LITHIUM IRON PHOSPHATE: towards an universal electrode material

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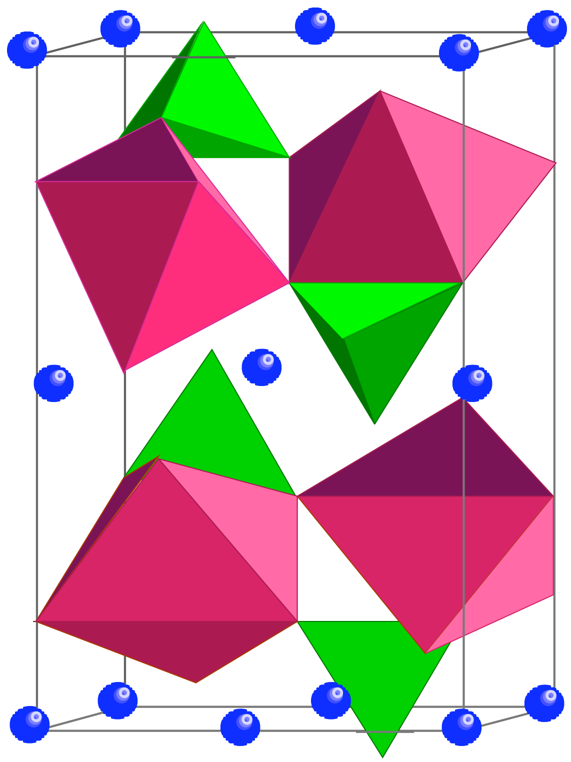
Olivine structure

heterosite structure



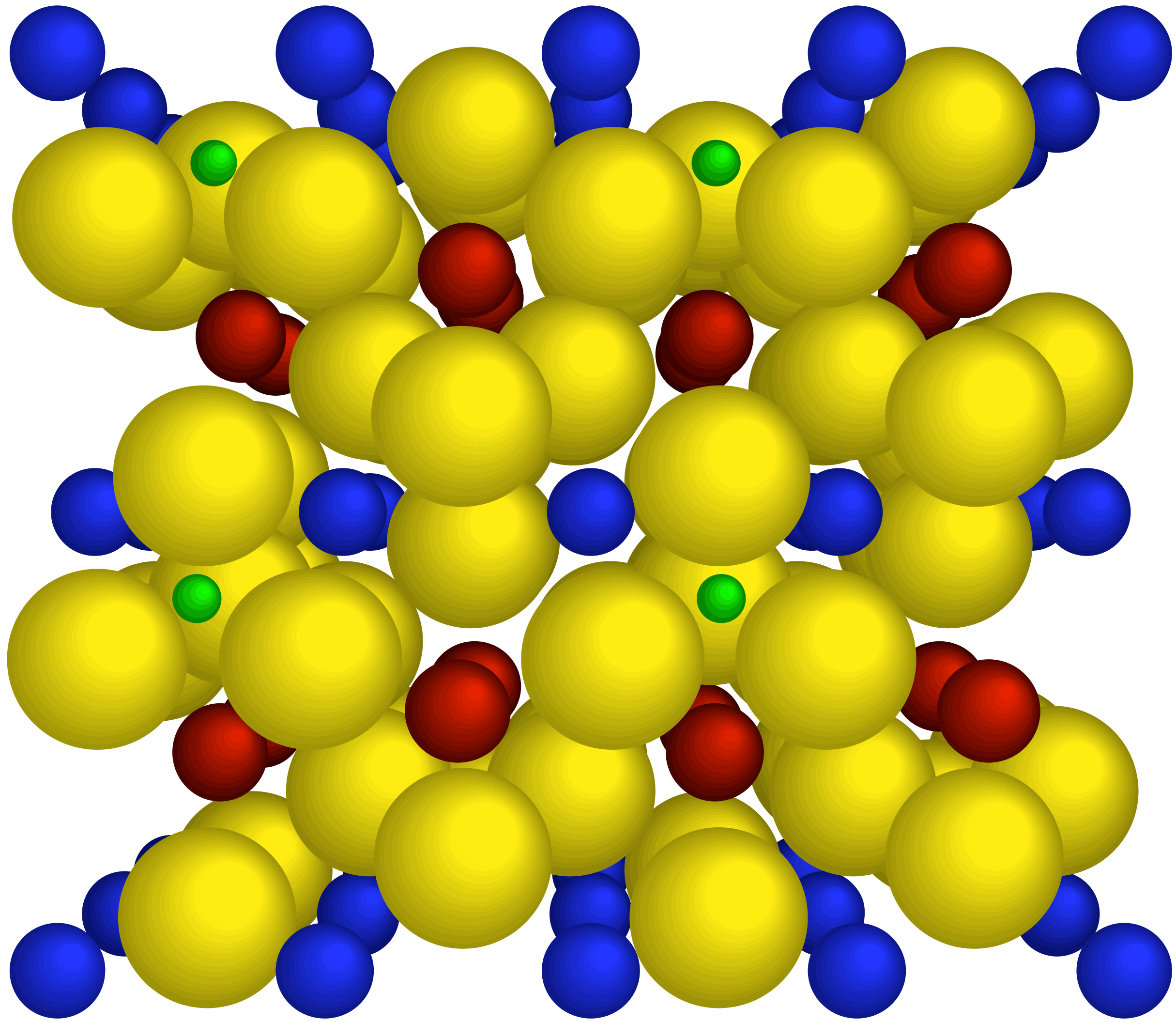
Li FePO$_4$

J. Goodenough and K. Padhi, 1996

Properties

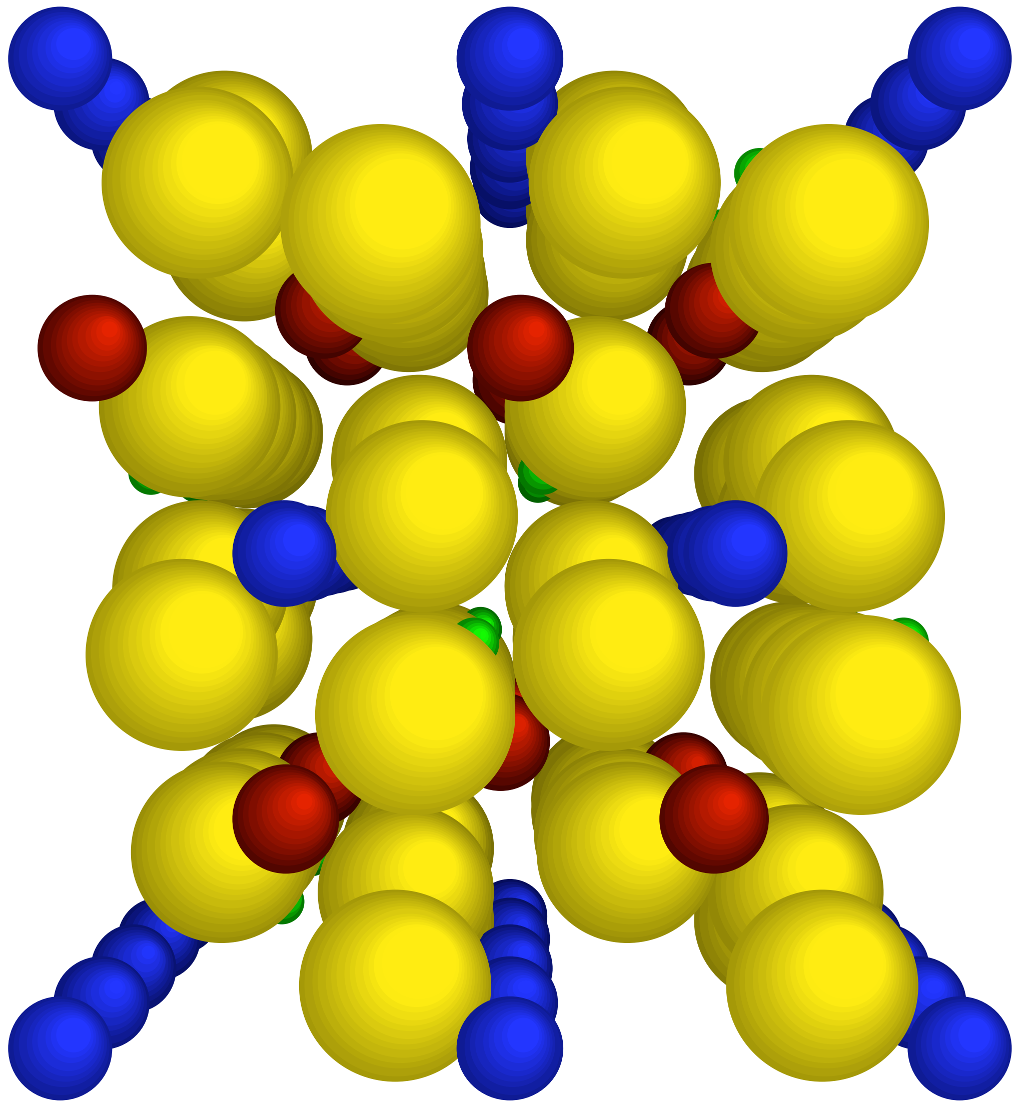
- ☑ **Thermal stability of LiFePO$_4$ and FePO$_4$ phases up to 400 ºC**
- ☑ **Inexpensive material**
- ☑ **Environmentally friendly**
- ☑ **High theoretical capacity**
- ☹ **Low electronic conductivity**

