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Improved Iron Based Cathode Material

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Transition metal-based intercalation compounds are suitable materials for cathode in lithium batteries.

Recently Padhi et al.[1-2] suggested the use of a new compound having the olivine structure: $LiFePO_4$. This iron based compound is environmentally benign and inexpensive. Insertion of lithium occurs reversibly with a very flat discharge plateau at about 3.4 V vs. Lithium. $LiFePO_4$ and delithiated $FePO_4$ though not intermiscible belong to the same space group with only small change in the unit cell parameters; this makes the material stable upon cycling. Unfortunately the limited accessibility of 0.6 Li atoms per formula unit of $LiFePO_4$ found by these authors limits the practical capacity to 100-110 $mAh.g^{-1}$ capacity, from the theoretical 170 $mAh.g^{-1}$.

Here, we report a new route for the synthesis leading to electronically conductive $LiFePO_4$ particles with outstanding electrochemical features.

An electronically conductive substance is added during the synthesis, before the formation of crystalline $LiFePO_4$. This substance represents less than 1% by weight of the final product. The crystallographic structure has been confirmed by X-ray.

Electrochemical tests were made at 80 °C, in coin type cells using a polymeric electrolyte.

The improvements of the material are summarized as follows:

- Voltammetric scans performed at 20 mV/h show that the intercalation / desintercalation of lithium is no longer limited (figure 1) and the capacity involved during the discharge process in these conditions is between 94 and 100 % of the theoretical capacity, i.e. 160-170 $mAh.g^{-1}$.
- The electronically conductive coating enhances the overall kinetics of the redox reactions. Figure 2 shows intentiostatic scans performed at 170 $mA.g^{-1}$ corresponding to a charge / discharge rate of C. Once again, the whole capacity is reached.

The addition of a conductive material during the synthesis of $LiFePO_4$ improves the practical capacity and the charge / discharge rate. Morever, the good reversibility of the redox reactions and its predicted low price make $LiFePO_4$ an attractive cathode for $3V^+$ lithium batteries.

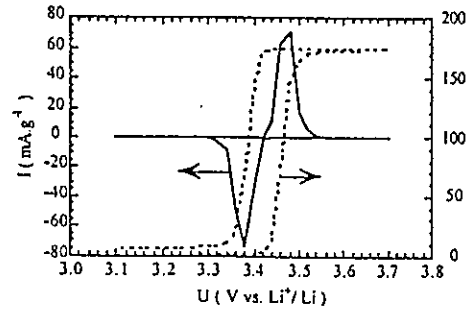

Fig. 1 : Potentiodynamic profiles for $LiFePO_4$. Scan rate 20 $mV.h^{-1}$; temperature 80 °C; electrolyte PEO-Li salt O/Li = 20:1

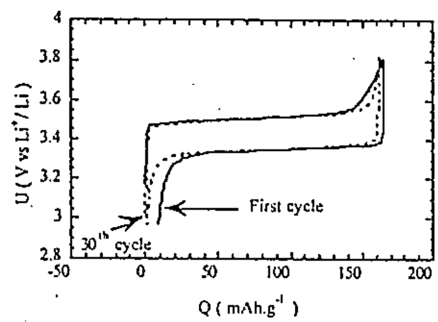

Fig 2 : Charge / Discharge curves of a $LiFePO_4$ cathode. Discharge rate C, Temperature 80 °C.

References:
1. A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, Proc. 189th ECS Meeting, L.A., May 5-10 (1996).
2. A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 144, 1188 (1997).

