Gerhard Nuspl, Süd-Chemie





## **1. Overview of LiFePO<sub>4</sub> Phostech's grades performances**

Charge and discharge capabilities

High temperature behaviour

Low temperature behaviour

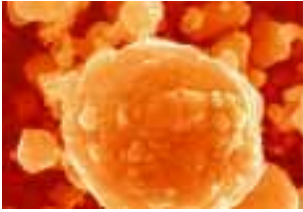
## **2. Stability**

What is damaging LiFePO<sub>4</sub> ?

## **3. Availability**

What IP is required to commercialize LiFePO<sub>4</sub> ?

Update on Phostech's facilities and production

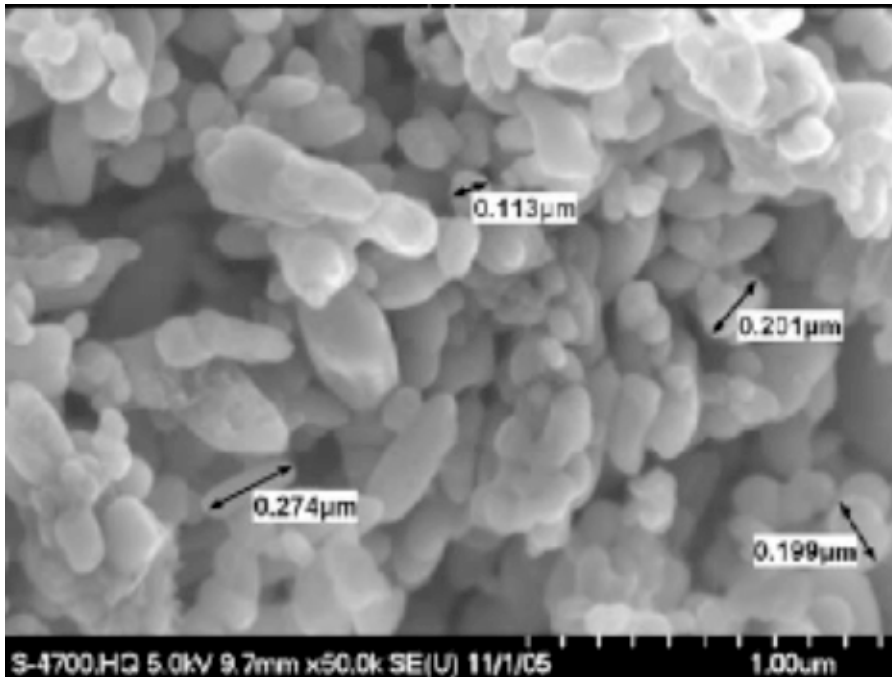


# Phostech's grades

## Morphology

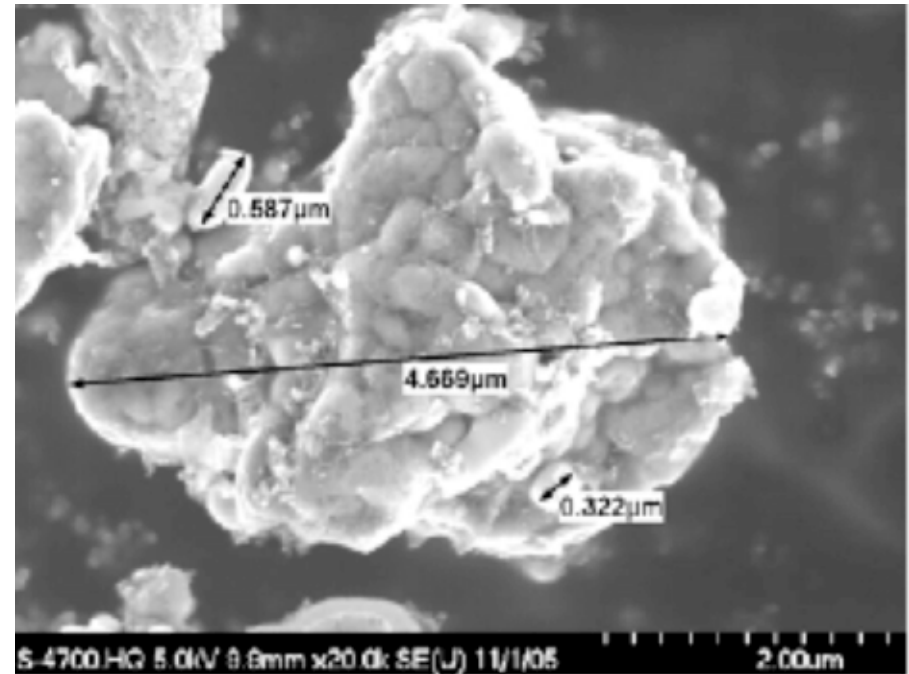


### Power grade (nano-sized material)

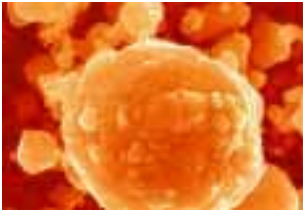


**Life Power® P2**

### Energy grade (micro-aggregates)



**Life Power® P1**



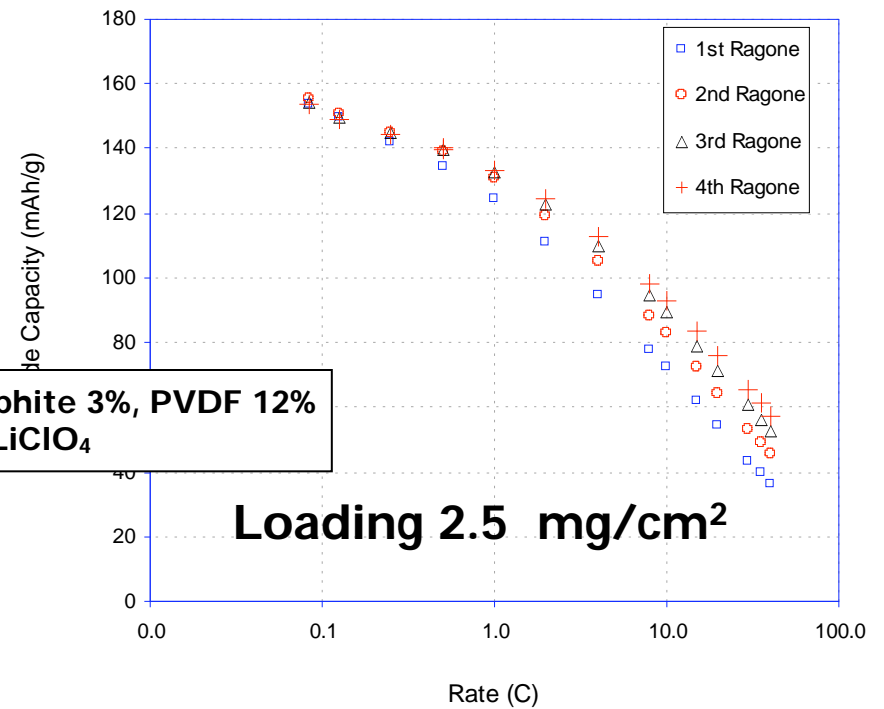
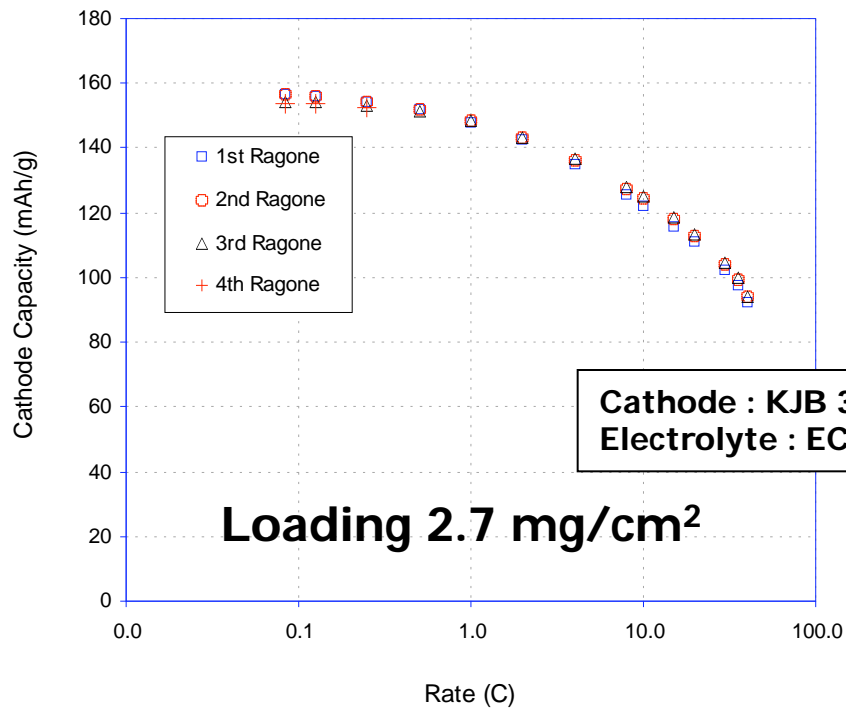
# Phostech grades

