US-China Electric Vehicles and Battery Technology Workshop, Chicago 2010

Fundamental Studies on Li-ion Battery Materials

Zhaoxiang Wang

Laboratory for Solid State Ionics
Institute of Physics, Chinese Academy of Sciences

Outlines

1 About Laboratory for SSI, IPCAS
2 Structural design and performance prediction of battery materials
3 Surface modification mechanism
4 Application of spectroscopy in material characterization

About Laboratory for SSI, IPCAS
Founded in 1982, one of the earliest SSI labs

Directions: fundamental and applied studies on materials for new energy sources

Applied: materials and material interfaces
manual assembly of Li-ion batteries in 1994
Pioneer production of Li-ion batteries in 1997
Foundation of Beijing PhyLion Power Sources Company in 1999

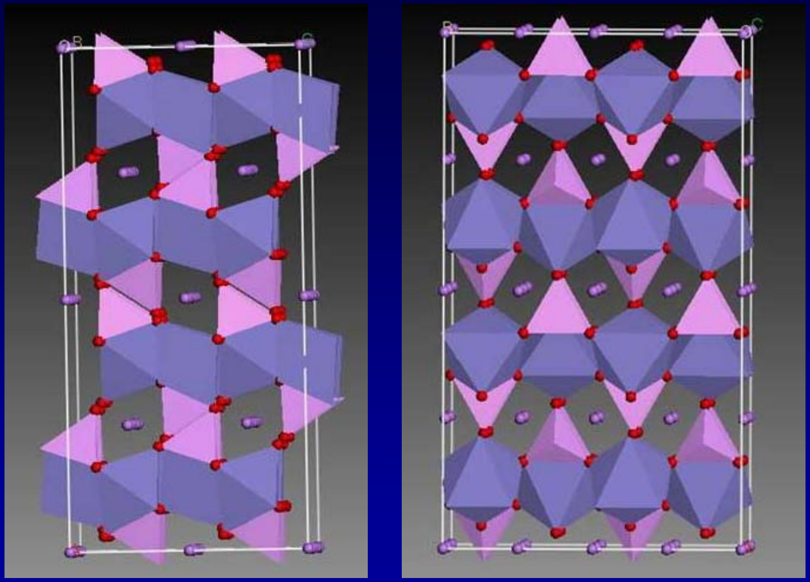
Fundamental: transport of electrons and ions in bulk and at interfaces
fast ion conductors/super-fast ion conductors (before 1990)
(gel) Polymer electrolytes since 1990
Electrode materials since 1992
SOFCs since 1996
Structural design and performance prediction
(first-principle's calculations) since 2002
Li-air cells since 2006

Members
Staff: 8
PhD students: 25-30 in Lab.