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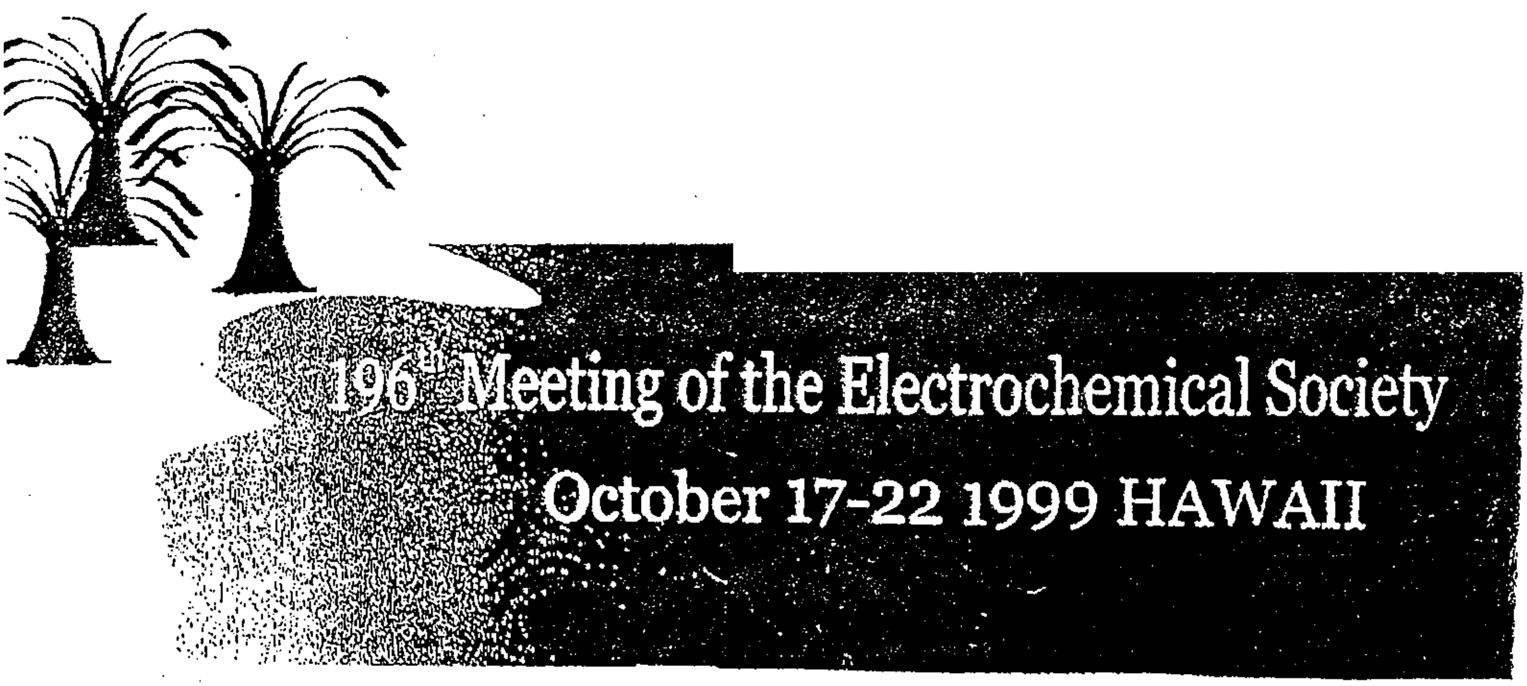
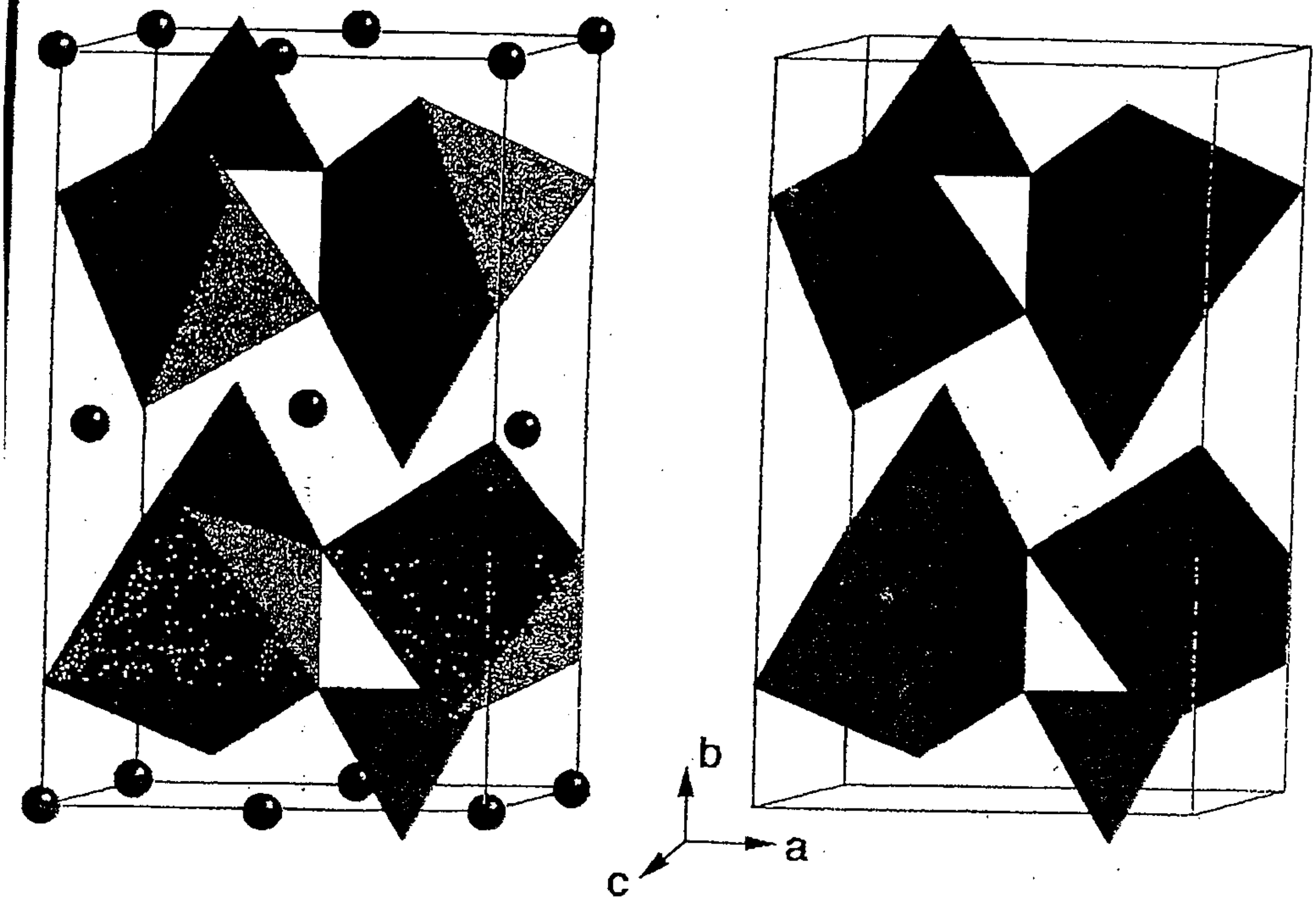