## Rate capabilities



### Power grade (nano-sized material)

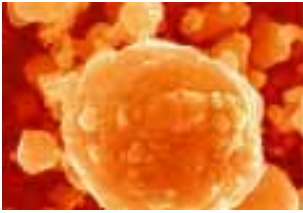
### Energy grade (micro-aggregates)



**40C <=> 94 mAh/g**

**40C <=> 57 mAh/g**

Rate capability maintained even at higher loadings



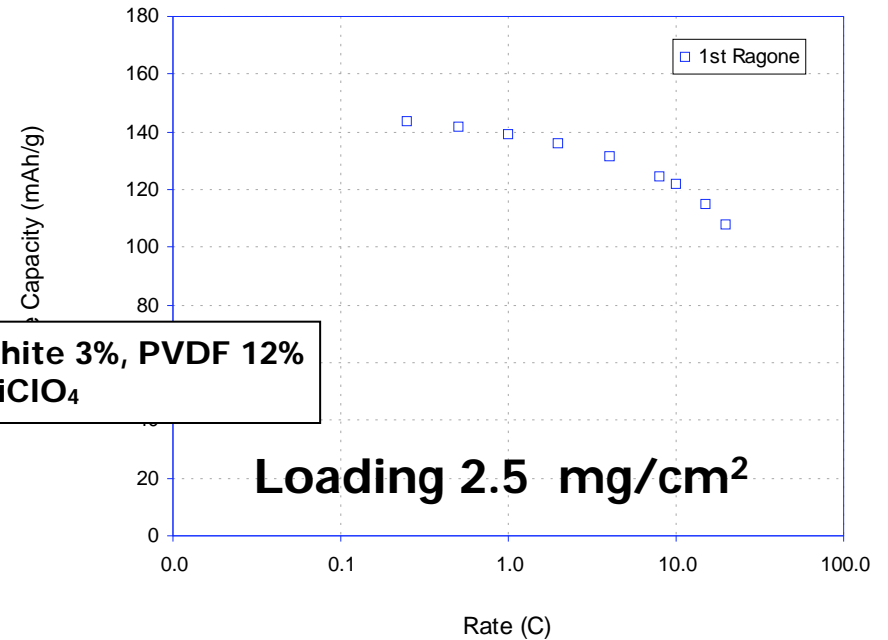
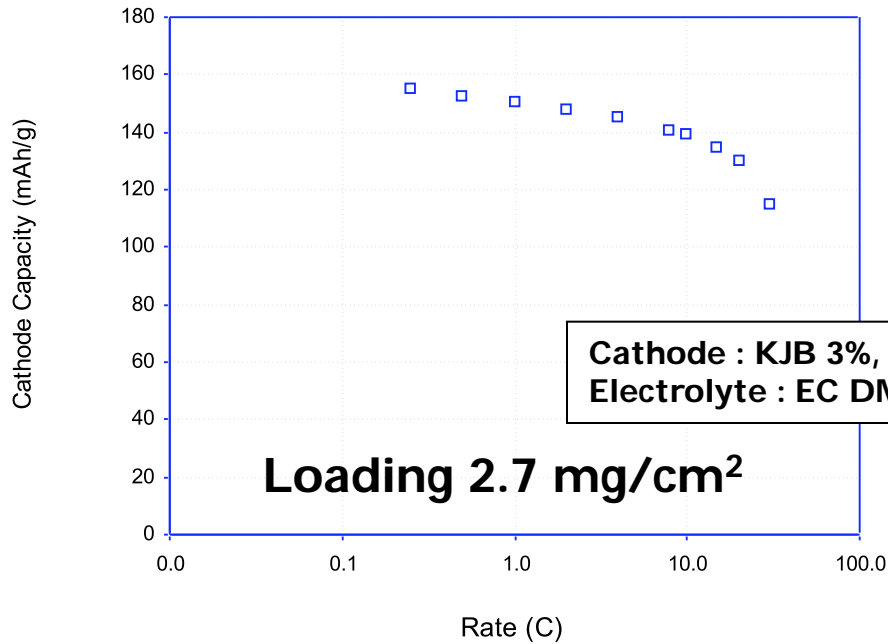
# Phostech grades

## Charge acceptance



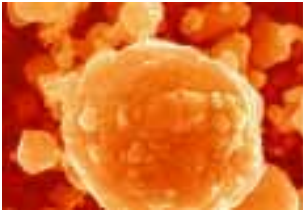
### Power grade (nano-sized material)

### Energy grade (micro-aggregates)



**75% of charge  $\Leftrightarrow$  2 mn**

**75% of charge  $\Leftrightarrow$  3 mn**



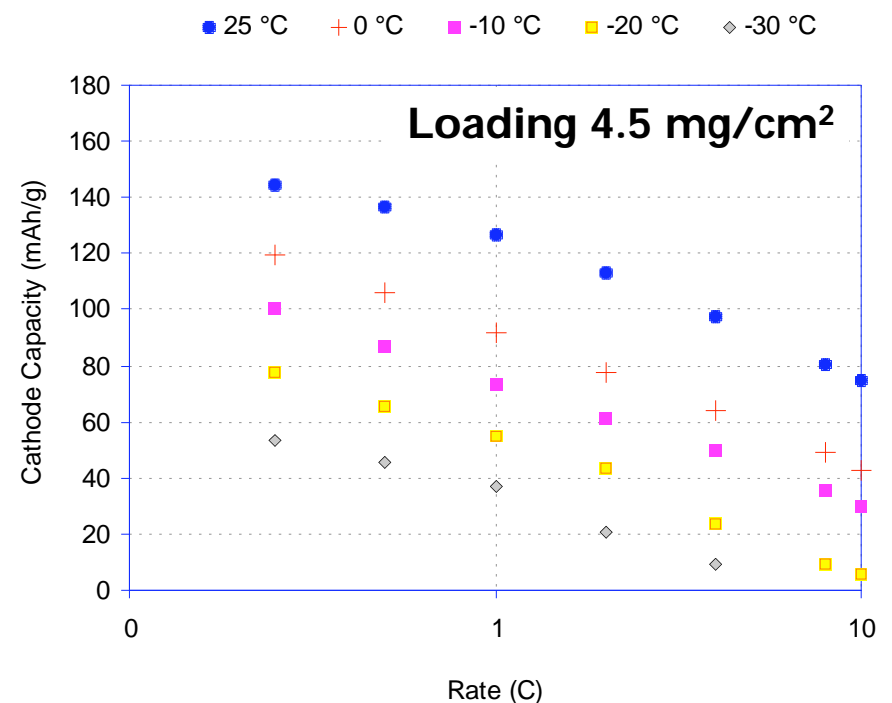
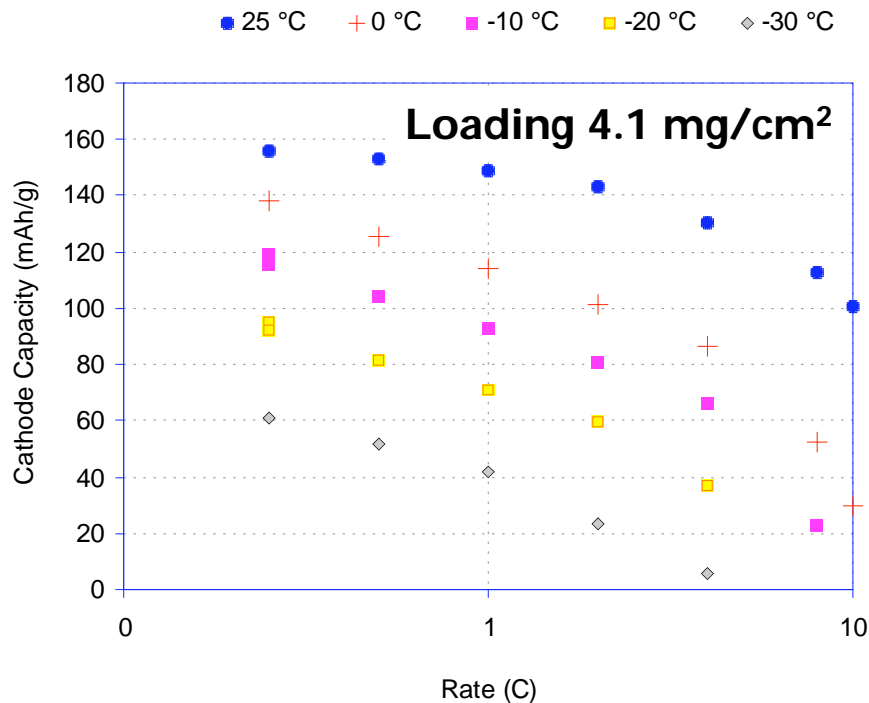
# Phostech grades