2 Structural design and performance prediction ($LiFePO_4$)

High safety
Low cost
Environmental benign

Low conductivity
Poor rate performance



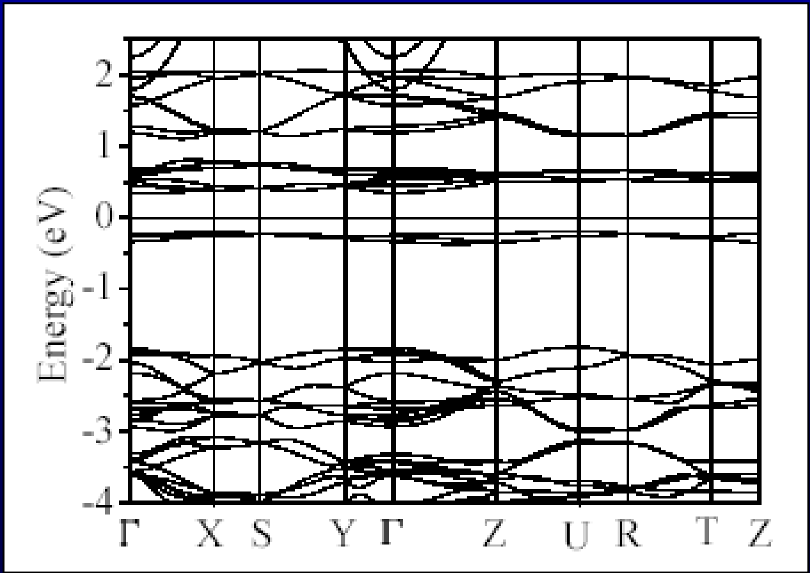
a-c plane *a-b plane*

Conventional solutions：

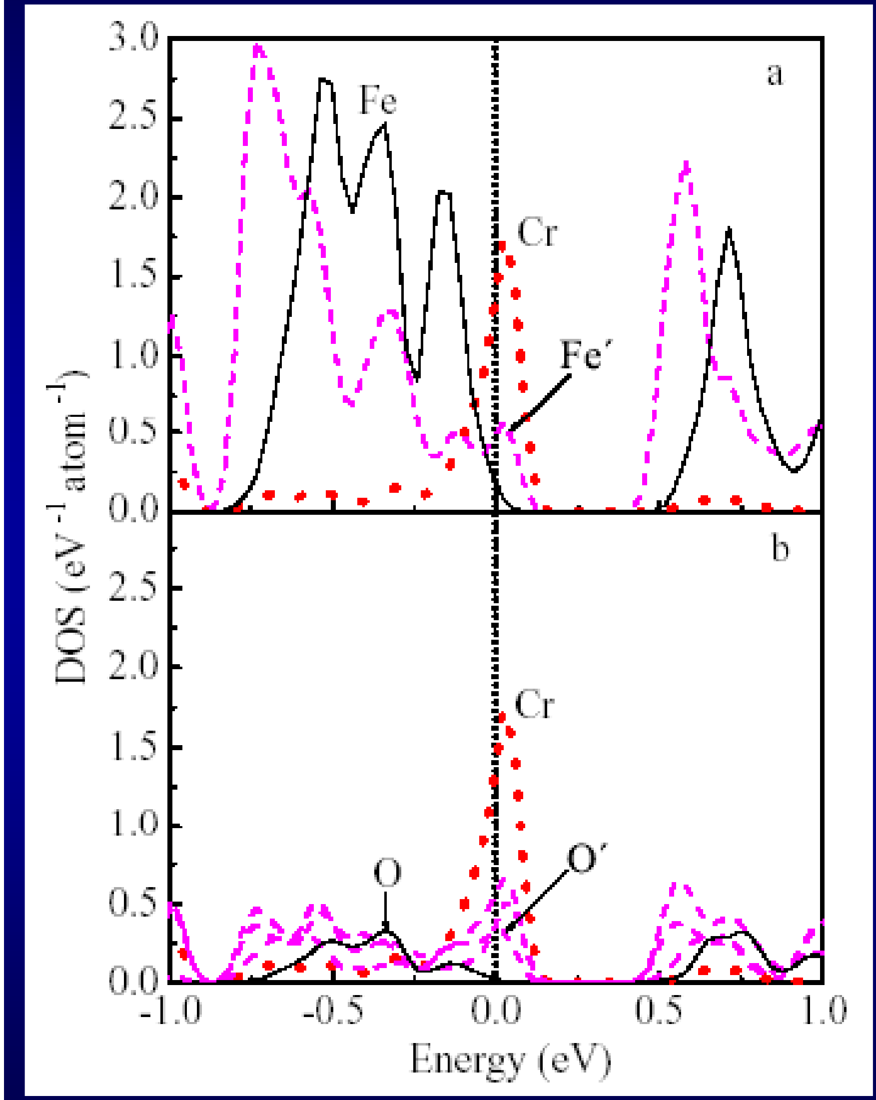
Carbon coating: patented

Nanosization: low tap density
side reations

Our strategy：atomic doping



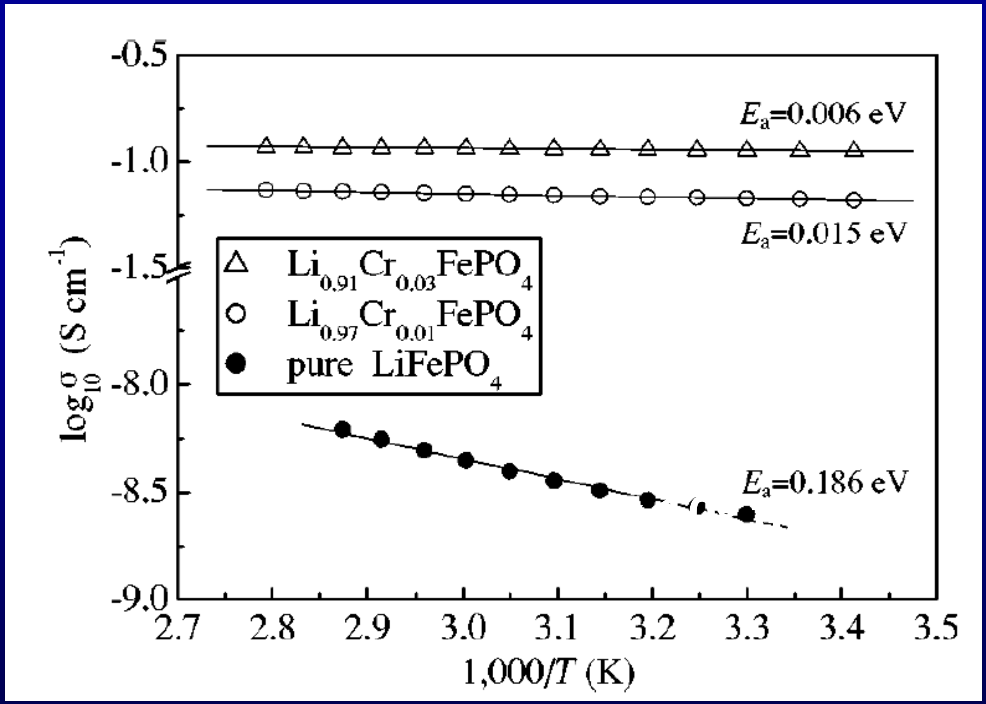
(a) Cr-doping at Li site: electronic conductivity enhanced



Possible mechanisms:

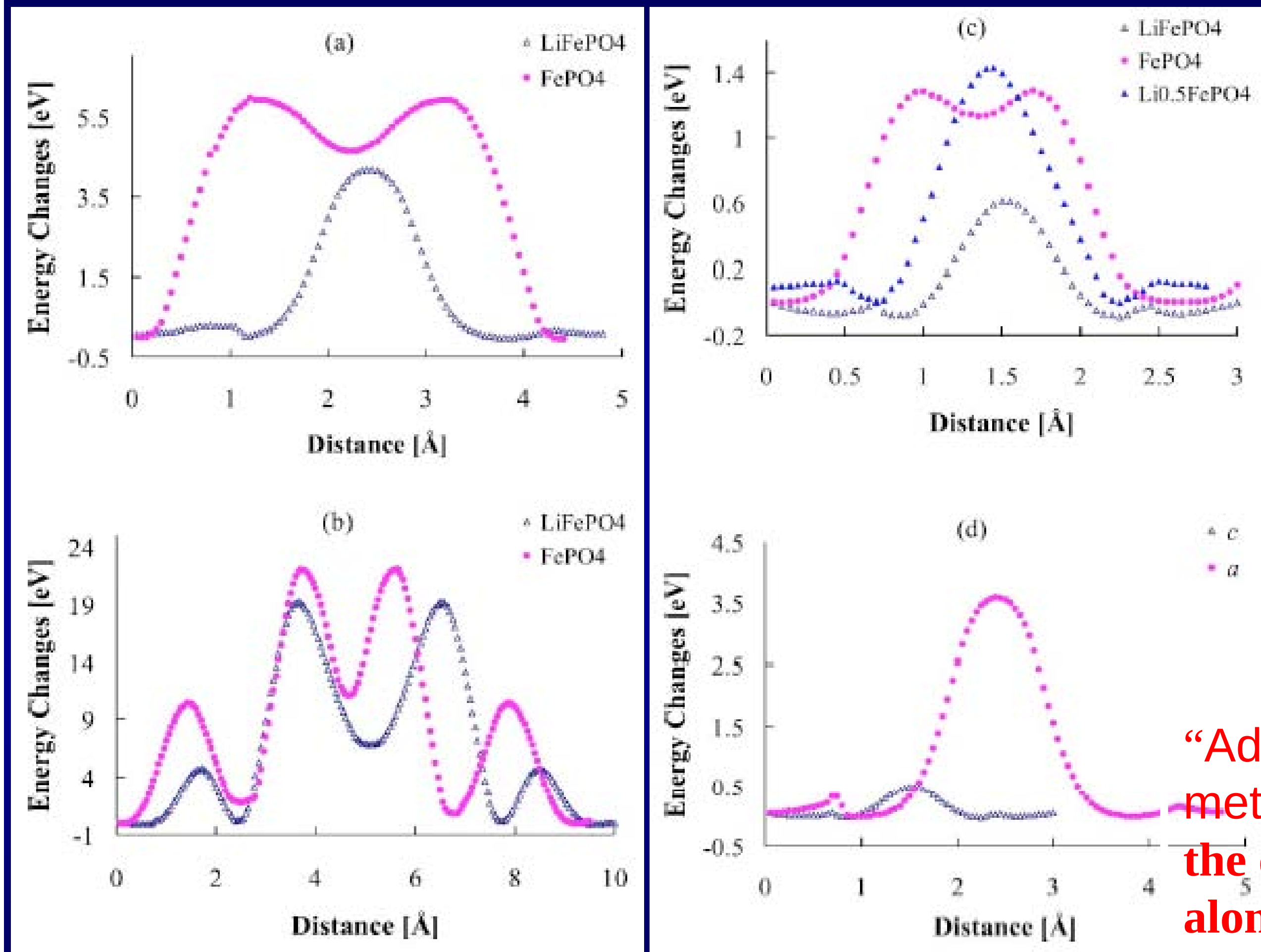
(1) Electrons are activated from valence band to the empty states of Cr (vacancy) (P-conduction) ;

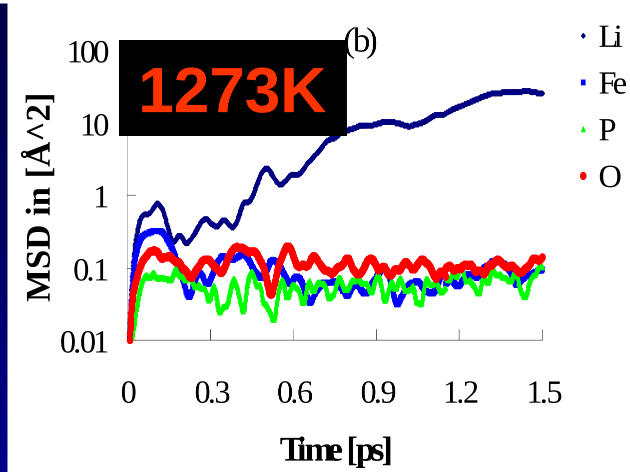
(2) Penetration paths.