Olivine structure



$LiFePO_4 \underset{}{\overset{-e^-}{\rightleftharpoons}} FePO_4 + Li^+$

	$LiFePO_4$	$FePO_4$
a (Å)	6.008	5.792
b (Å)	10.334	9.821
C (Å)	4.693	4.788

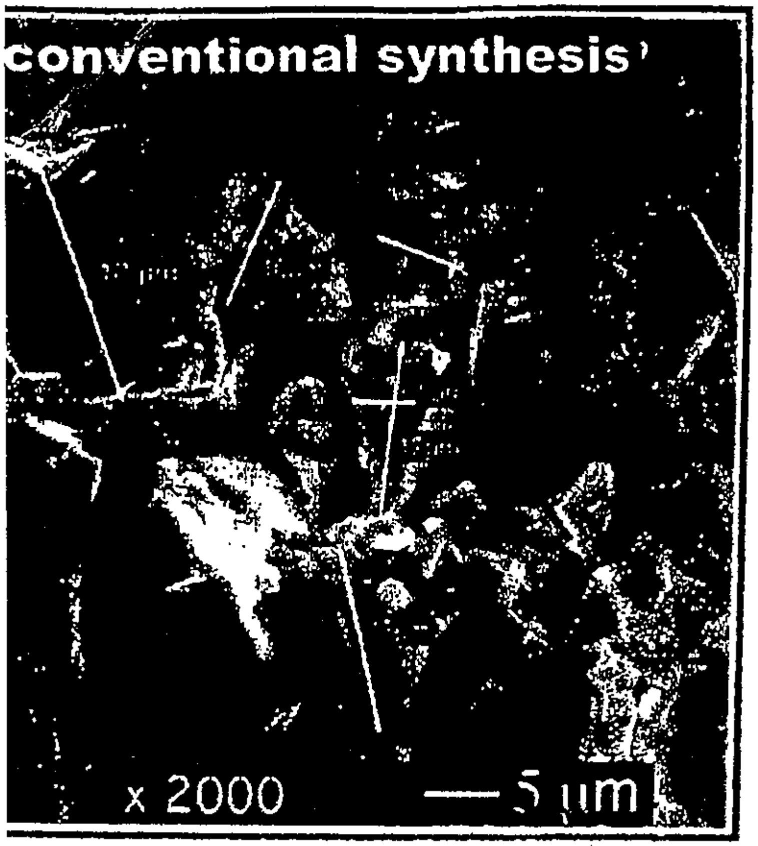
J. Goodenough and K. Padhi, 1996

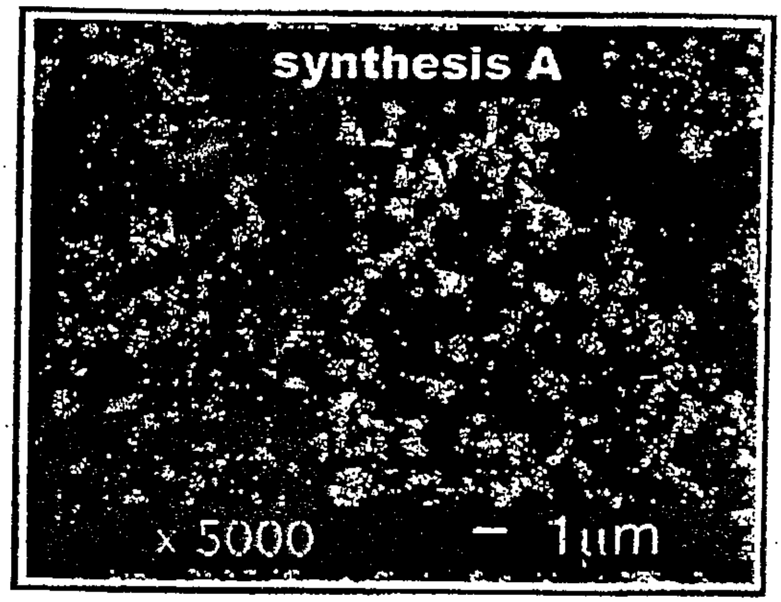
New syntheses of $LiFePO_4$

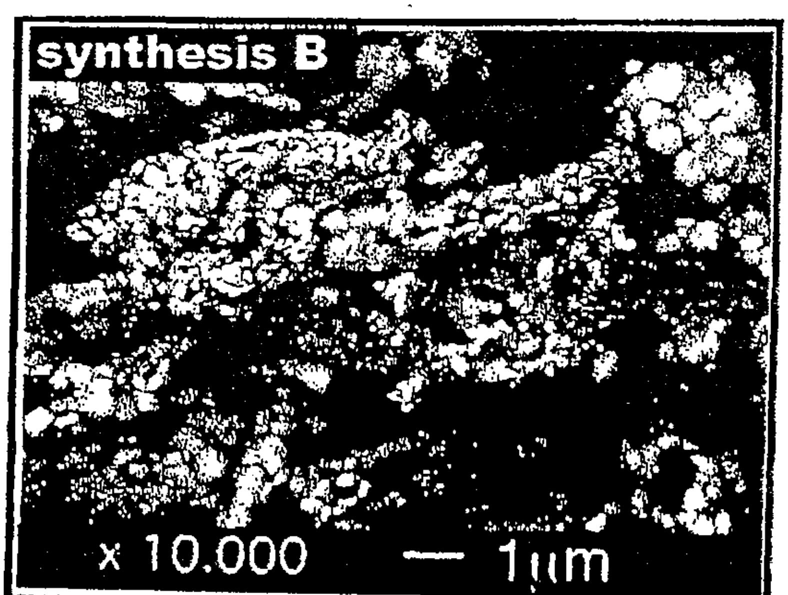