## Low temperature behaviour



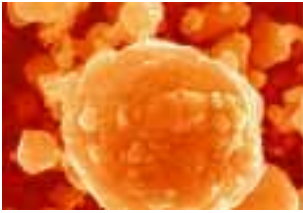
### Power grade (nano-sized material)

### Energy grade (micro-aggregates)



Cathode : EBN1010 10%, PVDF 10%  
Electrolyte : EC DEC LiPF<sub>6</sub>

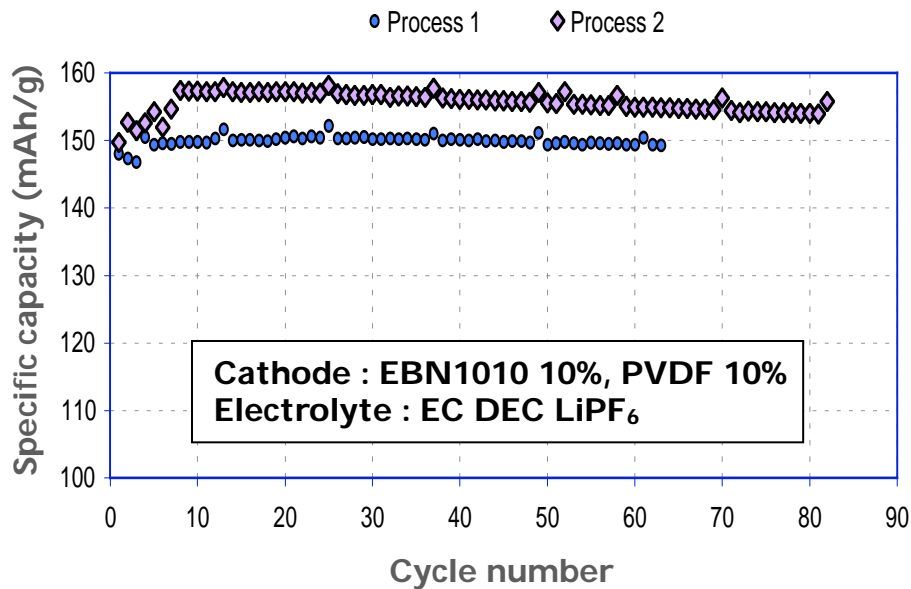
**Both grades can sustain continuous C-rate at -30°C during 15 mn**



# Phostech grades Cyclability at 60 °C



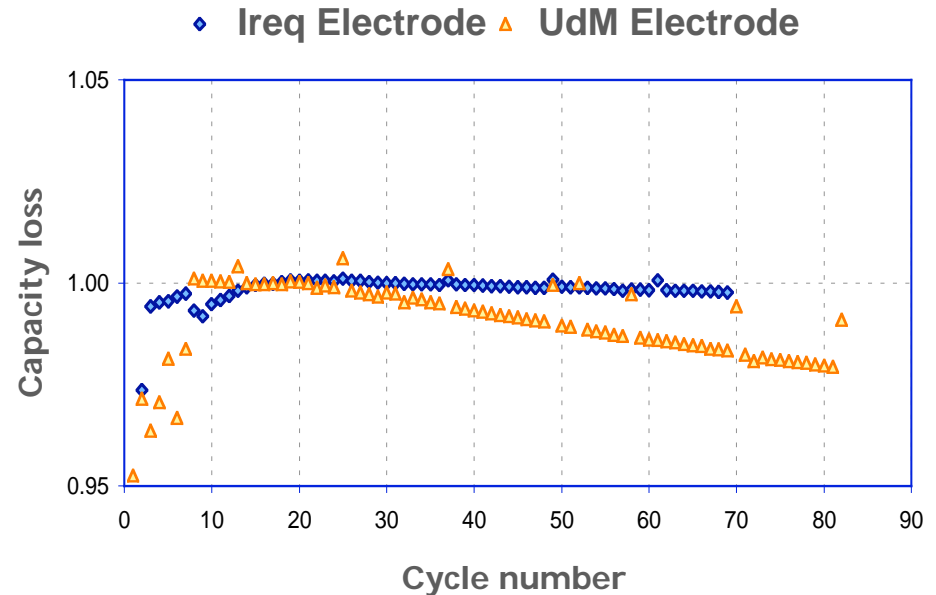
## Power grade (nano-sized material)



Slope: 1.5-3.5% of capacity lost after 100 cycles for both processes

(UdM Electrode)

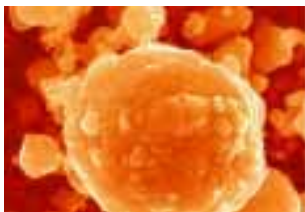
## Energy grade (micro-aggregates)



Stability depends on the electrode

# Aging





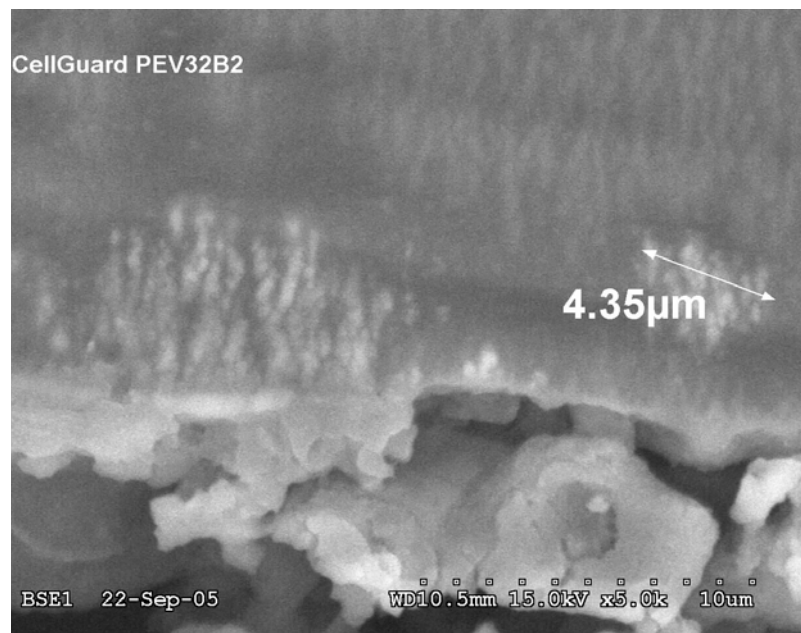
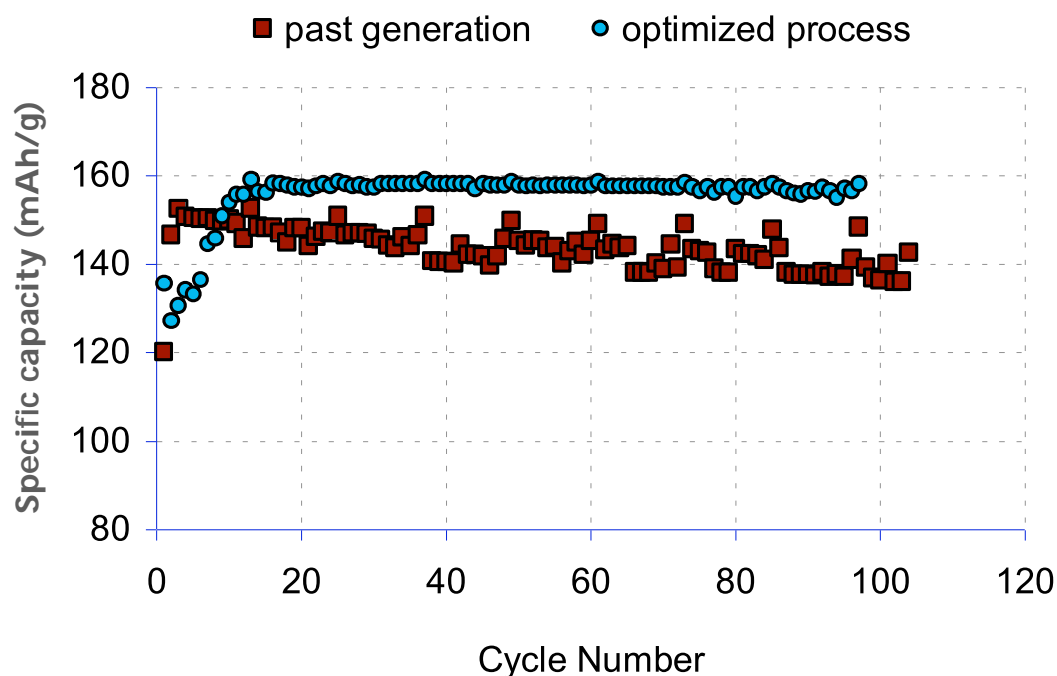
# Iron dissolution at 60°C in LiPF<sub>6</sub> electrolytes