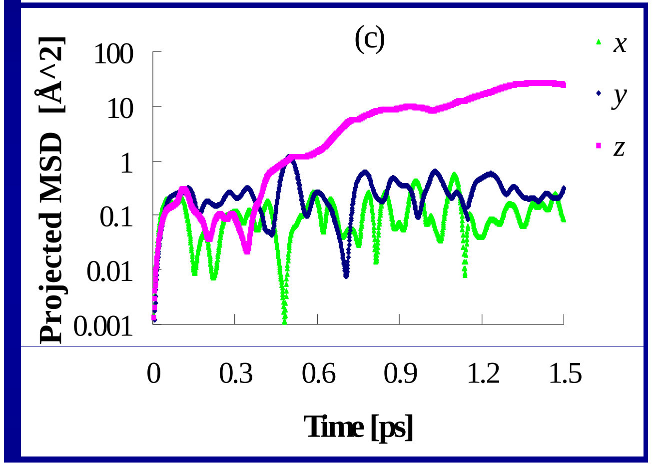


Physical Review B 68(2003)195108

(b) 1-D diffusion in $LiFePO_4$

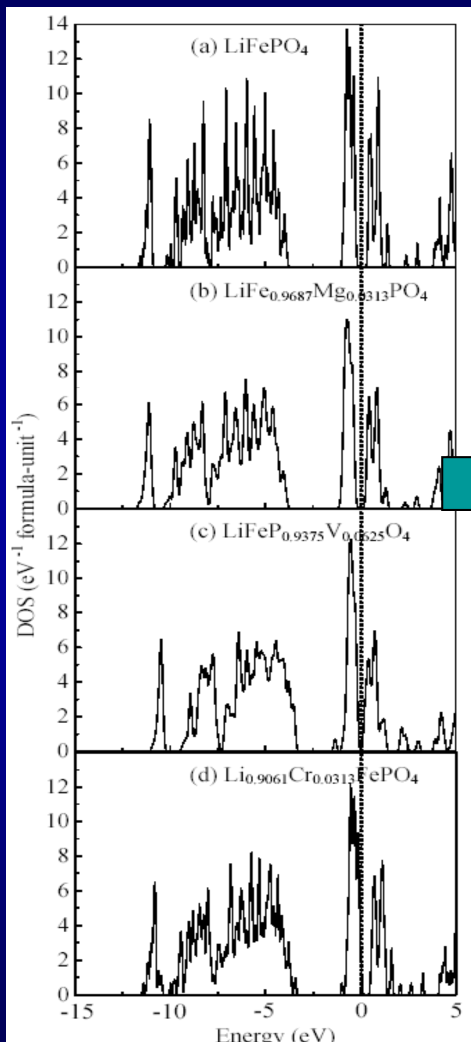


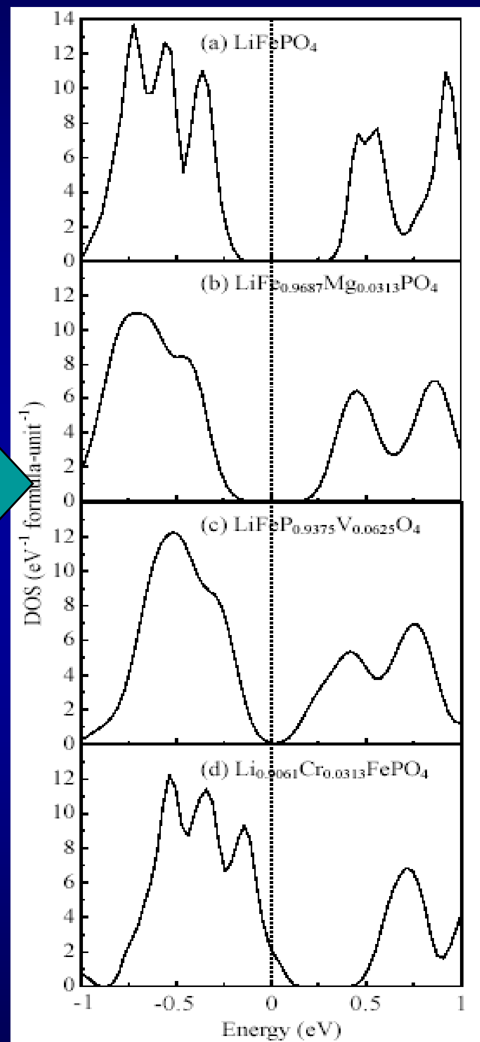


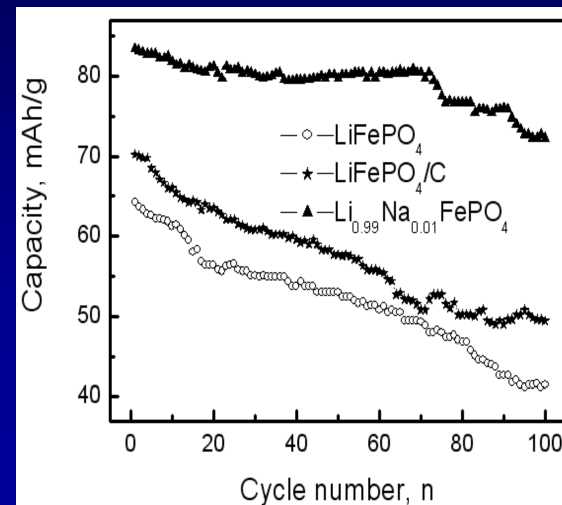


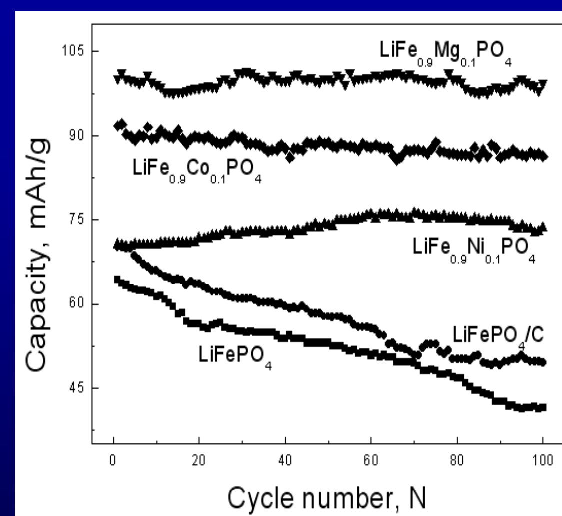
"Adiabatic trajectory method"calculations **indicate that the diffusion barrier of the Li ions along the b direction in $LiFePO_4$, $FePO_4$ and $Li_{0.5}FePO_4$ are 0.6, 1.2 and 1.5eV, while that along the *a* and *c* directions are much higher than that along the *b* direction**

(c) Small atoms doping at Li or Fe sites









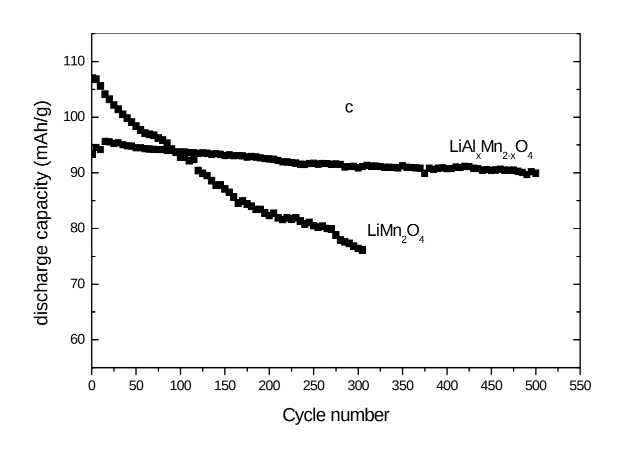
Summary

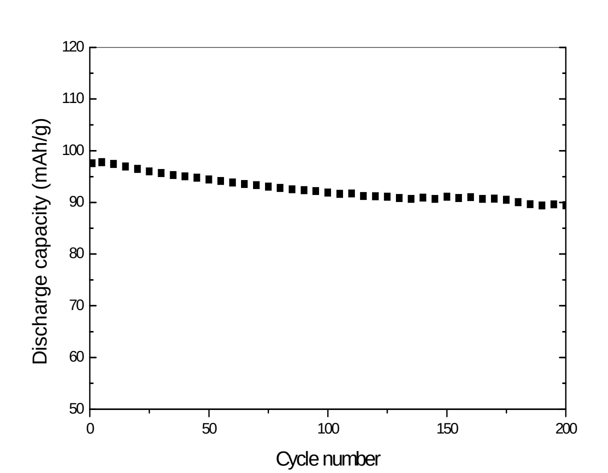
First-principle's calculations indicate that lithium diffuses in $LiFePO_4$ along the *b*-direction. Heavy atom doping at Li sites can enhance the electronic conductivity of $LiFePO_4$ but the heavy atoms will block the 1-D diffusion path of the Li ions. Small atom doping at Li improves the rate performance of $LiFePO_4$.