Synthesis A

Synthesis B
electronicaly conductive $LiFePO_4$

- Inexpensive route
- Electronic conductivity of sample B : 2.10^{-5} S.cm^{-1}


conventional synthesis
x 2000
5 μm

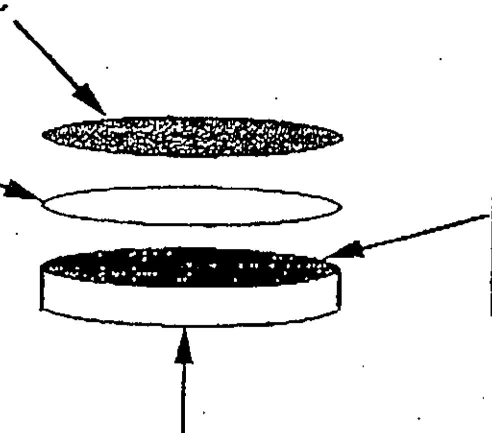

synthesis A
x 5000
1μm


synthesis B
x 10.000
1μm

Electrochemical experiments
Cell and setup

- Electrochemical cell

Coin cell type



⚠ Mass of active material : 1-3 mg
0.170 - 0.510 mAh

- experimental setup

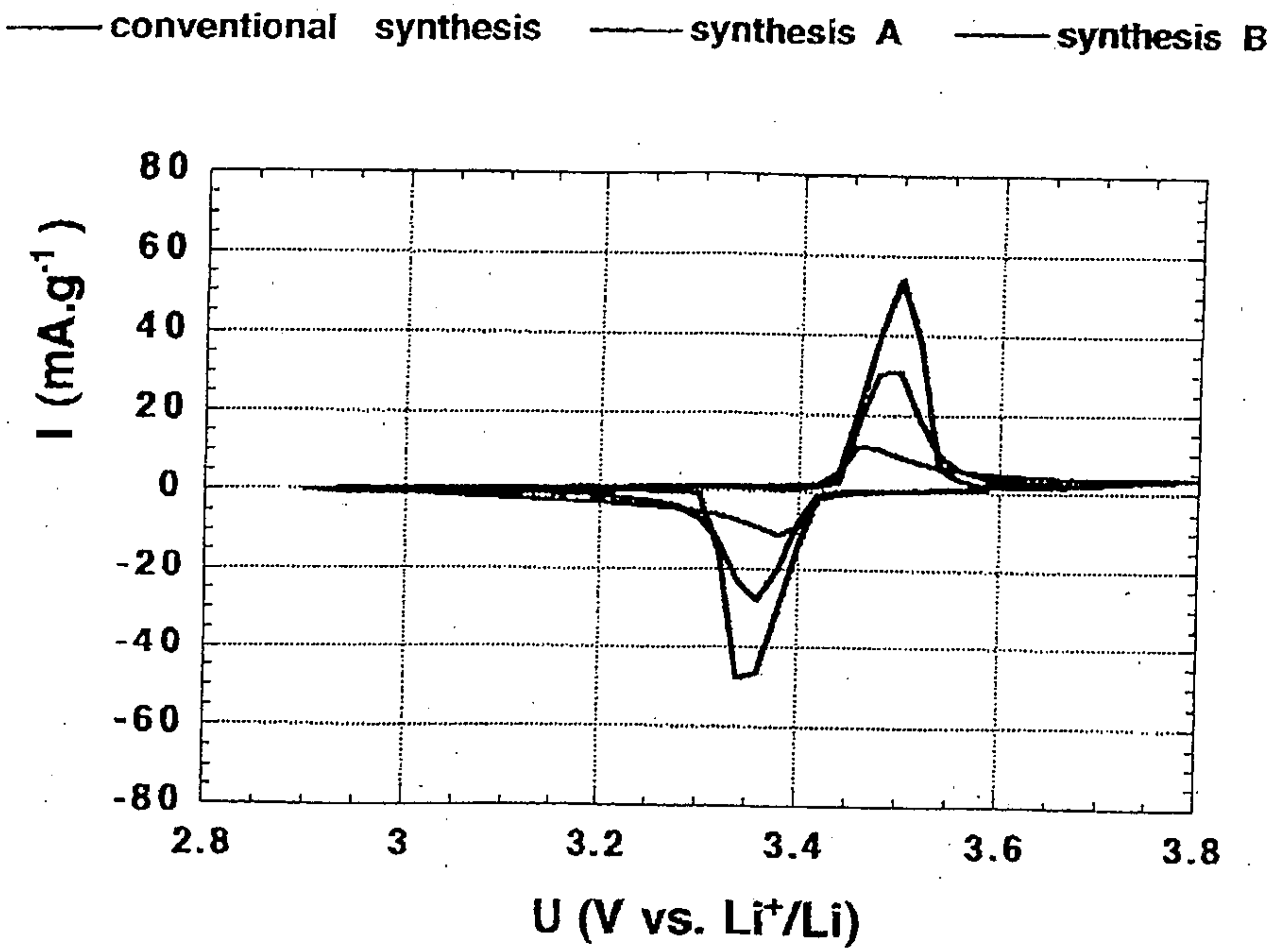
Experiment temperature : 80 °C

Slow scan Macpile® voltammetry (20 $mV.h^{-1}$)
3 - 3.7 V

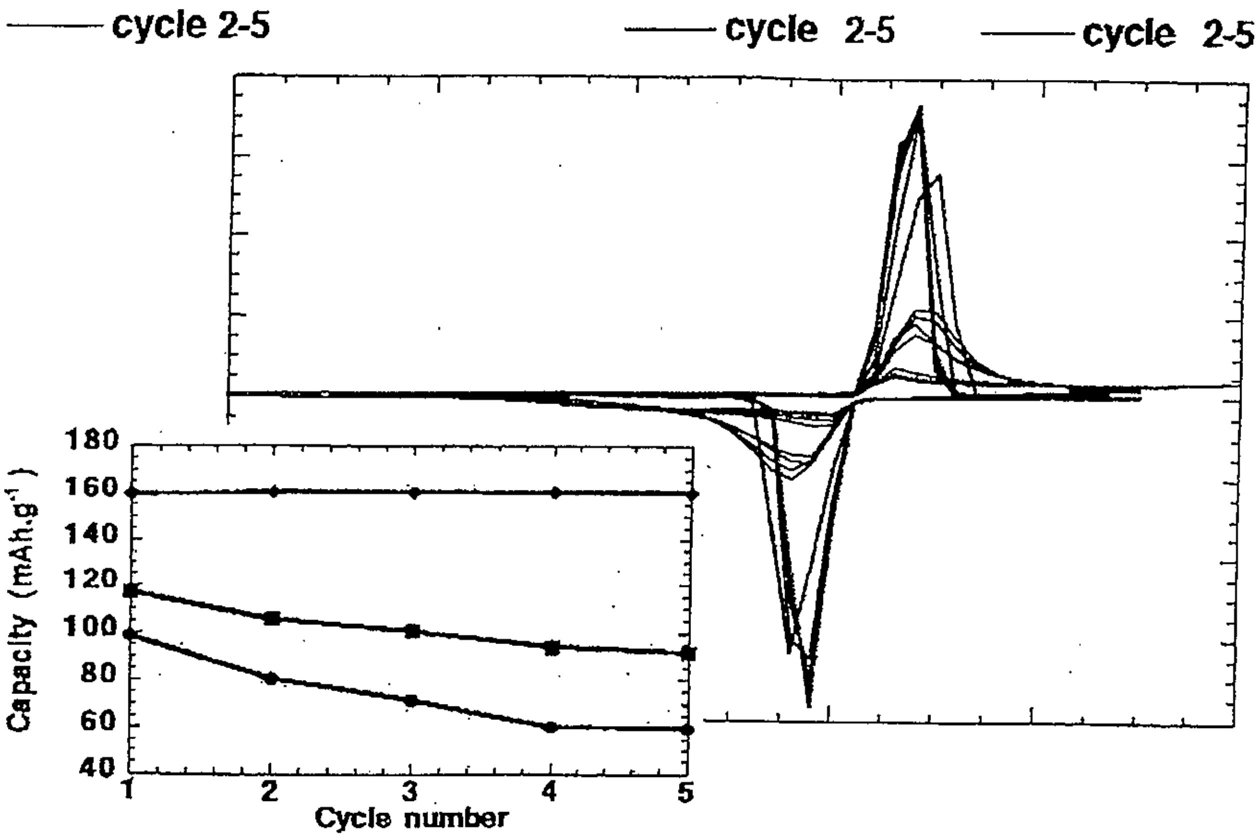
Galvanostatic Charge and discharge
3 -3.8 V

Electrochemical behaviour

Comparison of the 3 syntheses (voltammetric scans)