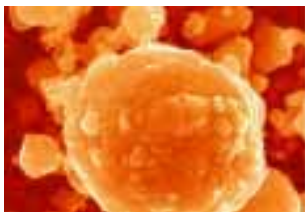
## Coffee-bag cells : Capacity evolution over 47 days at 60°C

**Past generation:** 8% loss of capacity after 100 cycles

**Optimized process:** 1% loss of capacity after 100 cycles



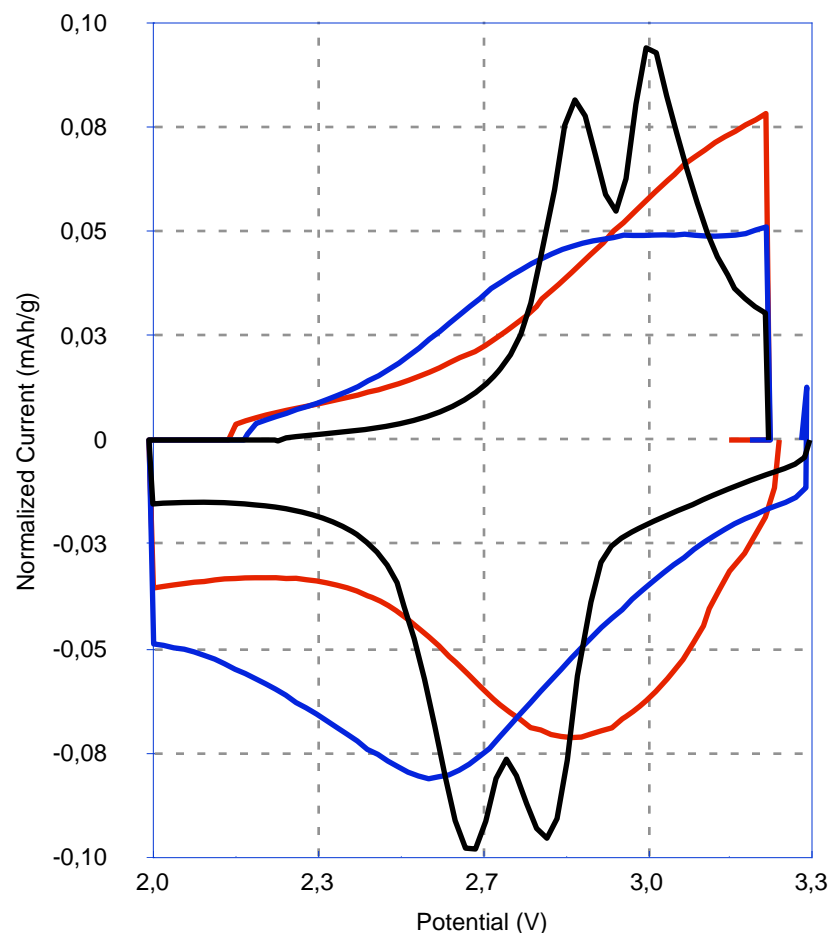
- After post mortem **no iron** could be detected in the battery cycling without capacity loss
- In the battery losing capacity **iron particles** were detected at Li/separator interface



# Iron III species **were** present in both grades



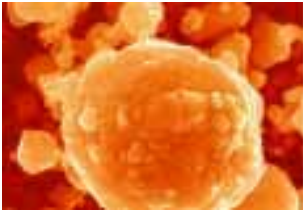
- LiFePO<sub>4</sub> with Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>
- Power grade
- Energy grade



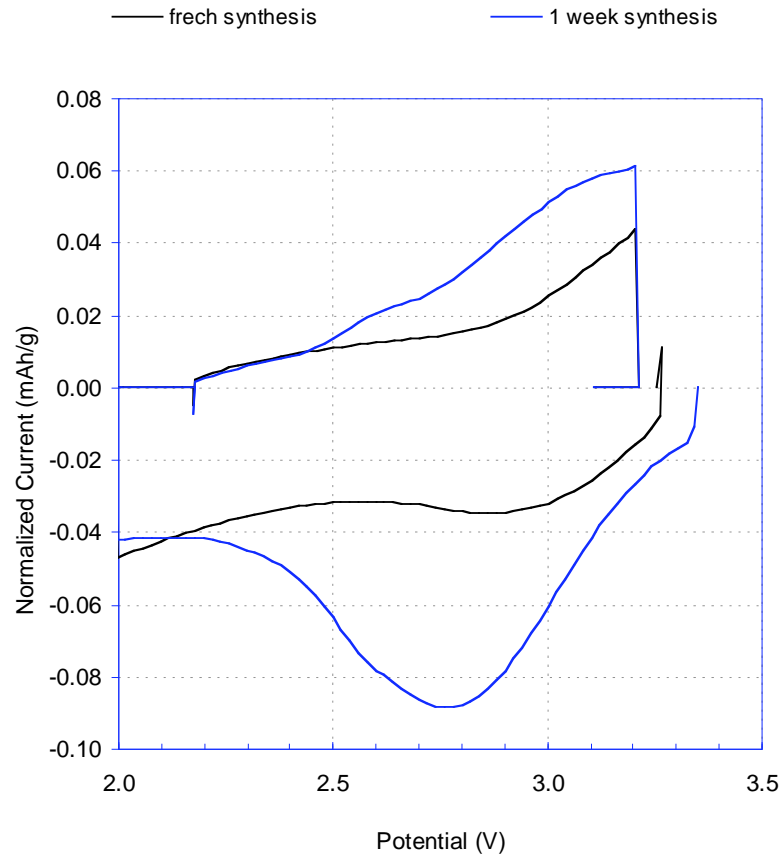
## Slow scan voltammetry (20mV/100s) at RT on new batteries

- Reversible peaks: 1-3% of specific capacity
- Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and LiFe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> detected in small quantities by XRD (less than 1%)
- Amorphous compounds such like FePO<sub>4</sub>·xH<sub>2</sub>O