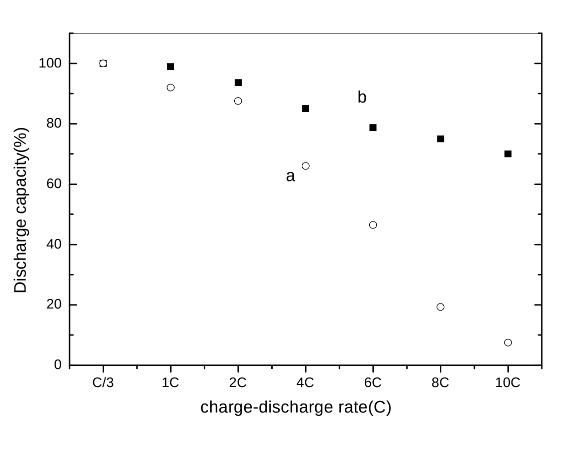
3 Surface modification to cathode materials

Performance improved with different modifications

(1) $LiAlO_2$ surface modification to $LiMn_2O_4$

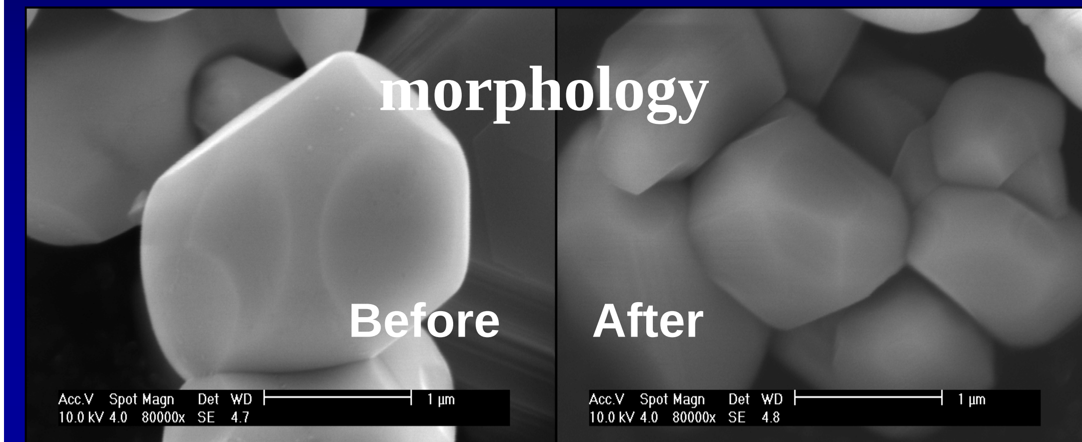


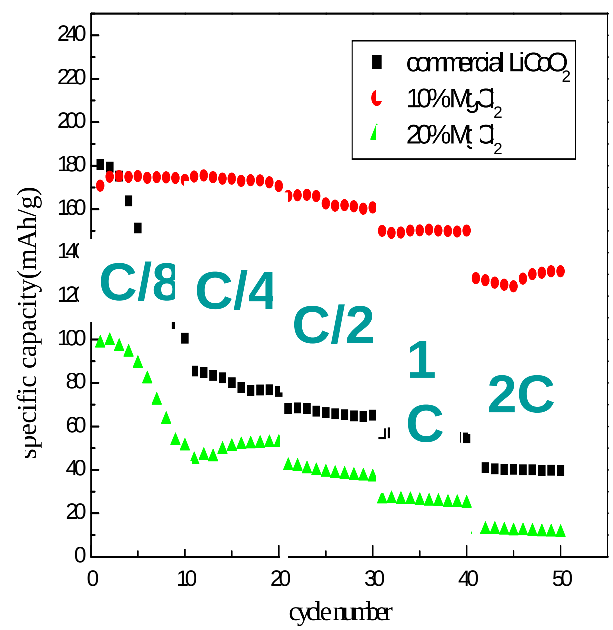


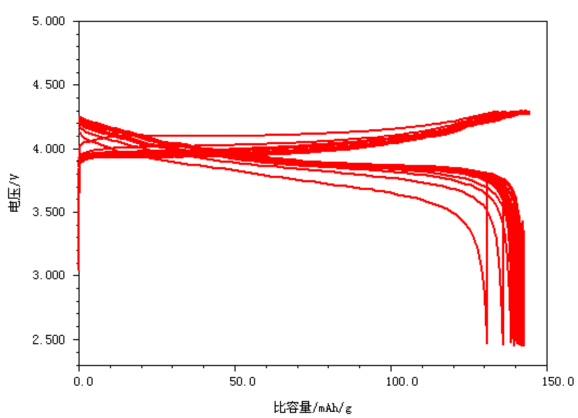


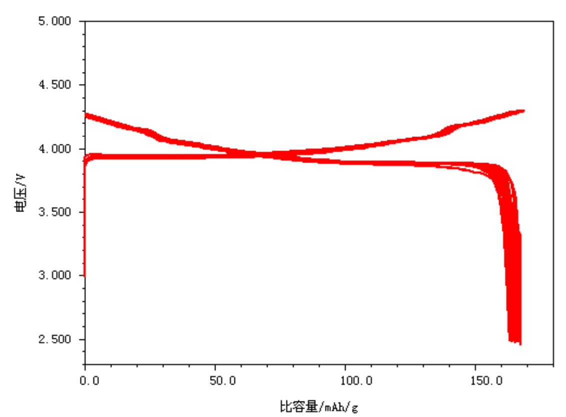
RT cycling **HT (55°C) cycling** **Rate performance**