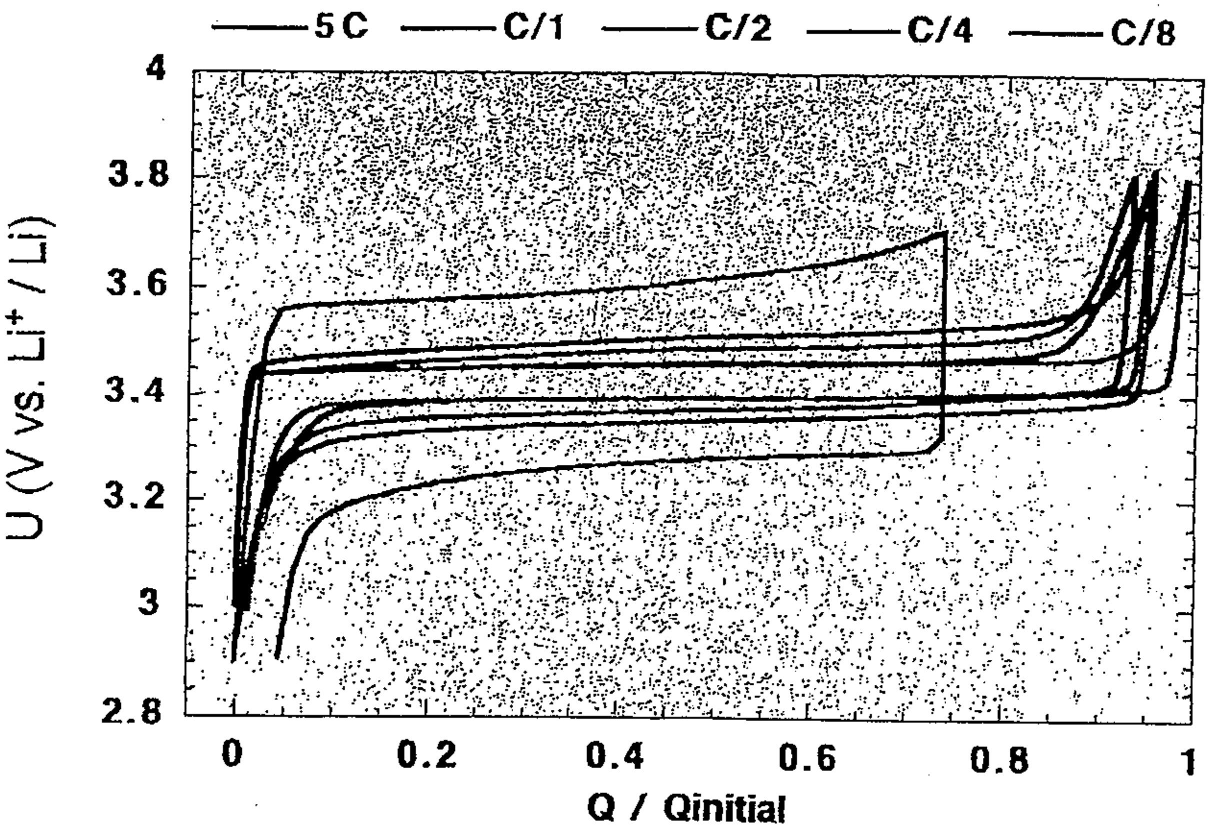


- Improvement of the reaction kinetics
- Improvement of the reversible capacity



- Capacity fade observed for non-conductive samples
- 160 - 170 mAhg^{-1} reversibly exchanged for synthesis B