Olivine structure



View along the c axis

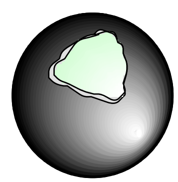
Olivine structure



View along the a axis

Our strategy to counter the lack of electronical Conductivity of $LiFePO_4$

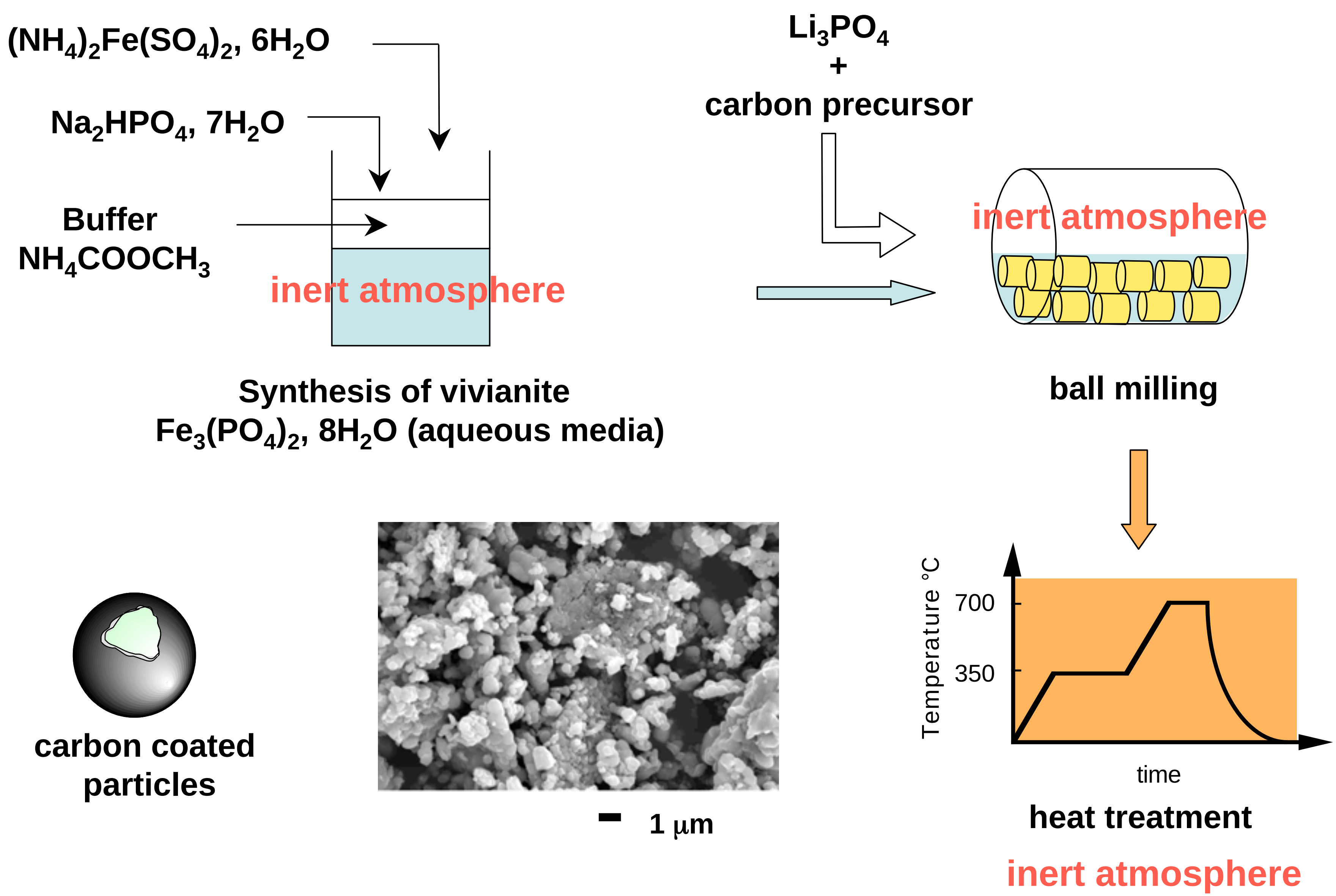
Nano-painting with inexpensive electronic conductor