(2) Surface modification to $LiCoO_2$ in ($LiNO_3$+$MgCl_2$) molten salt





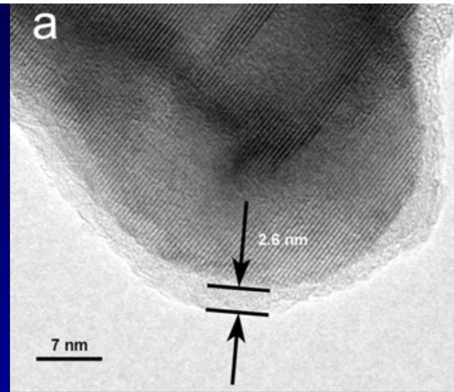


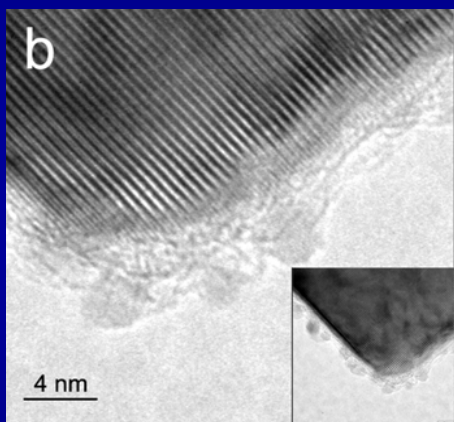


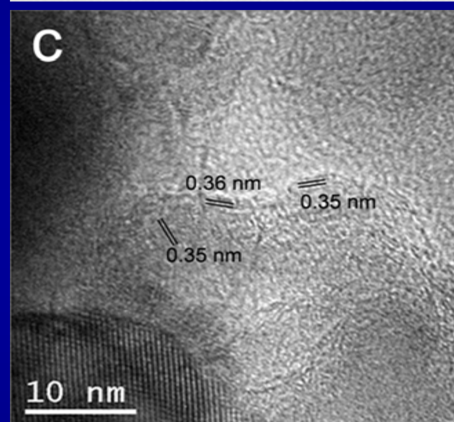
Before After

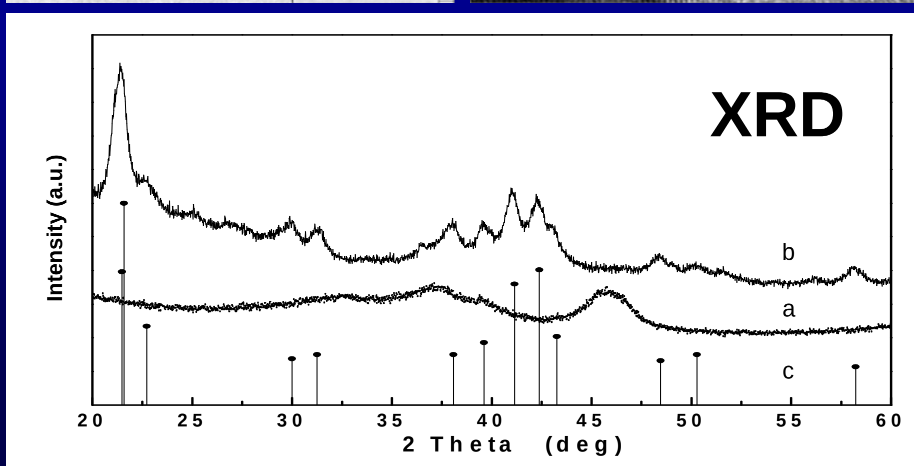
(3) Mechanism of surface modification

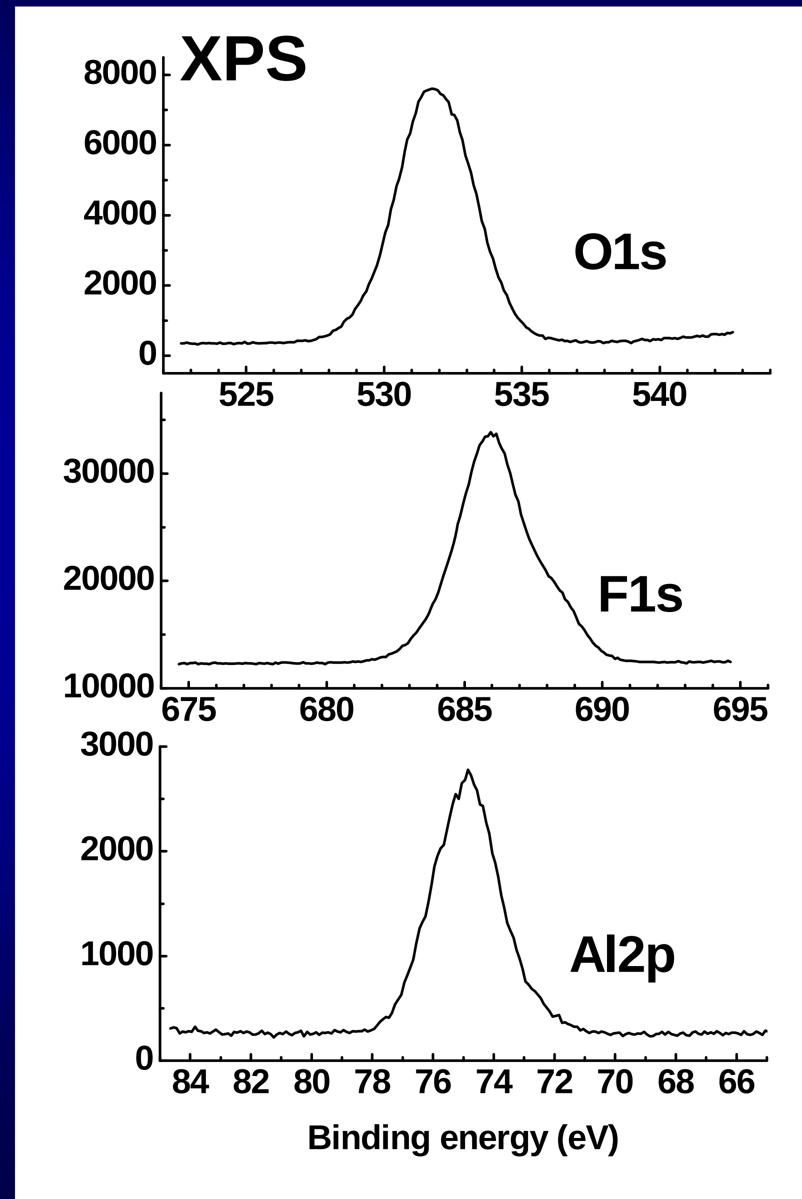
Product recognition: AlF_3

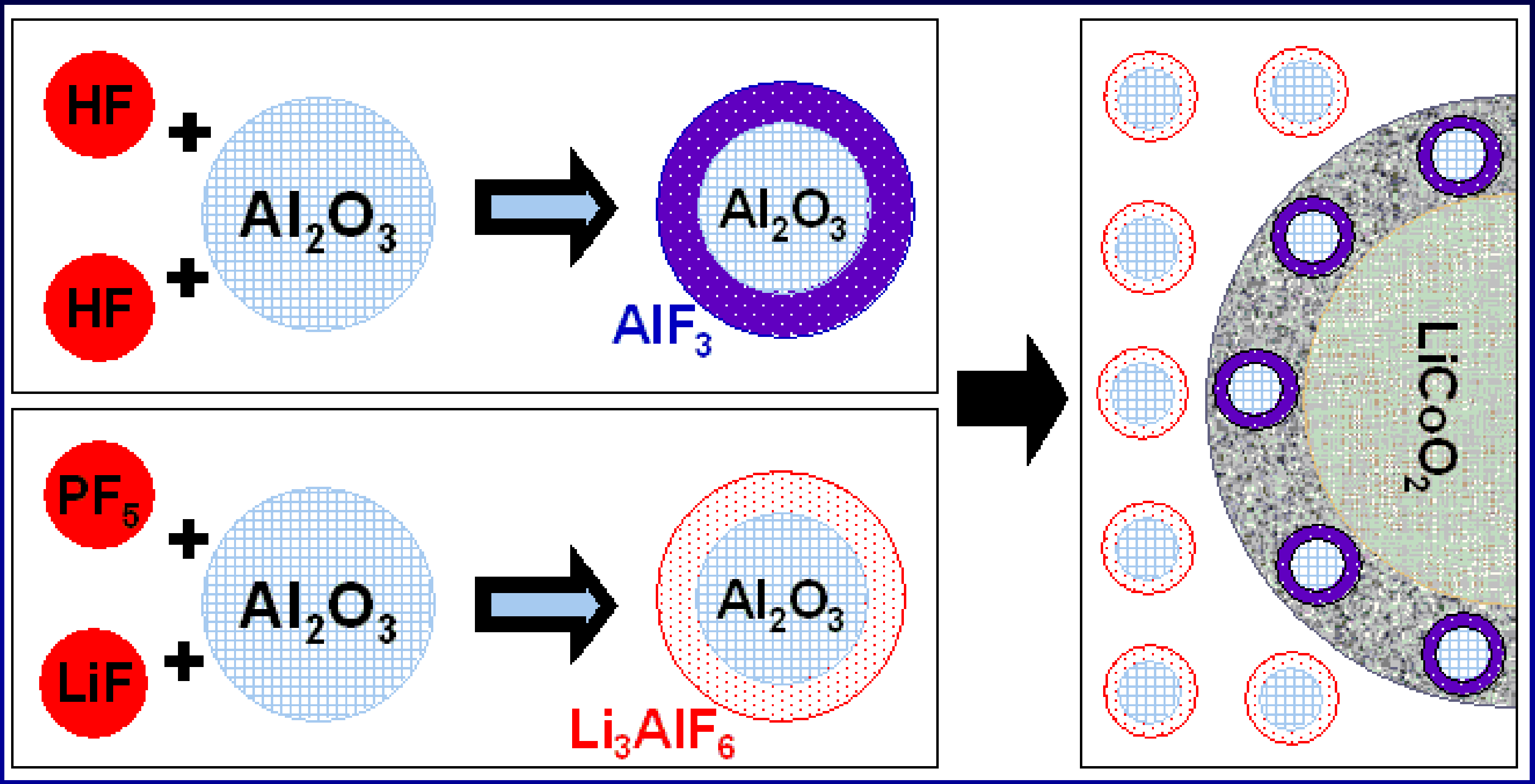












$LiPF_6 \leftrightarrow PF_5 + LiF$ (1)

$PF_5 + H_2O \rightarrow 2HF + POF_3$ (2)

$6HF + Al_2O_3 \rightarrow 2AlF_3 + 3H_2O$ (3)

$3PF_5 + Al_2O_3 + 6LiF \rightarrow 2Li_3AlF_6 + 3POF_3$ (4)

$Li_3AlF_6 \rightarrow AlF_3 \cdot 3LiF$ (solid solution)

Roles of Lewis acids

1) Corrosion to basic surface species；
2) Corrosing material surface and forming solid solution on surface solution;
3) Enhancing conductivity of SEI layer.