**Impurities from synthesis or from degradation process ?**

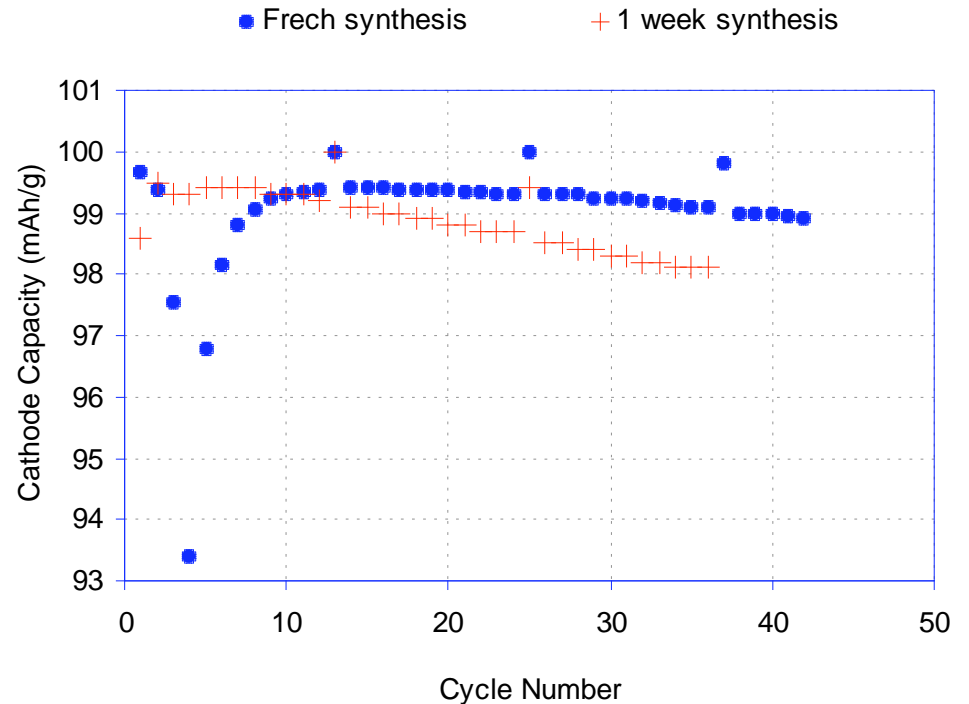


# Lab synthesis aging



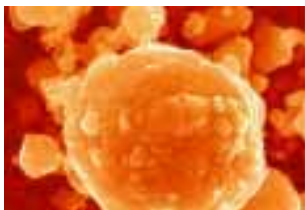
**Fe(III) compound:**

**1.2% after synthesis  
2.4% after one week**

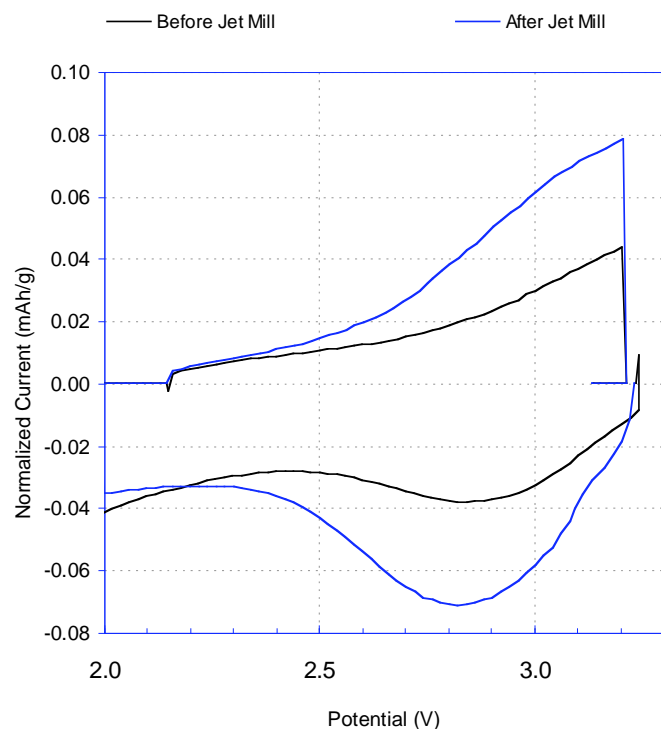


**Slope on 100 cycles:**

**1.1-1.9% after synthesis  
4.0-5.1% after one week**

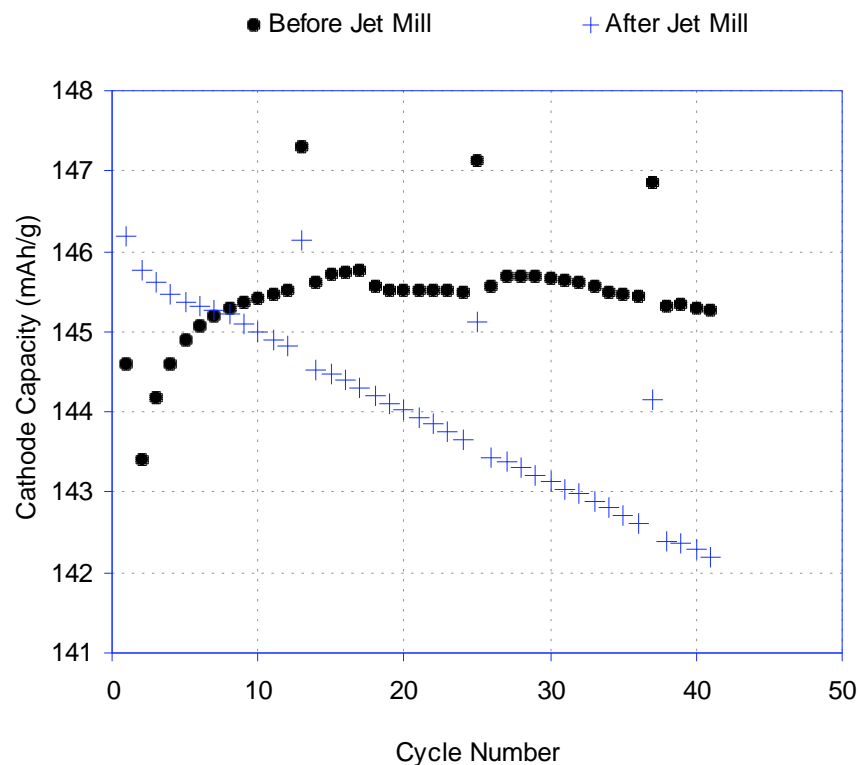


# Iron III species present in energy grade (until mid 2006)



**Fe(III) compound:**

**1.3% before,  
2% after Jet Mill**



**Slope:**

**2.5 % before  
6.1% after Jet Mill**

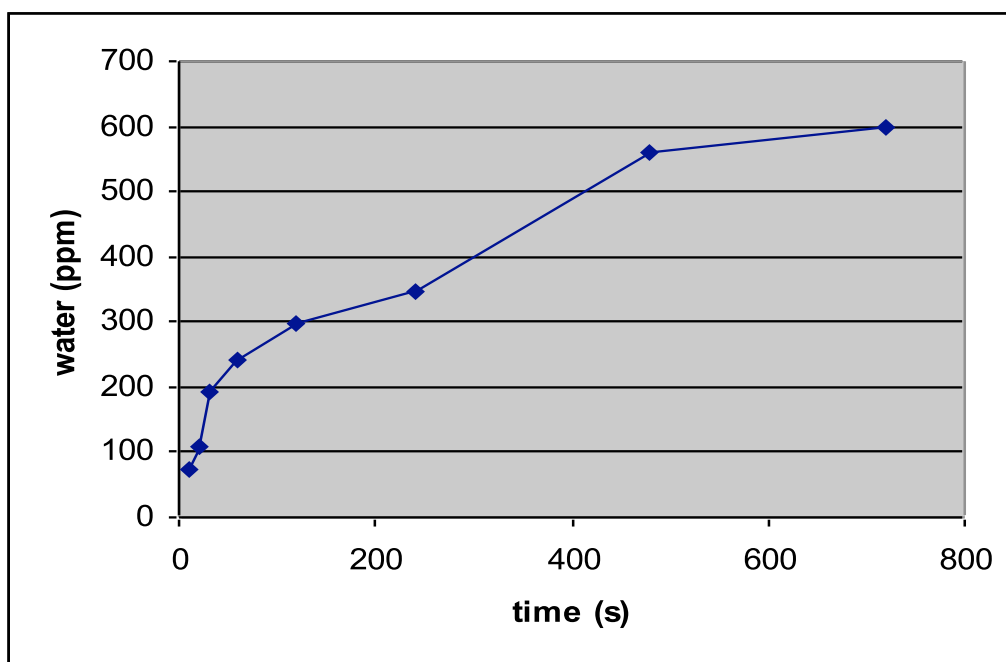
**Does the Fe(III) compound responsible for the bad cyclability or is it linked to the water content in the electrode ?**