carbon coated particles

Different routes for $LiFePO_4$ synthesis

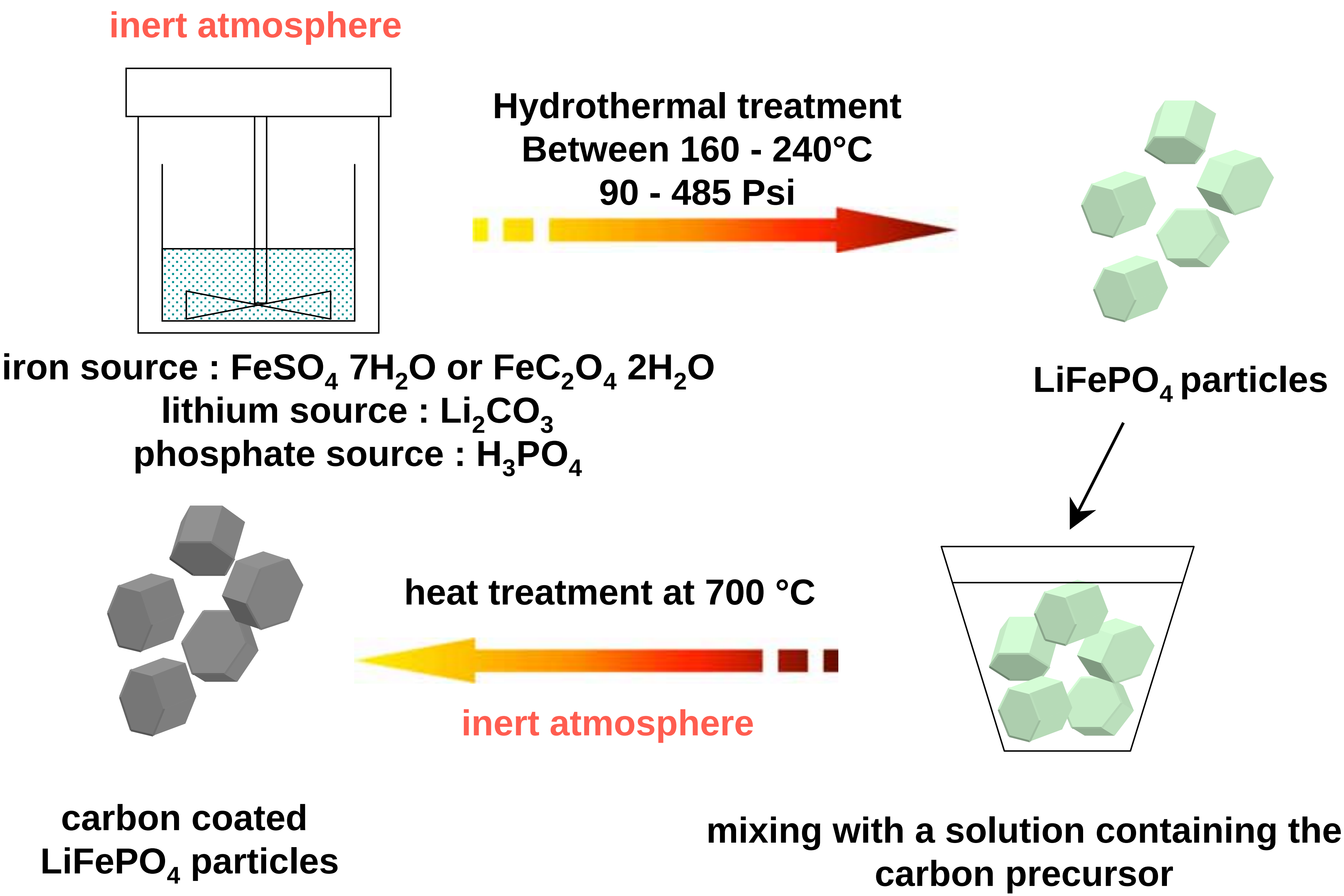
1) Synthesis from vivianite



Synthesis from vivianite

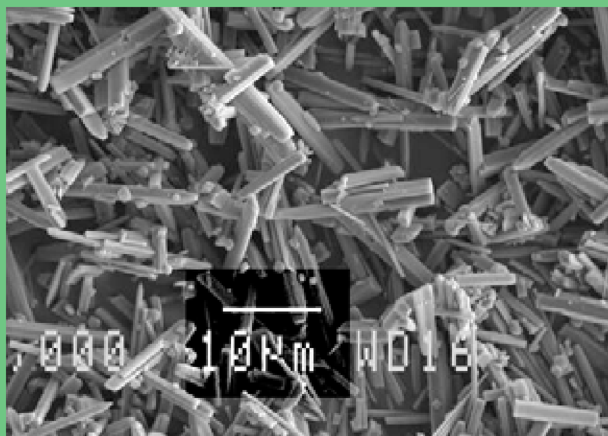
- ✓ Inexpensive precursors
- ✓ Micron size carbon coated particles
- ✓ High electrochemical performances
- ☹ Sensitivity of vivianite towards oxidation
- ☹ Poor reproducibility

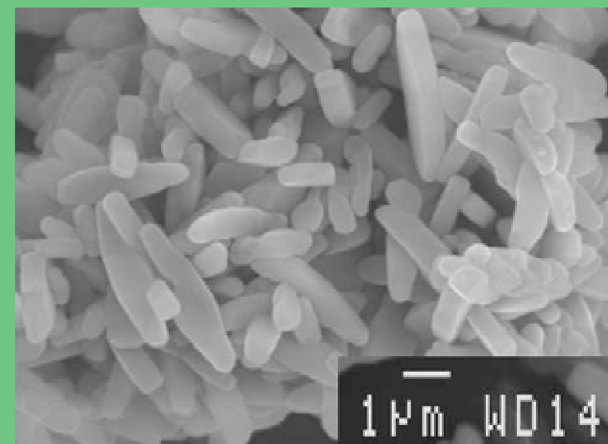
2) Hydrothermal synthesis



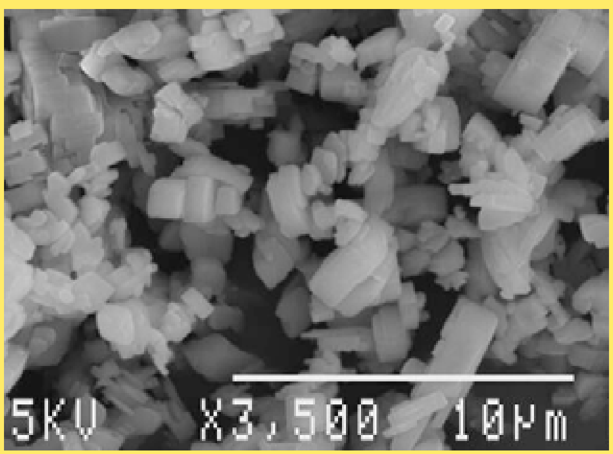
Hydrothermal synthesis

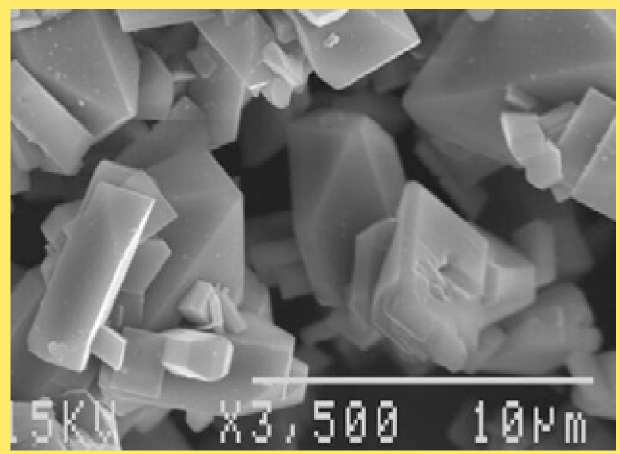
Some morphologies obtained by hydrothermal routes





From iron sulfate





From iron oxalate

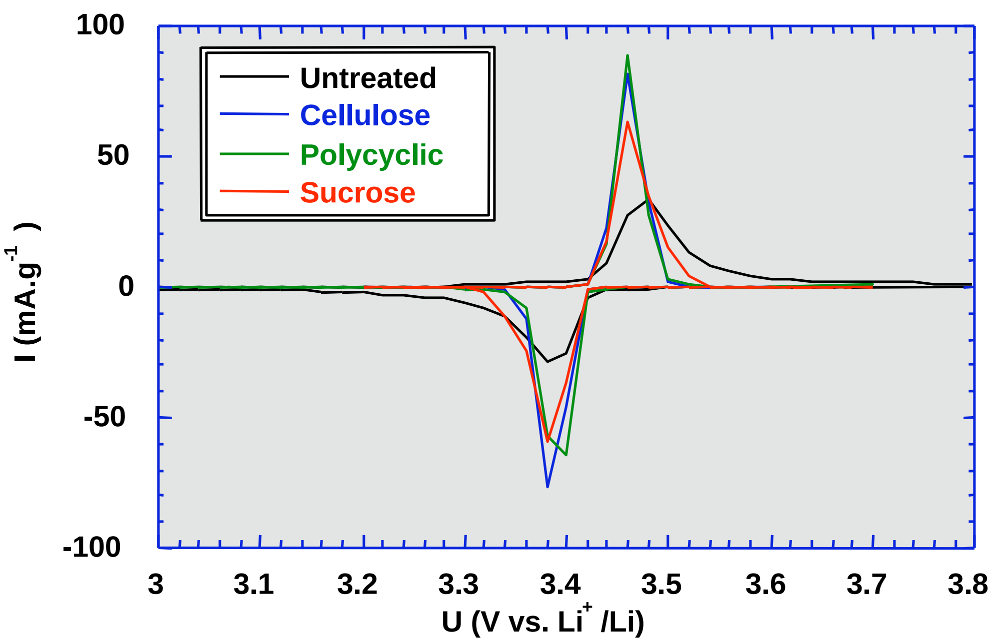
Hydrothermal synthesis

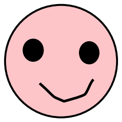
1) Influence of the carbon source on electrochemical behaviour in lithium battery