Galvanostatic experiments
experiments performed at different discharge rates

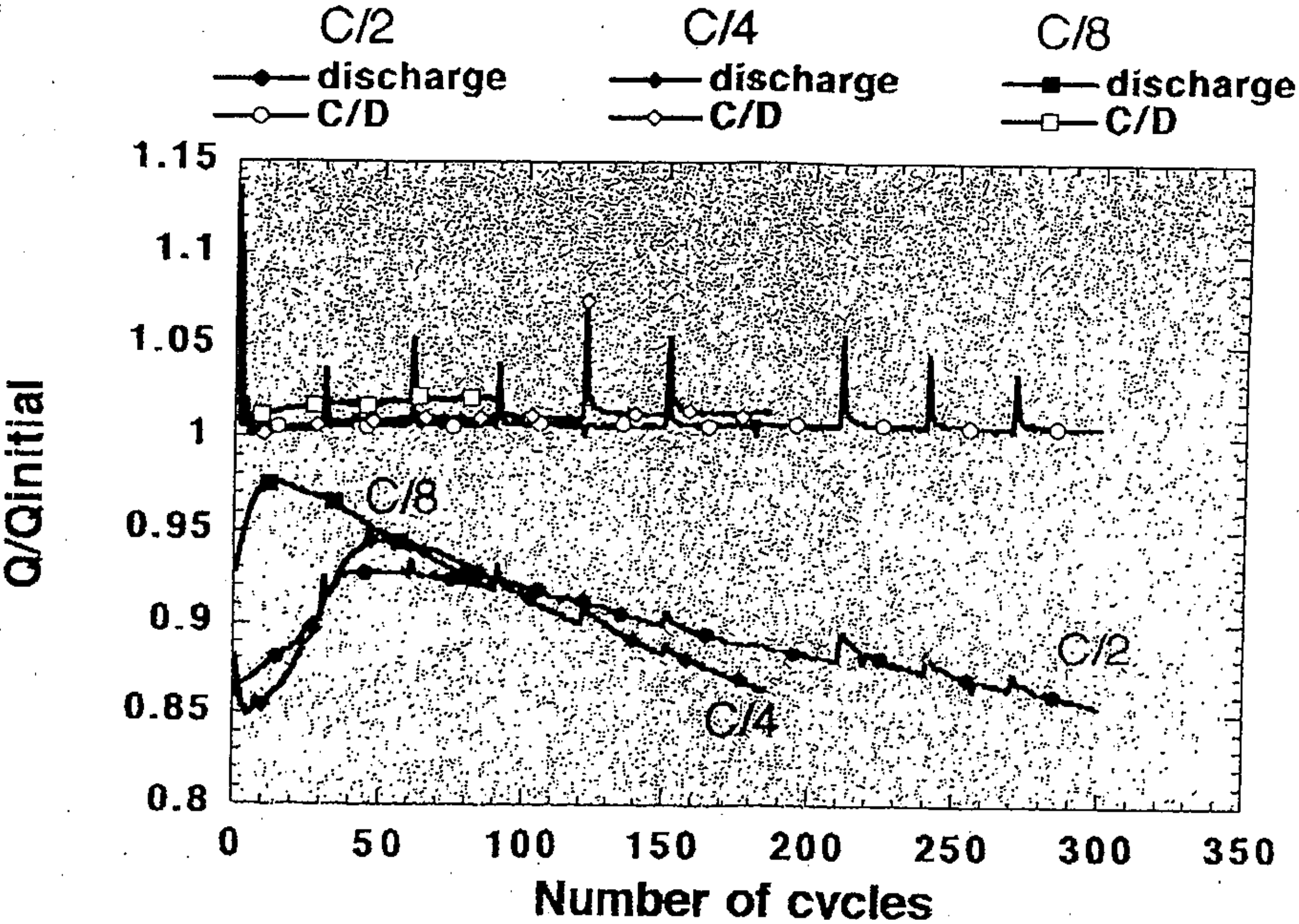


- 93 to 98 % of the initial capacity i.e. 158-166 $mAh.g^{-1}$ is involved in the rate range C/1 - C/5

- for the 5C rate 70 % of the initial capacity was exchanged i.e. 115 $mAh.g^{-1}$

⚠ For rates higher than C/4 the oxydo-reduction reactions are limited by the lithium diffusion

Behaviour upon cycling
at different charge / discharge rates



⚠ decreasing the charge /discharge rate

↓

increase of C/D ratio

increase of capacity fade

Oxydation secondary reaction

Voltammetric scans at different rates
self discharge tests

↓

secondary reaction during the oxydation process
reversible self discharge of $FePO_4$ at open circuit

↓

Oxydation of :

Electrolyte ?

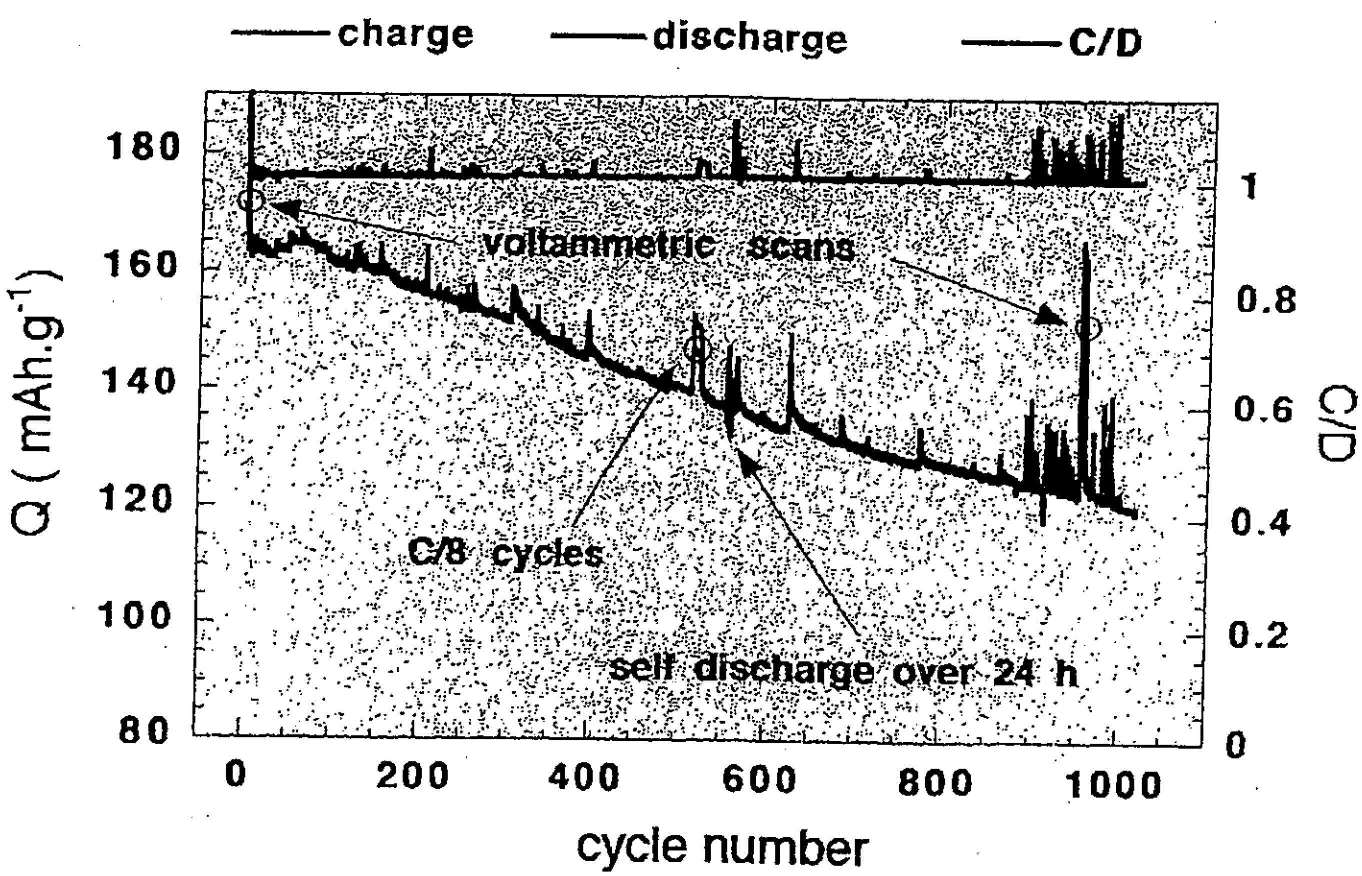
curent collector ?