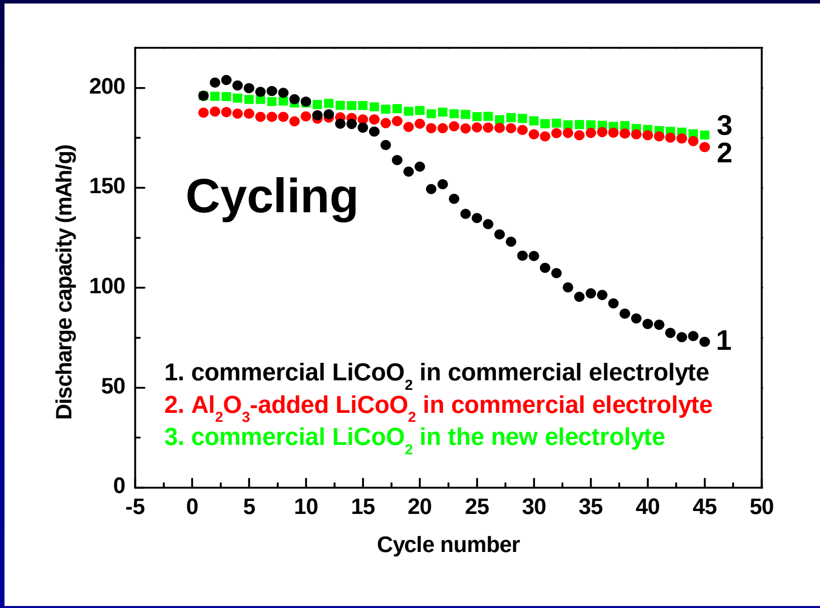
(4) Novel surface modification methods

1 Addition of Al_2O_3 nano-particles in $LiCoO_2$;

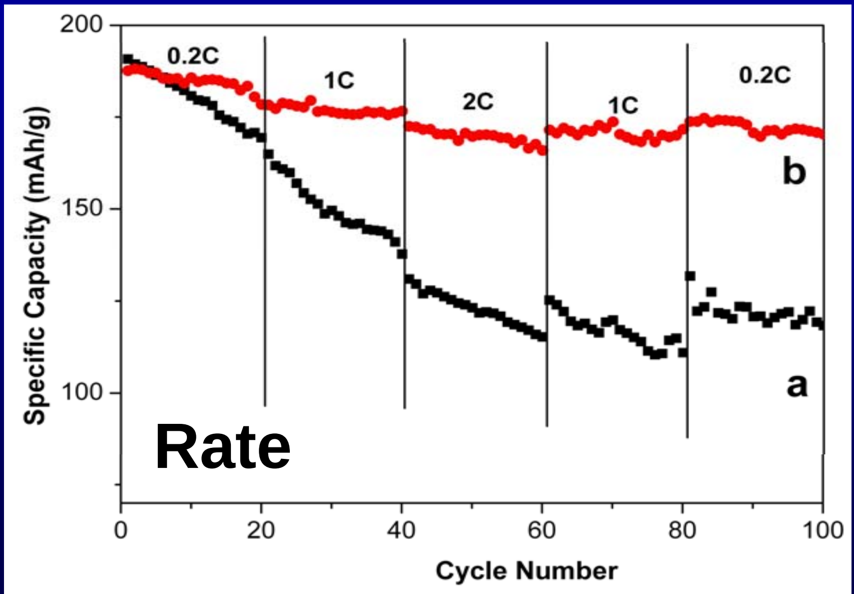
2 Add Al_2O_3 nano-particles in commercial electrolyte and use the liquid as new electrolyte after separation of the solid from the liquid;

3 Add Al_2O_3 in commercial electrolyte.

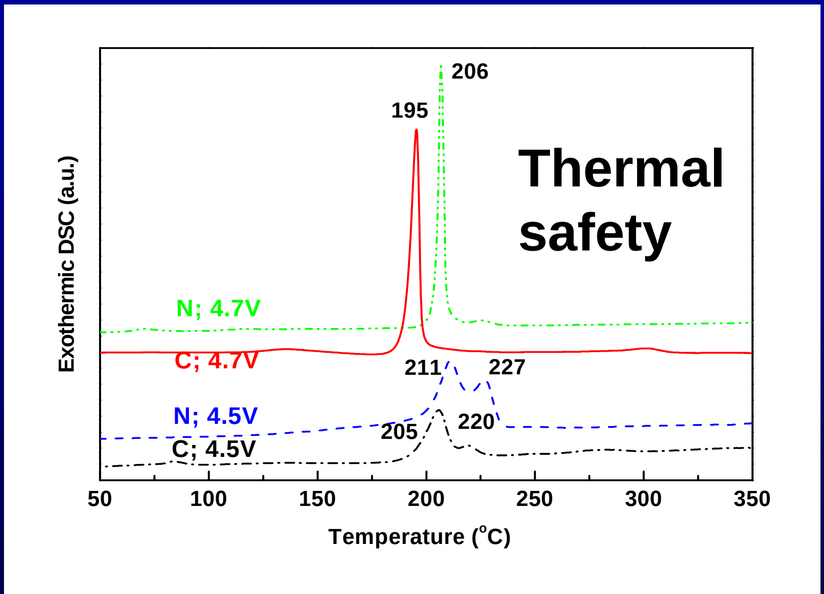
Easier operation
More improvements



Cycling
Discharge capacity (mAh/g)
Cycle number
1. commercial $LiCoO_2$ in commercial electrolyte
2. Al_2O_3-added $LiCoO_2$ in commercial electrolyte
3. commercial $LiCoO_2$ in the new electrolyte
1
2
3



Rate
Specific Capacity (mAh/g)
Cycle Number
0.2C
1C
2C
1C
0.2C
a
b



Thermal safety
Exothermic DSC (a.u.)
Temperature (°C)
N; 4.7V
C; 4.7V
N; 4.5V
C; 4.5V
206
195
211
227
220
205

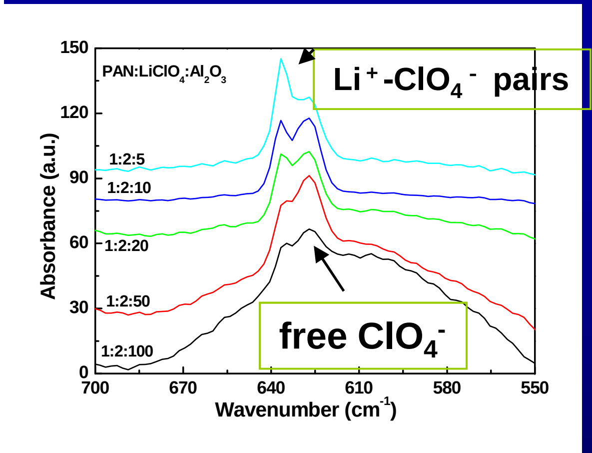
4 Application of spectroscopy in Material Characterization

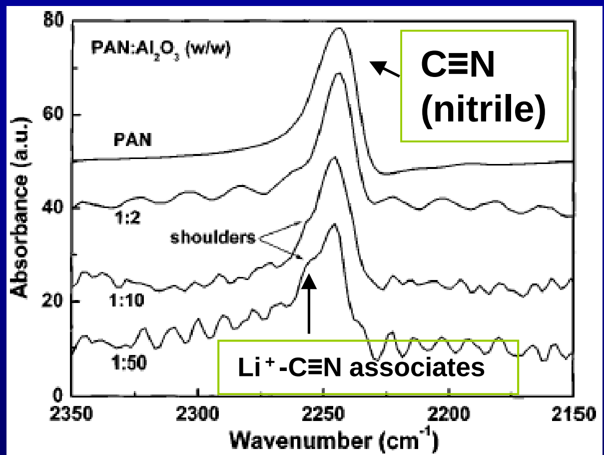
(1) Interactions among components in polymer electrolytes
(2) Decomposition of SEI on tin nanoparticles
(3) Capacitive lithium storage on nano-grain boundaries
(4) Spontaneous reaction between $LiCoO_2$ and electrolyte

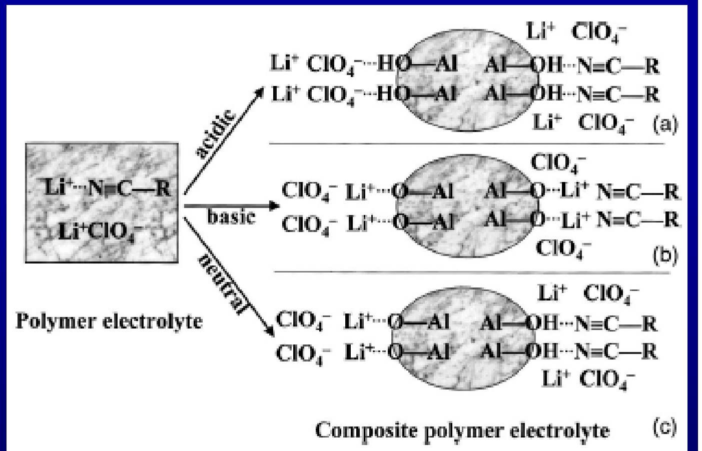
(1) Ceramic nano-particles on conductivity of polymer electrolytes

Addition of nanoparticles can enhance its conductivity of polymer electrolyte. The function of the nano-particles is unknown.