Slow scan voltammetry (v = 20 mv.h^{-1}) at 80°C

Investigated carbon precursors:

- Cellulose derivatives
- Sucrose
- Polycyclic compound





Carbon coating enhances kinetics

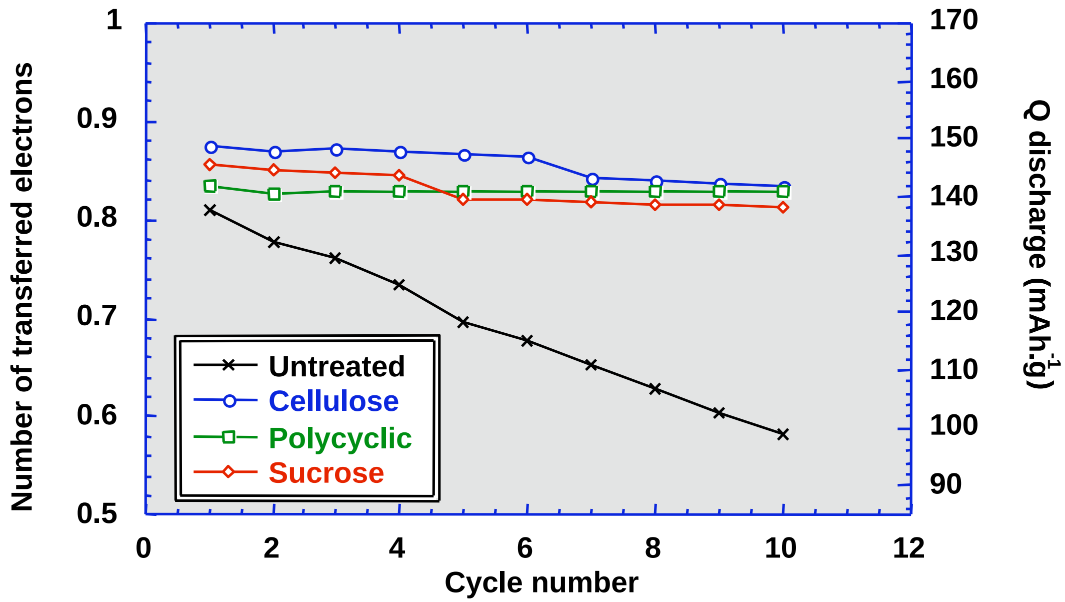
Hydrothermal synthesis

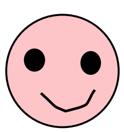
2) Influence of the carbon source on electrochemical behaviour in lithium battery

Slow scan voltammetry (v = 20 mv.h^{-1}) at 80°C

Investigated carbon precursors:

- Cellulose derivatives
- Sucrose
- Polycyclic compound





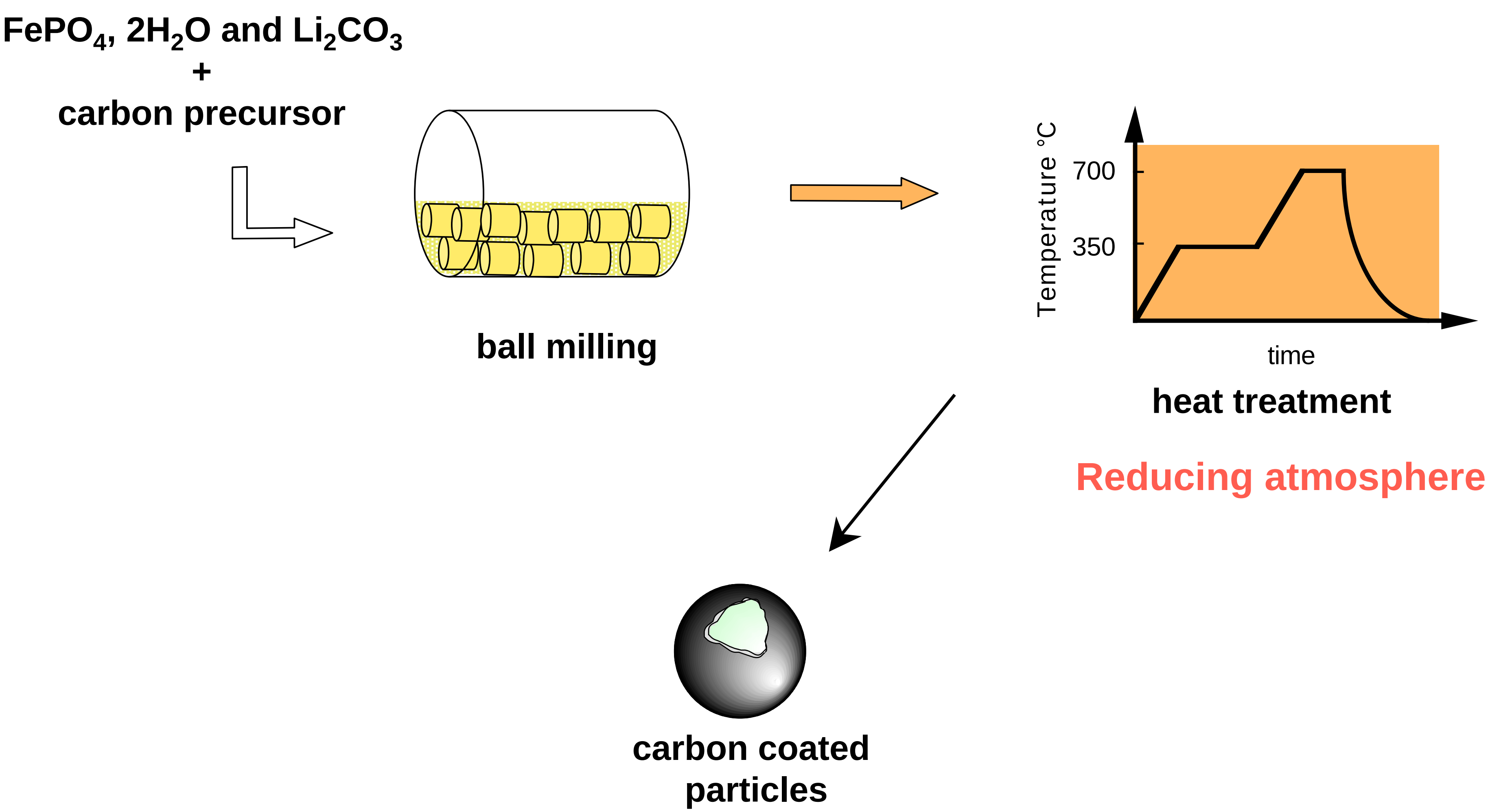
Carbon coating enhances cyclability

Hydrothermal synthesis

- ☑ Inexpensive precursors
- ☑ Control of particles morphology and size
- ☑ Good reproducibility