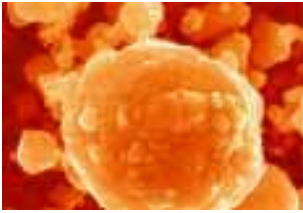
## LiFePO<sub>4</sub> aging at room atmosphere



- LiFePO<sub>4</sub> can be easily dried between 100-120°C under vacuum or dry gas flow
- How fast the powder is taking back water ? (room atmosphere at 20% of humidity)

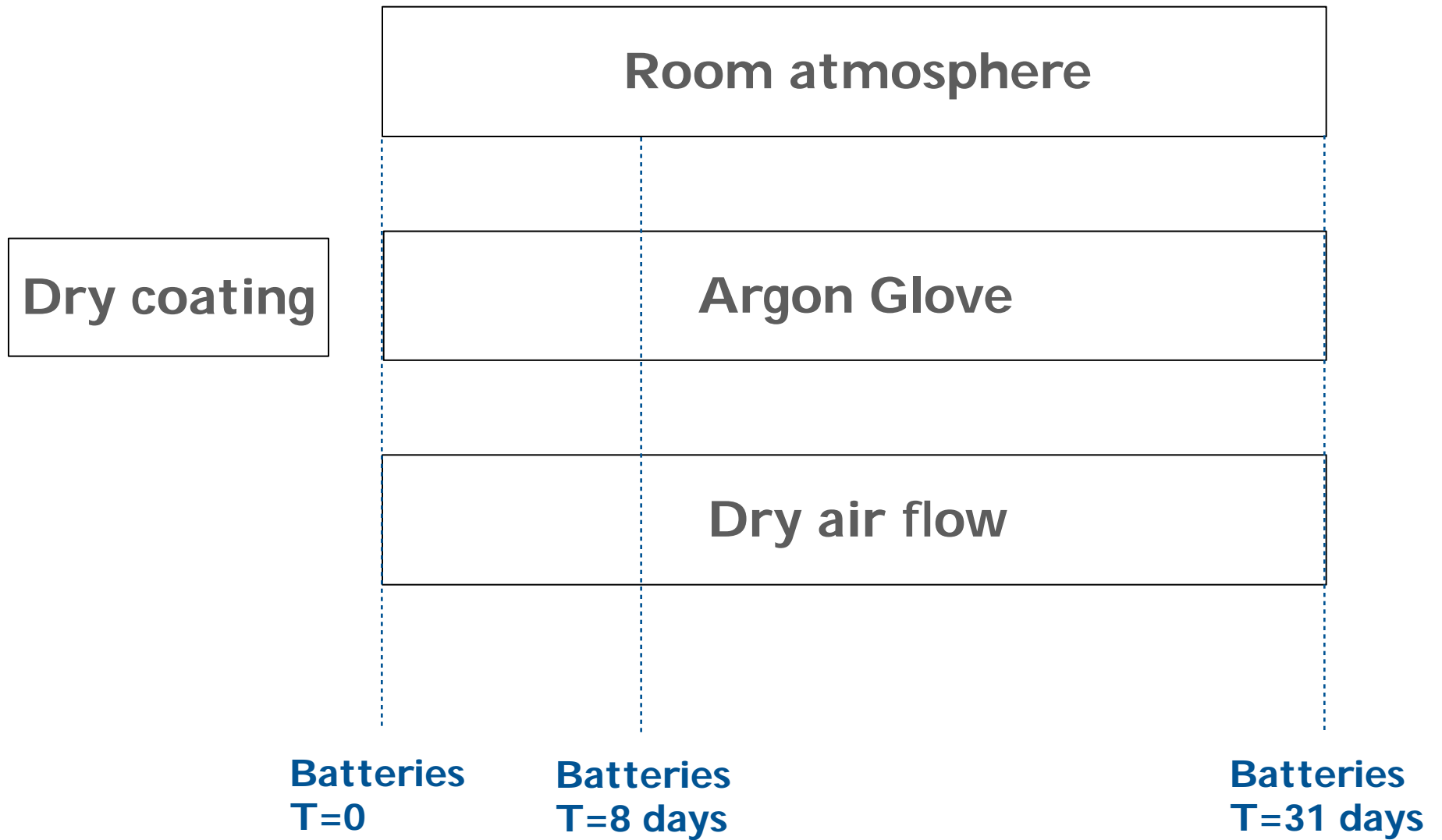


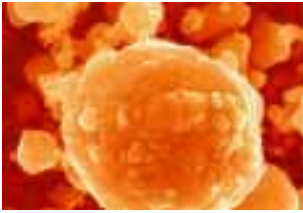
- After Jet Milling the powder is catching water fast. Special cares have to be taken during sampling to avoid contamination from room atmosphere (800-900 ppm achieved through sampling process)
- More than 1% of water was measured on powder kept unprotected in the lab



# Electrode Aging

## Energy grade



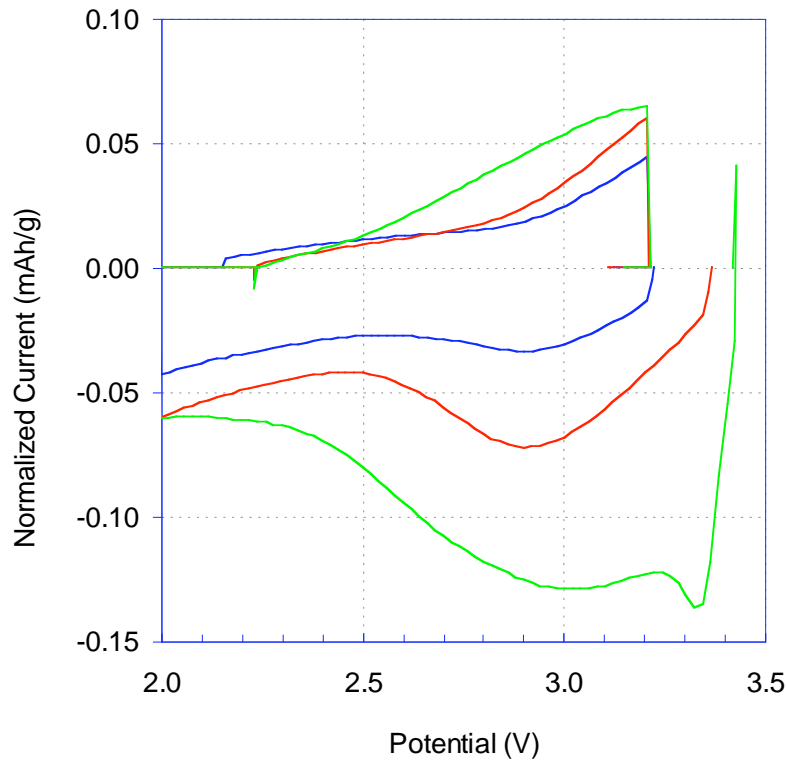


# Electrode Aging Energy grade



## Room atmosphere

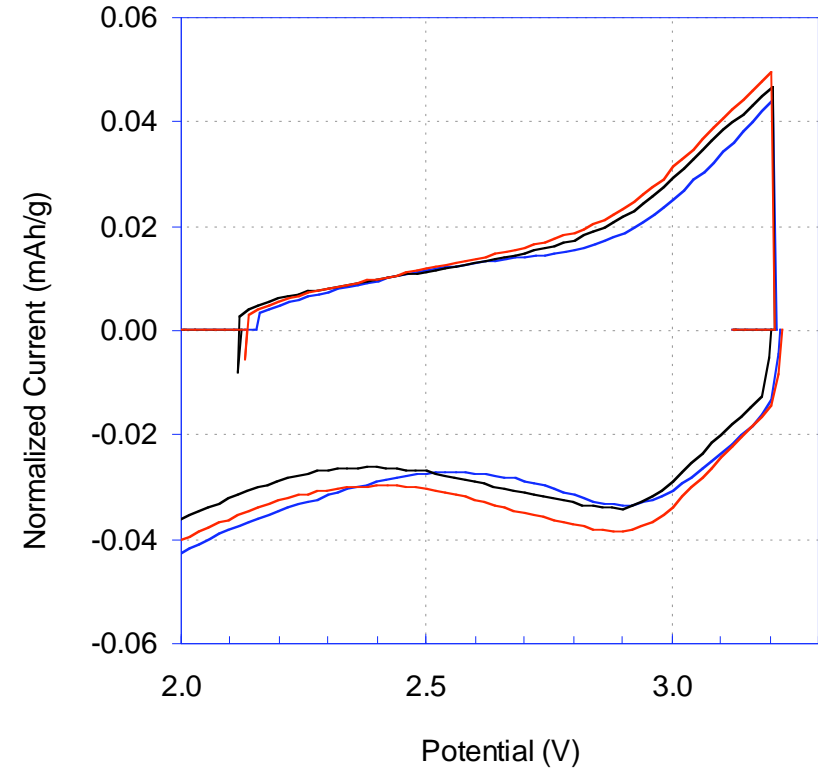
- T = 0
- T = 8 days
- T = 31 days



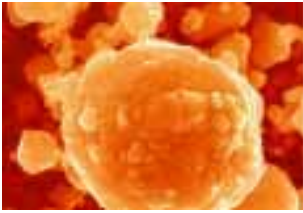
Fe(III) compound: 1.3% T = 0  
2.3% T = 8 days  
4.6% T = 31 days