Electrochemical tests with different substrats
shown the same self discharge

↓

One of the species presents in the electrolyte is probably involved in the secondary oxydation reactions

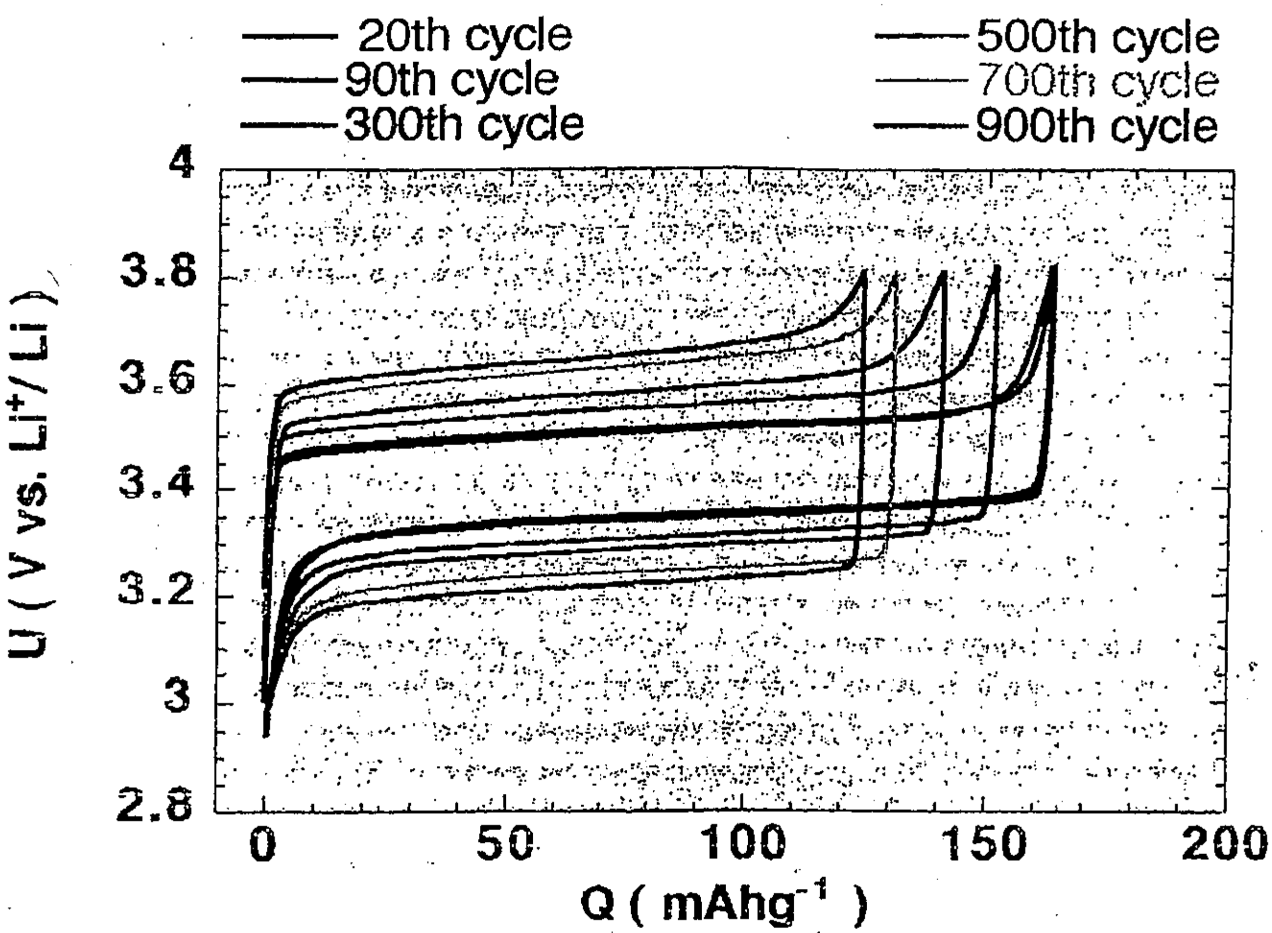
Behaviour upon cycling
experiments performed at a discharge rate of C/1



- 96 % of the initial capacity retained after 80 cycles and 70 % after 1000 cycles
- After 950 cycles 89 % of the initial capacity can be recovered at lower cycling rates

Galvanostatic experiments

experiments performed at a discharge rate of C/1



⚠ Power lost upon cycling