- ☹ Expensive equipment
- ☹ Post-synthesis heat treatment required
- ☹ Partially non-stoichiometric compound

3) Synthesis from iron III



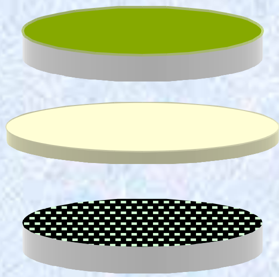
Synthesis from iron III

- ☑ Very simple one step route
- ☑ Inexpensive precursors
- ☑ Good reproducibility
- ☑ Excellent electrochemical behaviour

$LiFePO_4$ as cathode material in Lithium polymer batteries

1) High temperature applications

$LiFePO_4$ in lithium polymer batteries



lithium anode

electrolyte $PEO_{20}LiTFSI$

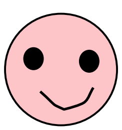
composite cathode

- $LiFePO_4$: 33.5 wt %
- PEO : 56.5 wt %
- Ketjen black : 10 wt %

experimental temperature : 80°C

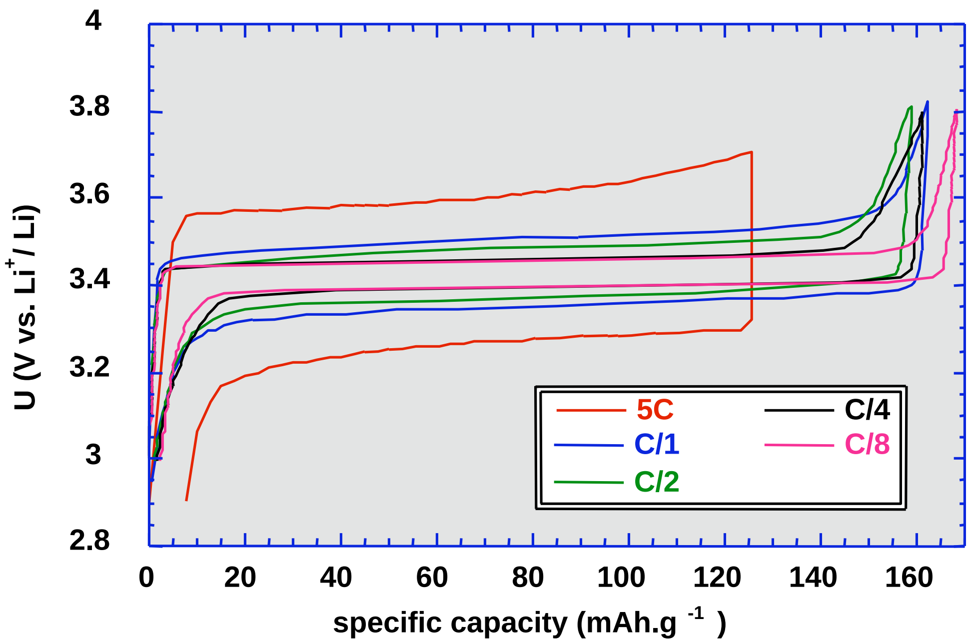
Charge and discharge profiles at various rates

(cut off values 3.8 and 3V)