## Dry air & argon

- T = 0
- T = 31 days argon
- T = 31 days dry air



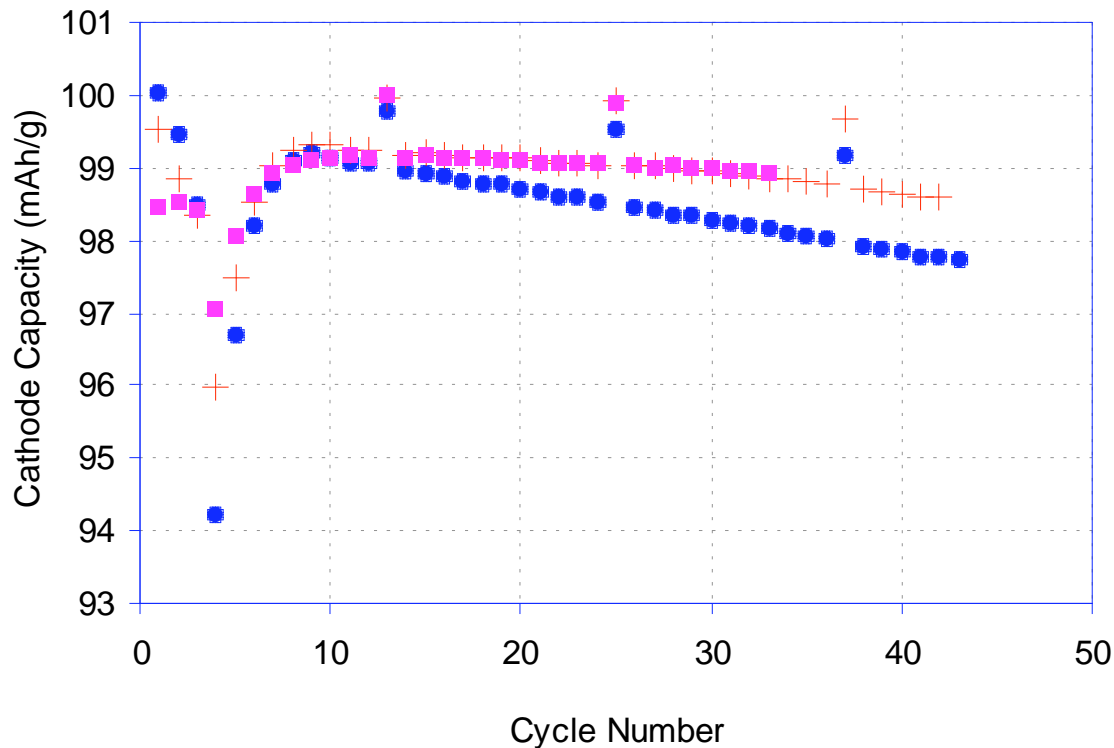
No degradation under dry air !



# Electrode Aging Influence on cycling (60°C)

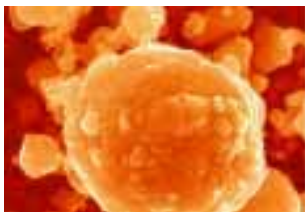


- T = 31 days room atmosphere
- + T = 31 days argon
- T = 31 days dry air



Slope on 100 cycles	
Room atmosphere:	3.9-4.3%
Argon:	1.2-1.7%
Dry air:	1.1-2.2%

After aging at room atmosphere our standard procedure to dry electrode was not efficient to remove water (300-400 ppm detected), that could explain the bad capacity retention



## What is clear ?



Carbon coated  $\text{LiFePO}_4$  stored at room atmosphere contain Fe(III)

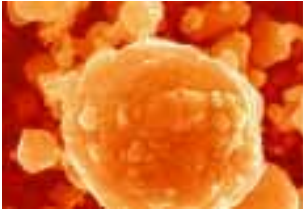
Oxidation of an impurity

Oxidation of  $\text{LiFePO}_4$

Powder slightly oxidized chemically in ACN just show  $\text{FePO}_4$

This Iron III Phase is not responsible for Fe(III) dissolution

Still present after cycling at  $60^\circ\text{C}$



# Possible corrosion mechanisms of LiFePO<sub>4</sub>



- $\text{LiFePO}_4 + 1/4 \text{O}_2 + 1/2 \text{H}_2\text{O} \longrightarrow \text{FePO}_4 + \text{LiOH}$  evolving as Li<sub>2</sub>CO<sub>3</sub>
- $3 \text{LiFePO}_4 + 3/4 \text{O}_2 + 1/2 \text{H}_2\text{O} \longrightarrow \text{LiFeP}_2\text{O}_7 + \text{Fe}_2\text{O}_3 + \text{Li}_2\text{HPO}_4$
- $3 \text{LiFePO}_4 + 3/4 \text{O}_2 \longrightarrow \text{Li}_3\text{Fe}_2(\text{PO}_4)_3 + 1/2 \text{Fe}_2\text{O}_3$