$LiClO_4$ + propylene carbonate (PC) + polyacrilonitrile (PAN) (+Al_2O_3) → remove PC → PAN + $LiClO_4$ (+ Al_2O_3)





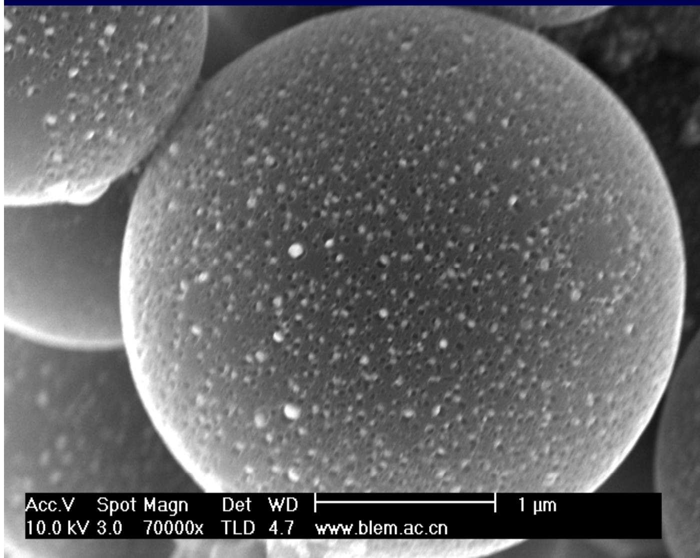


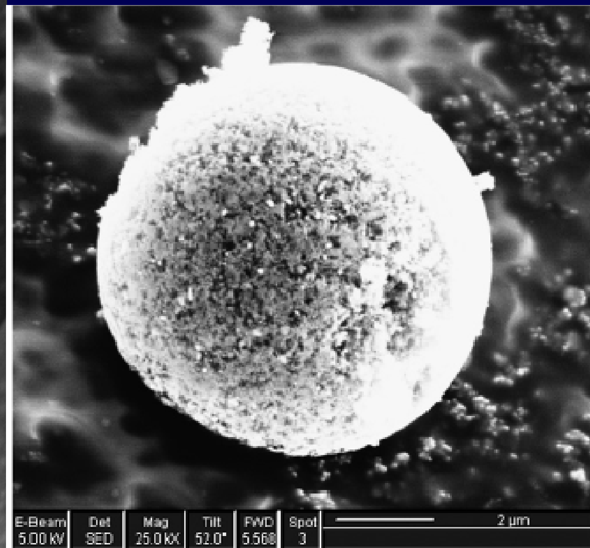
Nanoceramics helps to dissociate $LiClO_4$ salt.

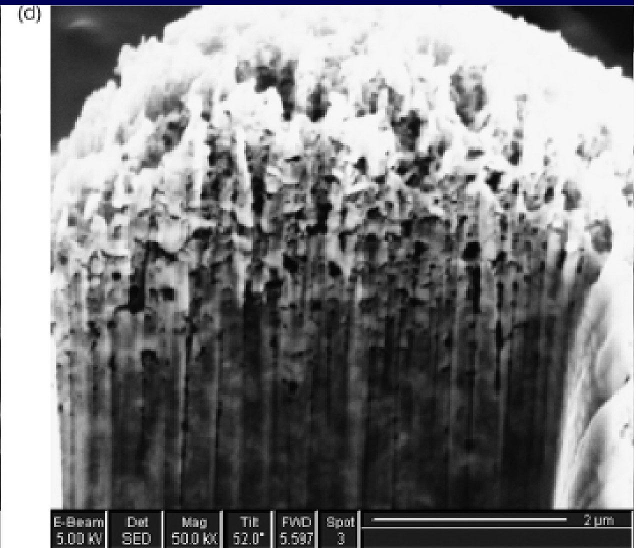
Nanoceramics suppresses the Li^+/PAN association

Interaction mode between Lewis: Li^+ and acids/bases. The role of the ceramics is like a solid solvent.

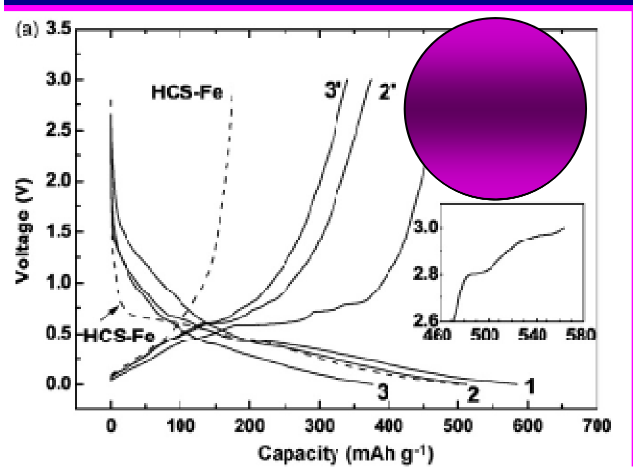
(2) Catalytic effect of nano-Sn to SEI

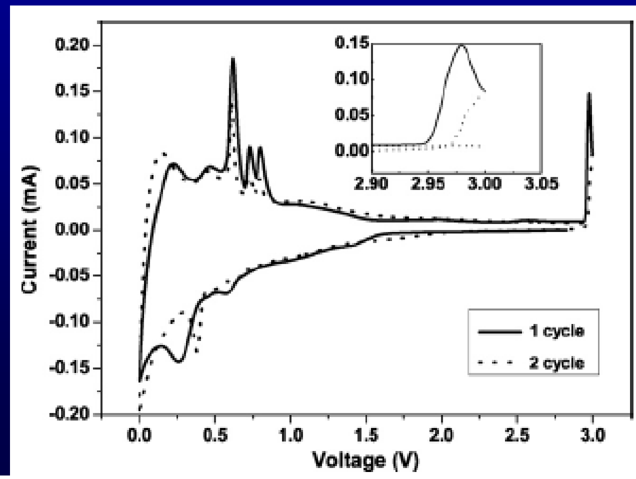


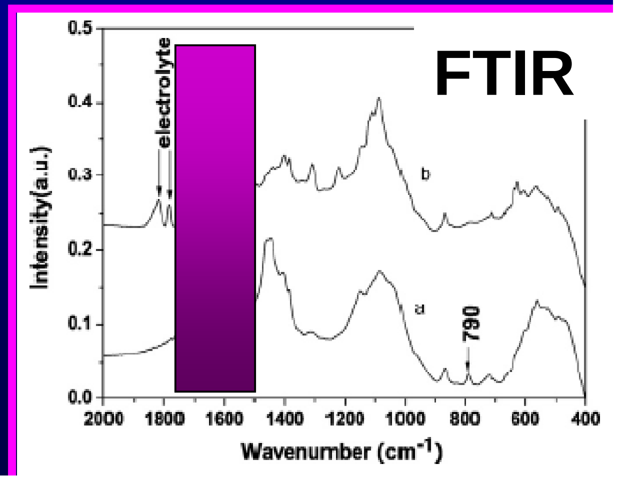




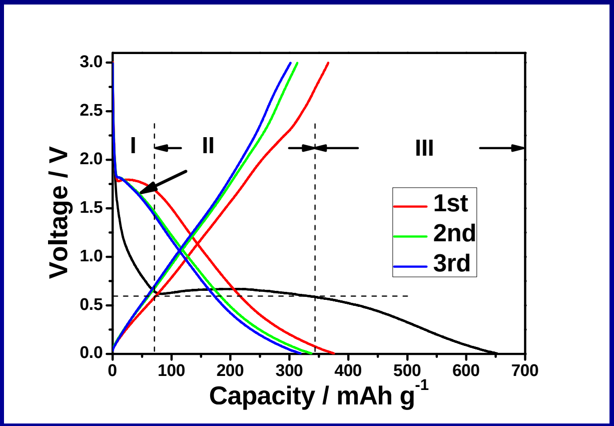
Nano-Tin embedded in porous hard carbon spherules