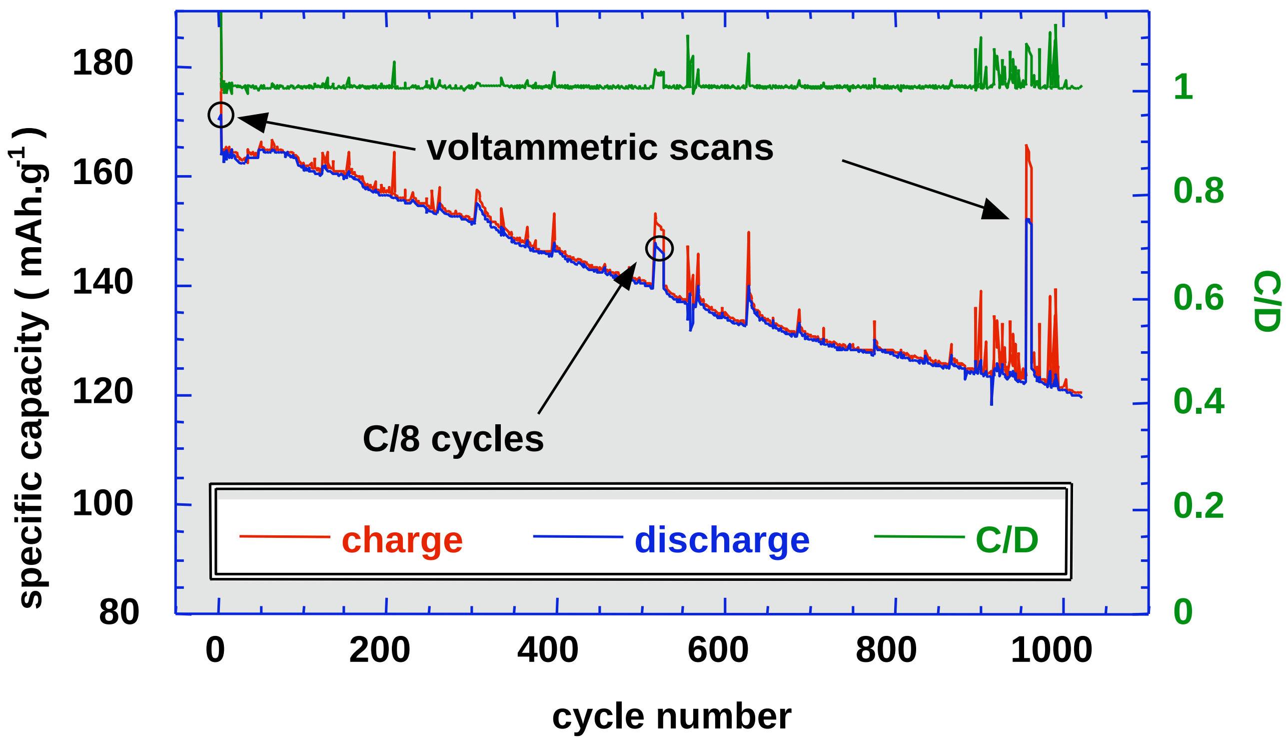
160 mAh.g^{-1} at C/1

120 mAh.g^{-1} at 5C



$LiFePO_4$ behaviour upon cycling

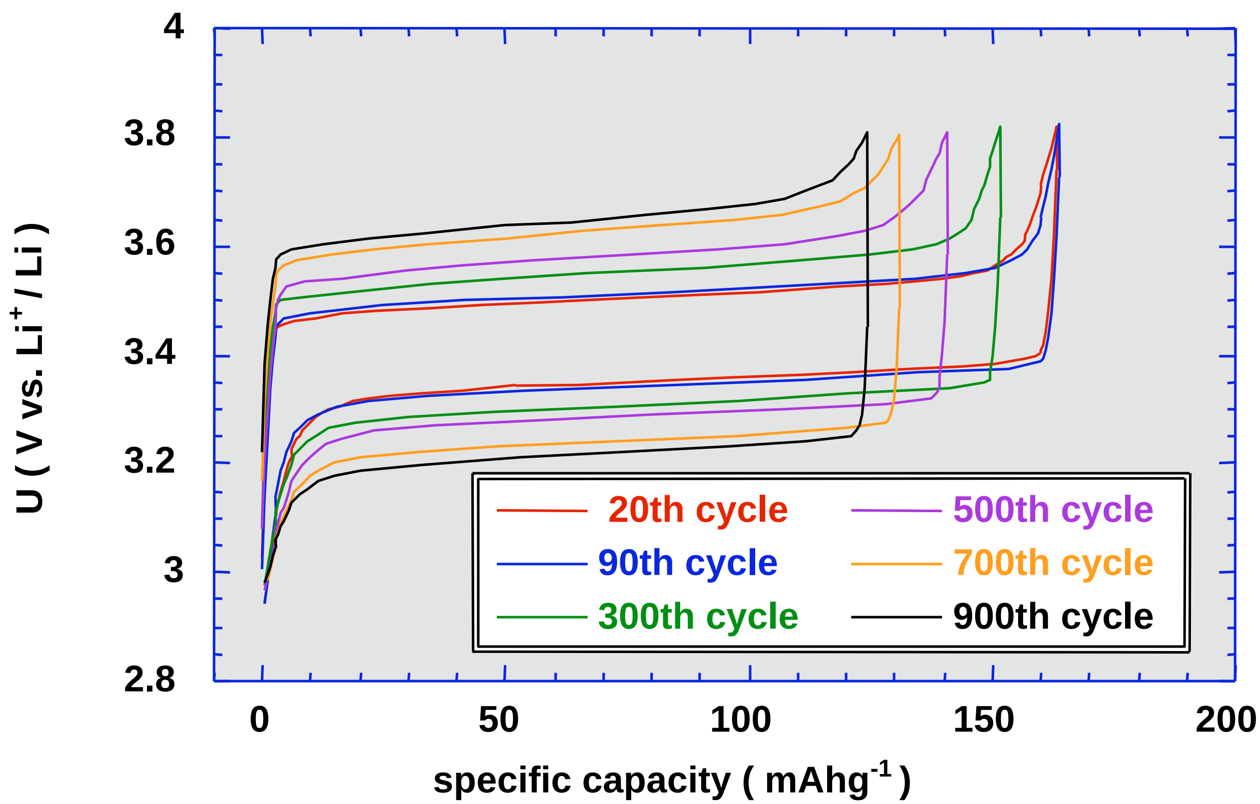
Evolution of battery features upon cycling at C/1
at 80°C (cut off values: 3.8 and 3V)

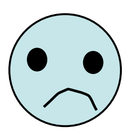


120 $mAh.g^{-1}$ after 1000 cycles at C/1
90% of initial capacity recovered at slower rates

LiFePO$_4$ behaviour upon cycling

Evolution of battery features upon cycling at C/1
at 80°C (cut off values 3.8 and 3V)