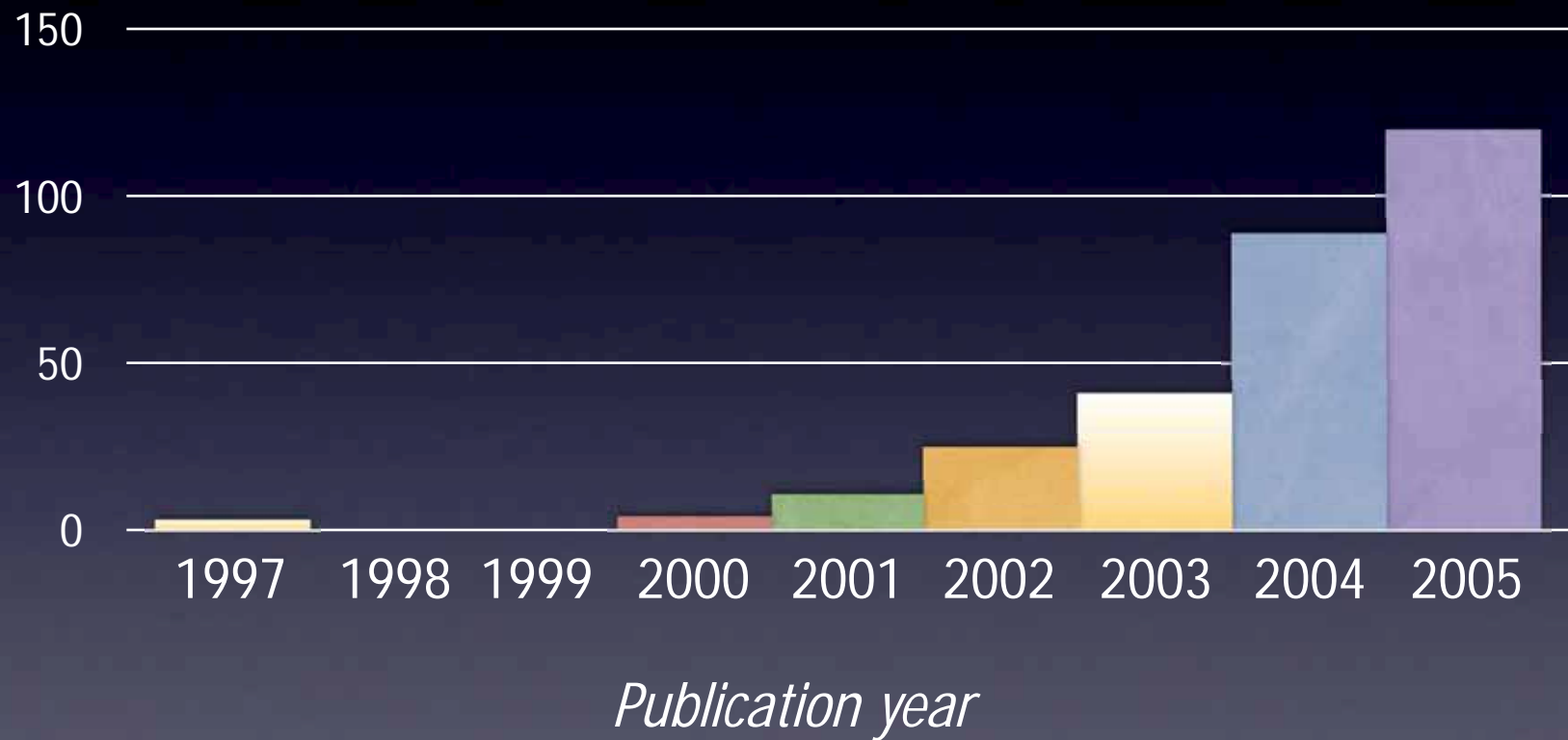


# Phostech's IP



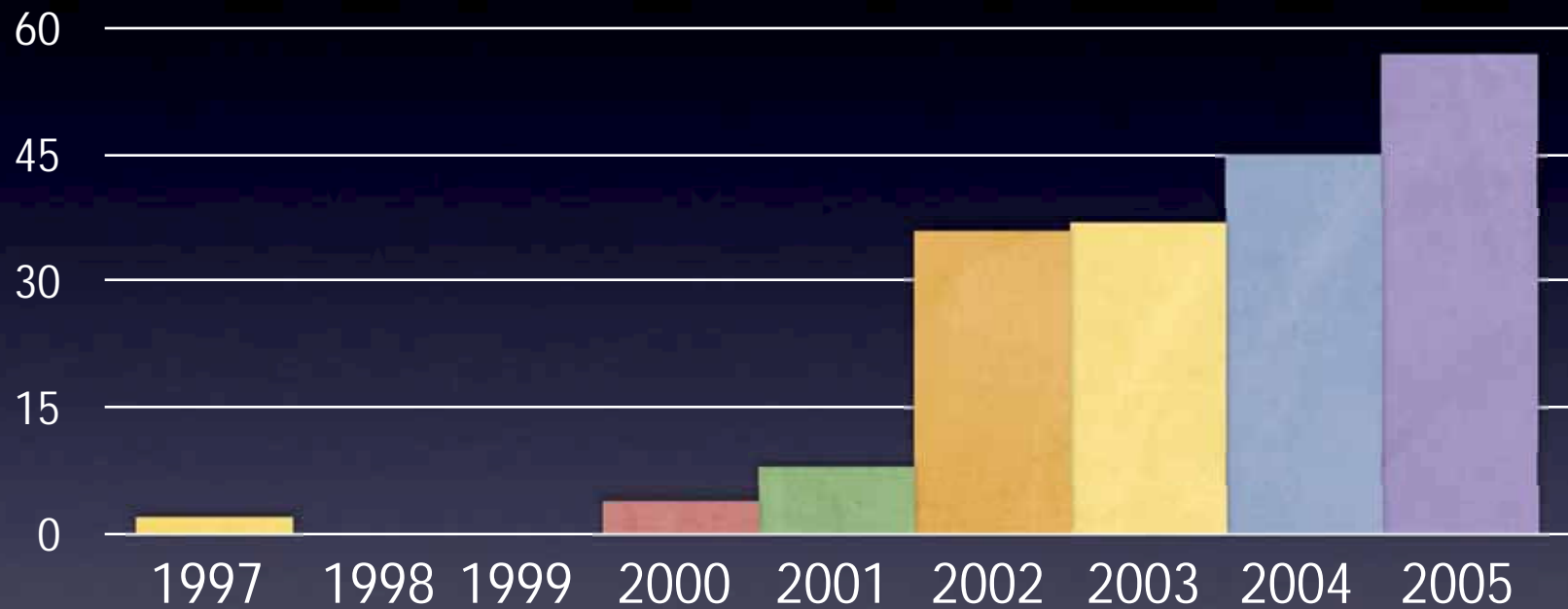
# Strong scientific activity on $\text{LiFePO}_4$

## Publications



# Strong patent activity on $\text{LiFePO}_4$

## Patents



*Publication year*

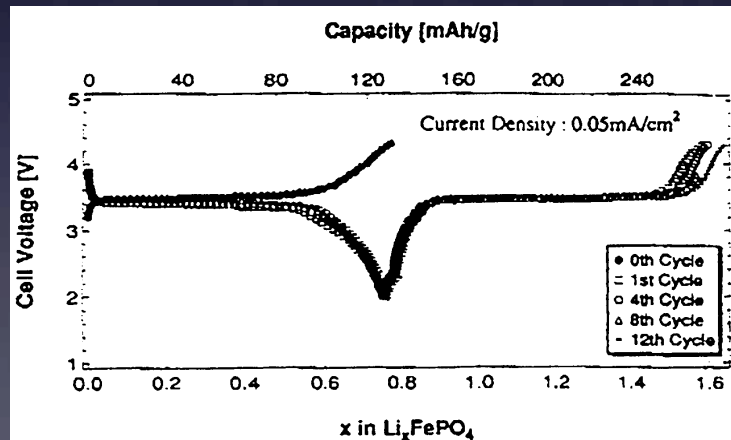
# Phostech core IP position

Combination of two patented key-innovation

## LiFePO<sub>4</sub>

- Application as cathode material  
**US 5,910,382**
- Optionally doped  
**US 6,514,640**

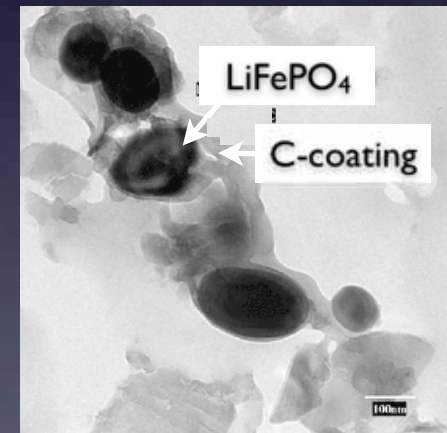
**Exclusive HQ/UT license**



## Carbon-coating

- Overcome low e<sup>-</sup> conductivity  
**US 6,855,273**

**Exclusive HQ/UdM/CNRS license**



**Necessary IP "TOOLBOX"** to commercialize battery grade product without infringing patents

**For more information on IP issue**

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*Phostech Lithium*

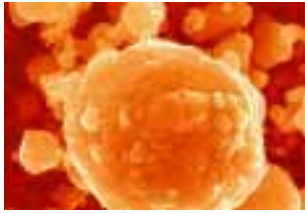
**Thorsten.Lahrs@phostechlithium.com**

**www.phostechlithium.com**

**(1) 450 653 1810**

# Availability of $\text{LiFePO}_4$





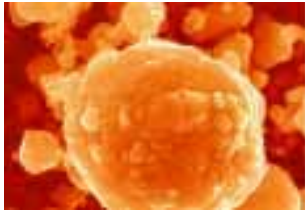
# Availability of $\text{LiFePO}_4$ Energy grade



**Boucherville, Quebec, Canada**

**100 to/year**

**Used in e-bikes etc. by PHET**

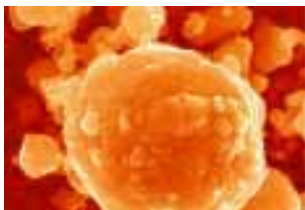


# Availability of $\text{LiFePO}_4$ Energy grade in St-Bruno, Qc



**400 to/year capacity in 2007**





# Availability $\text{LiFePO}_4$

Power grade



*Moosburg, Germany (Toll operation Süd-Chemie)*

<b>Actual</b>	<b>200 kg/month</b>
<b>Dec. 2006</b>	<b>3 to/month</b>
<b>April 2007</b>	<b>&gt; 10 to/month</b>

*Québec, Canada*

**Plant extension envisioned in Québec  
in the future for Life Power® P2**