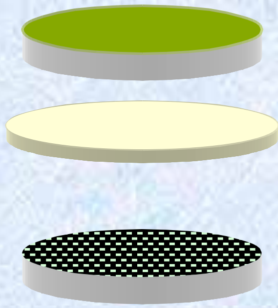


Loss of power upon cycling

$LiFePO_4$ as cathode material in Lithium liquid electrolyte batteries

2) room temperature applications

$LiFePO_4$ in liquid batteries



lithium anode

Celgard separator

- $LiPF_6$ 1M in EC:DMC 1:1
- $LiClO_4$ 1M in EC:DMC 1:1

composite cathode

- $LiFePO_4$: 85 wt %
- PVDF : 10 wt %
- carbon black : 5 wt %

Experimental temperature : 20°C

$LiCoO_2$ grade used in commercial batteries
Particles size 5-6 μm

$LiFePO_4$ obtained via vivianite synthesis

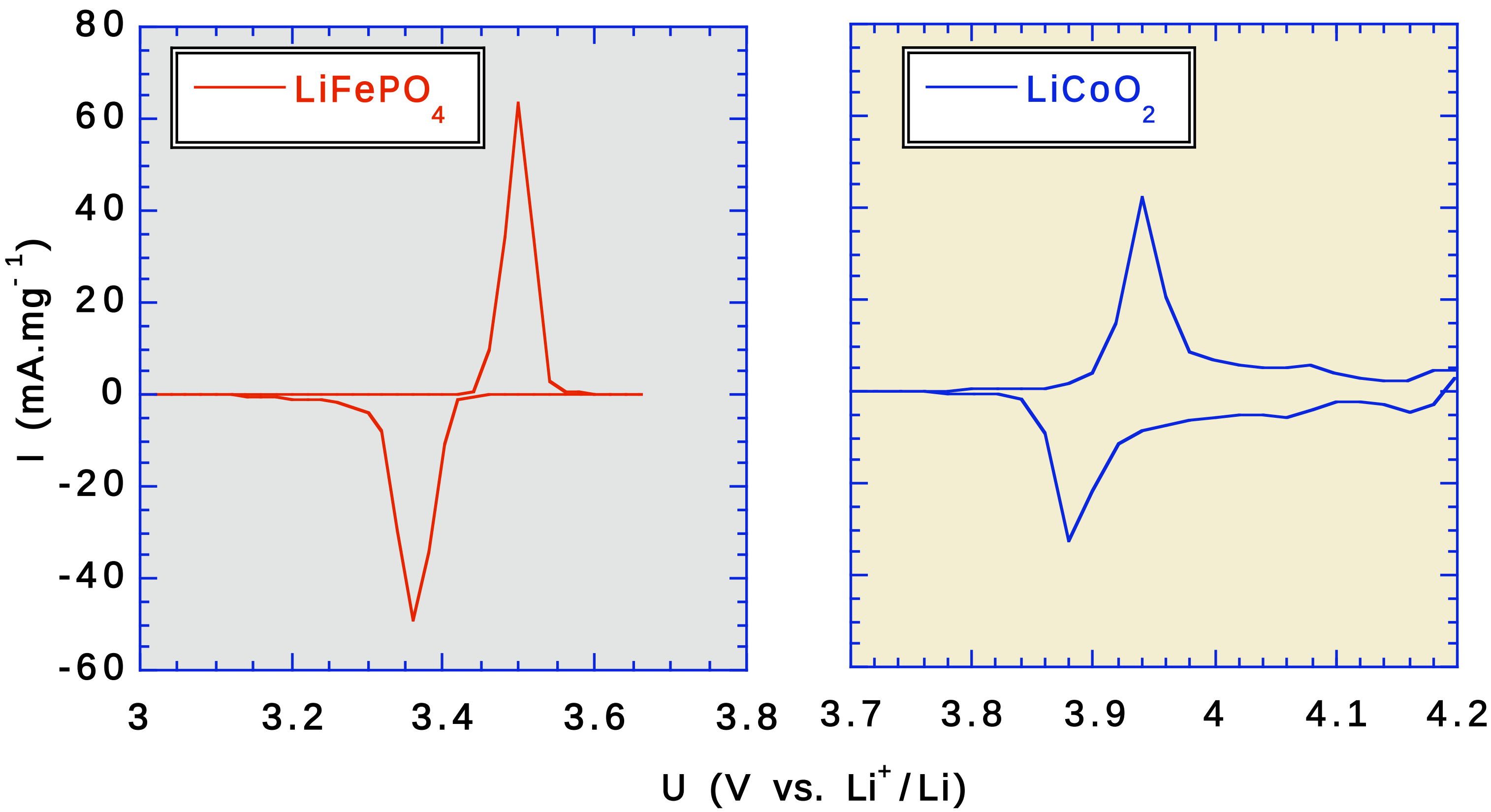
$LiFePO_4$ in liquid batteries

Electrochemical behaviour of $LiFePO_4$ and $LiCoO_2$

Slow scan voltammetry (v = 20 mv.h^{-1}) at 20°C

$LiFePO_4$ cathode :
7.5 mg.cm^{-2}
↓
1.25 mAh.cm $^{-2}$

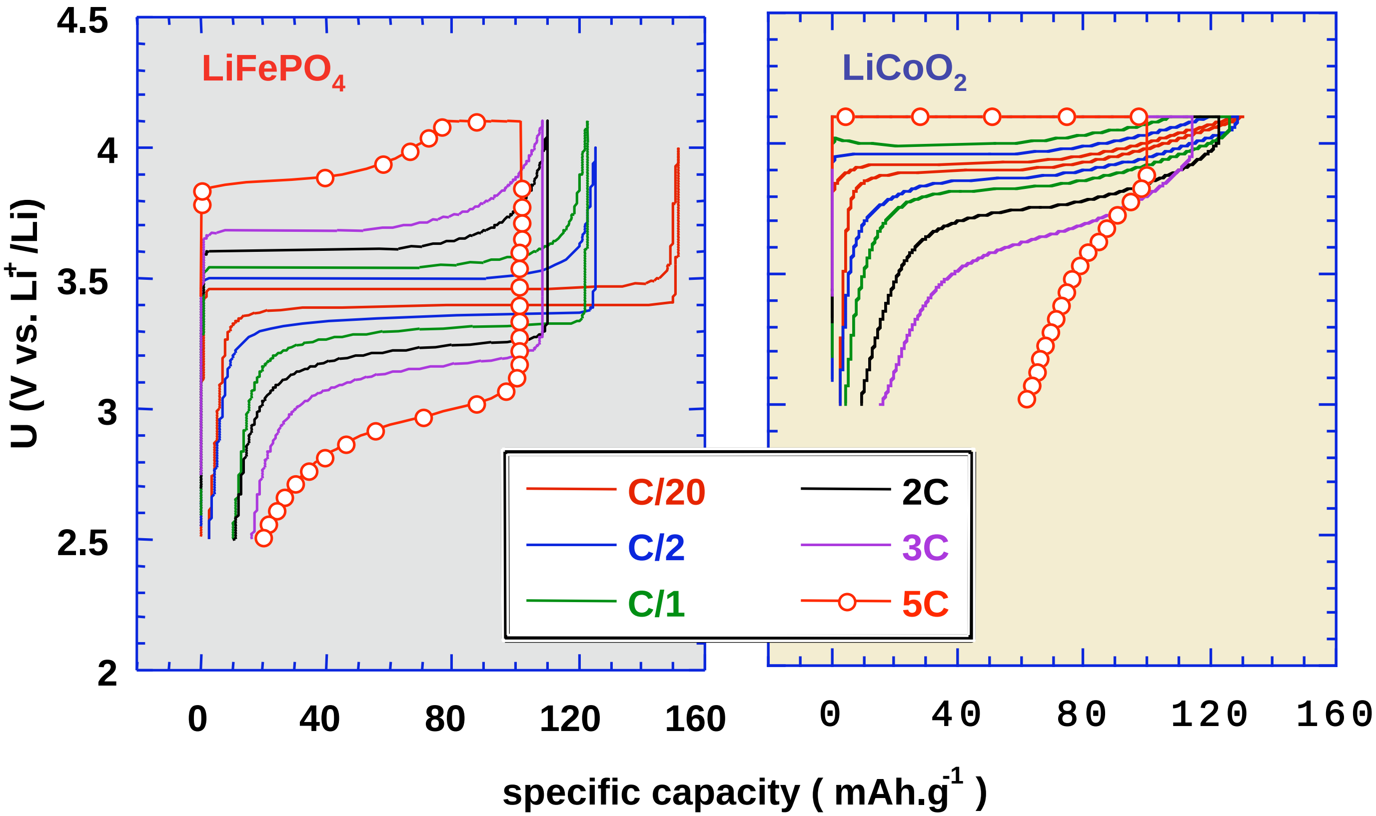
$LiCoO_2$ cathode :
7.7 mg.cm^{-2}
↓
1.05 mAh.cm $^{-2}$



$LiFePO_4$ in liquid batteries

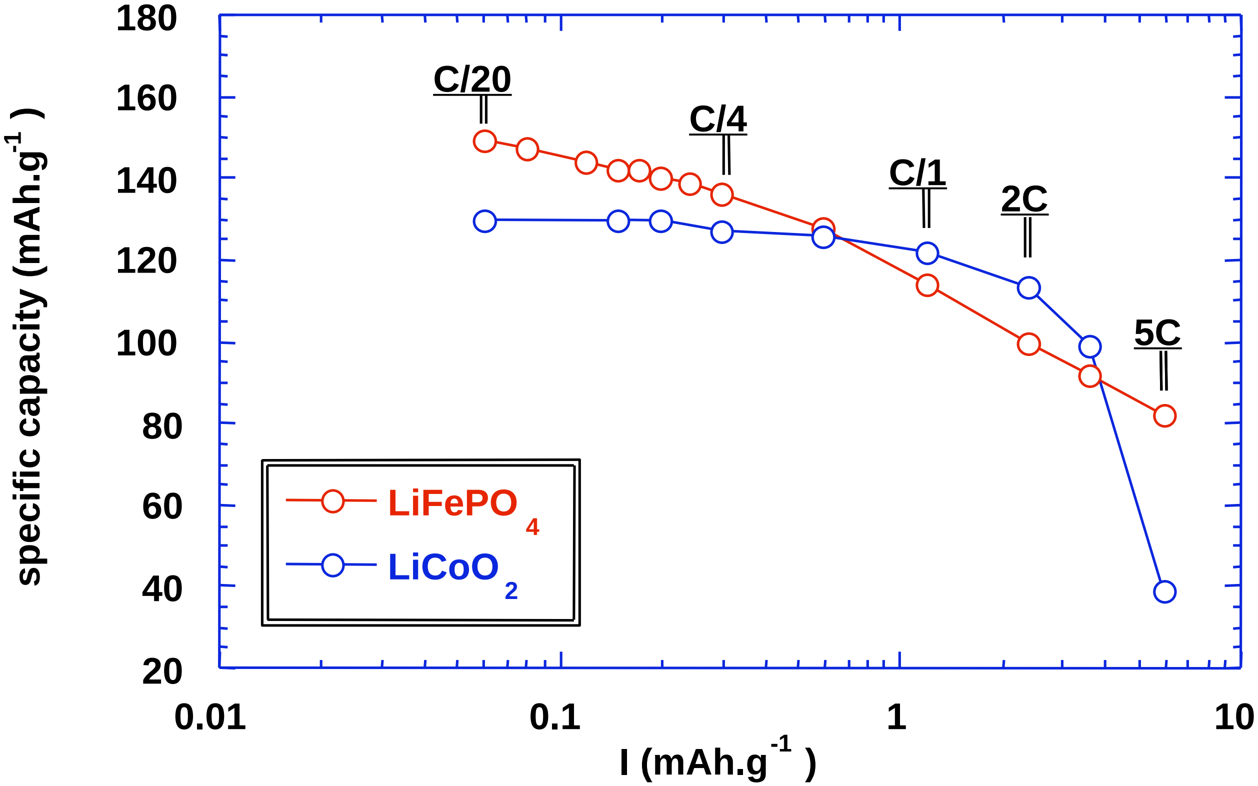
Charge and discharge profiles at various rates
at 20°C (cut off values 4.1 and 2.5V)

$LiFePO_4$ cathode : 7.5 mg.cm^{-2} → 1.25 mAh.cm $^{-2}$	$LiCoO_2$ cathode : 7.7 mg.cm^{-2} → 1.05 mAh.cm $^{-2}$



$LiFePO_4$ in liquid batteries

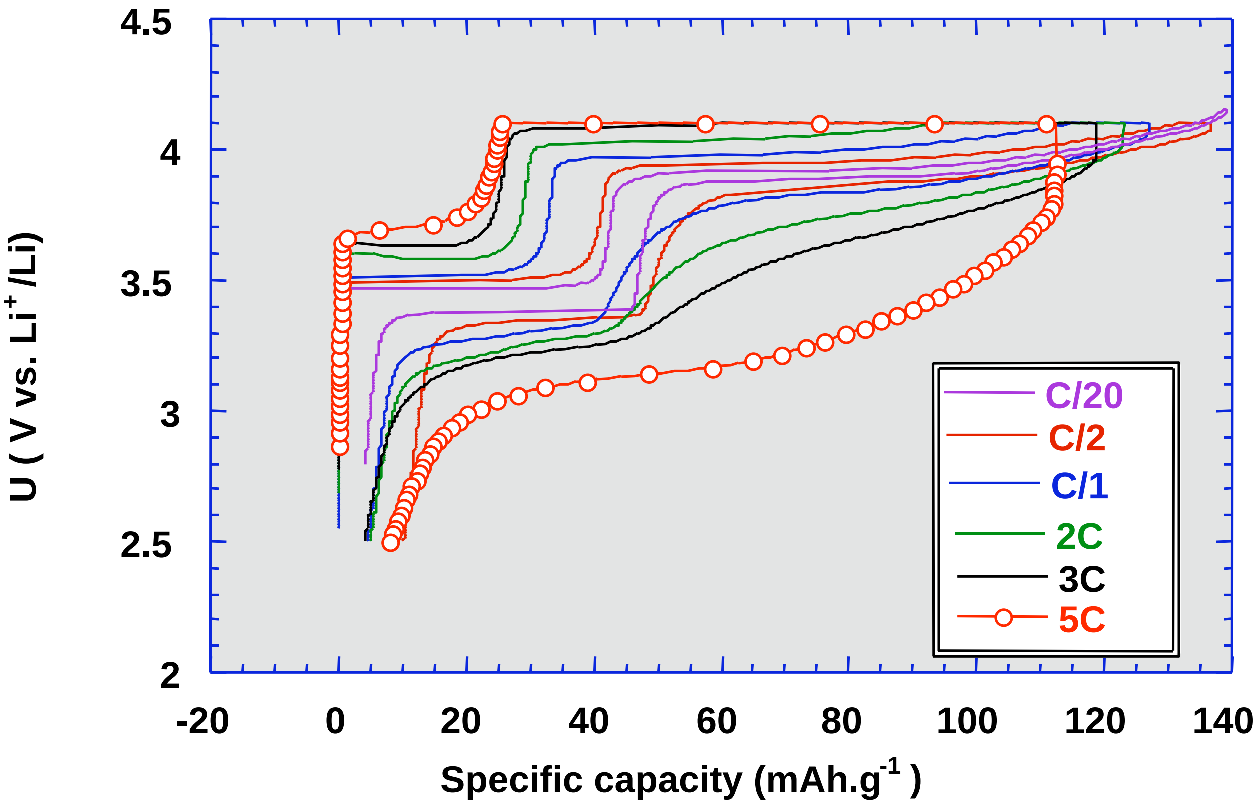
Evolution of specific capacity with current density



Blending cathode materials

Electrochemical behaviour of cathode materials blends in liquid battery at various rates (T = 20°C)

$LiFePO_4$	: 2.8 $mg.cm^{-2}$	0.47 $mAh.cm^{-2}$
$LiCoO_2$	: 7.2 $mg.cm^{-2}$	0.98 $mAh.cm^{-2}$
Total	: 10 $mg.cm^{-2}$	1.45 $mAh.cm^{-2}$



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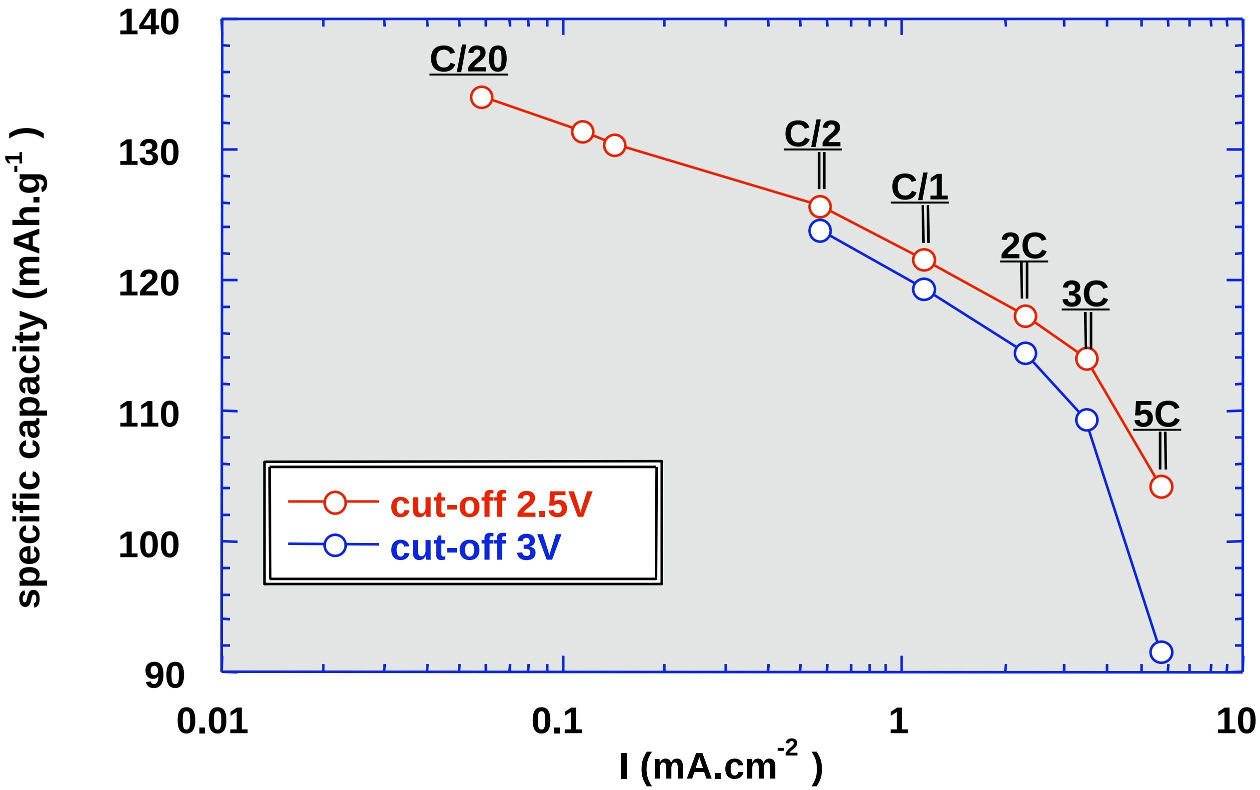

Conclusions

Lithium iron phosphate

\+ Carbon coating (“nano painting”) compensates for lack of electronic conductivity => very fast kinetics (5C !)

\+ Facile synthetic routes offer a choice of morphologies without compromising on price nor performances

\+ With manganese phosphates, the future source of inexpensive safe electrode materials

\- Drawback of lower specific gravity and tap density

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