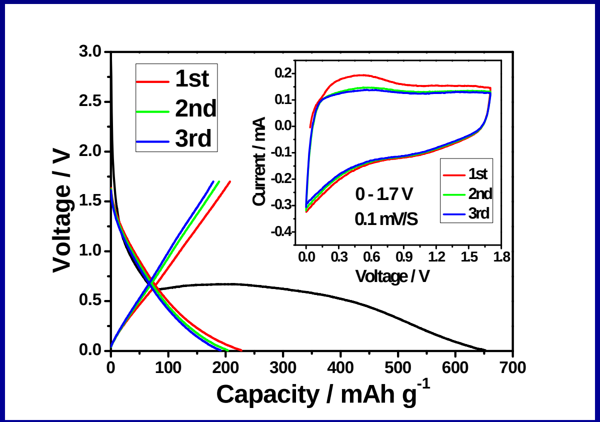


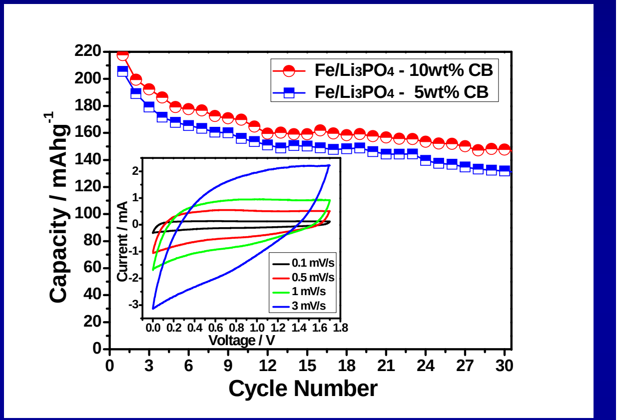




(3) Capacitive lithium storage on grain boundaries





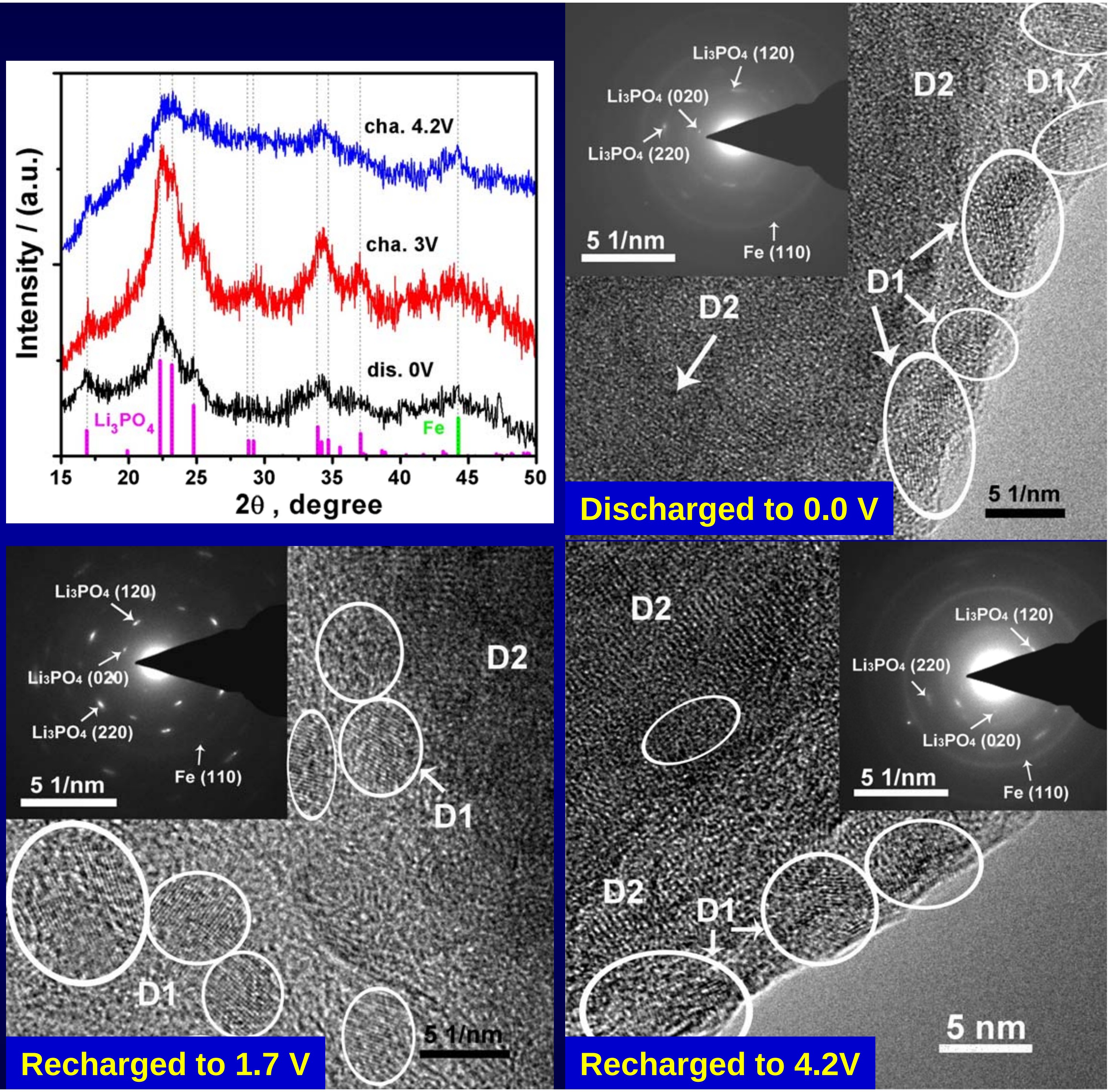


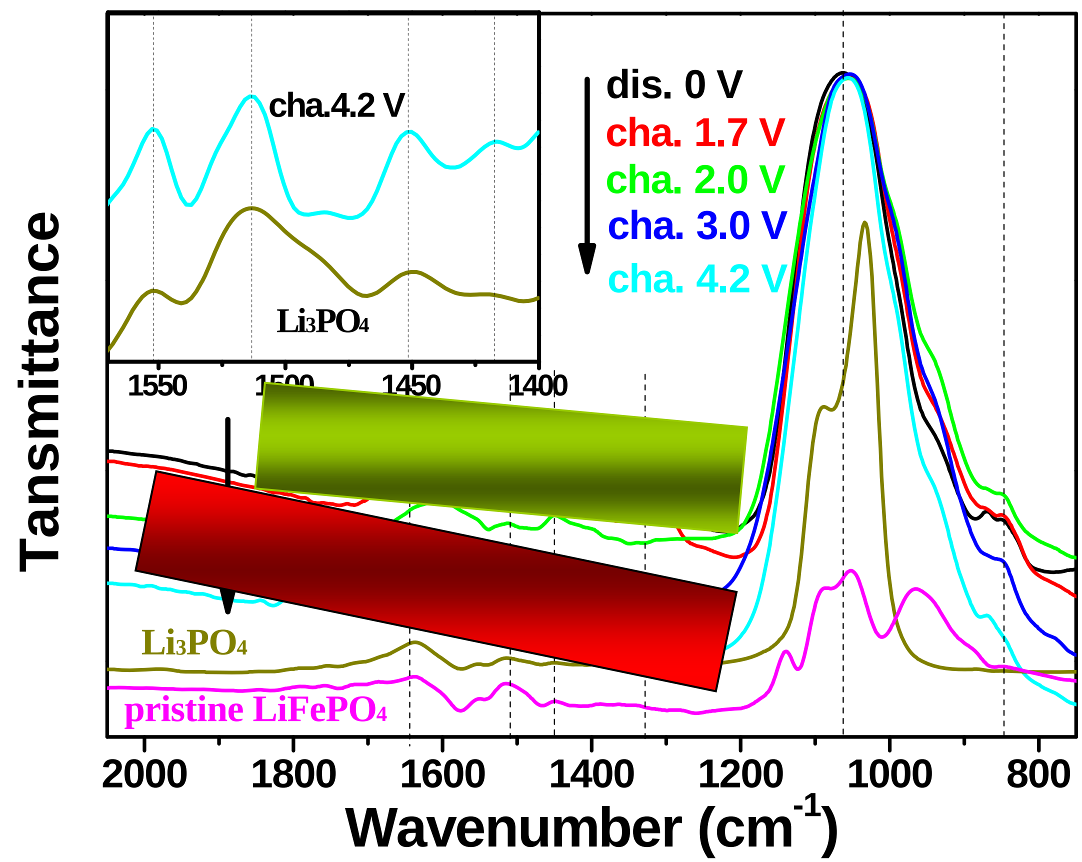
$$LiFePO_4 + Li^+ + e^- \longrightarrow Fe + Li_3PO_4$$

Discharge products: $Fe+Li_3PO_4$

$D_1 = Fe$

$D_2 = Li_3PO_4$





Charge state dependent FTIR

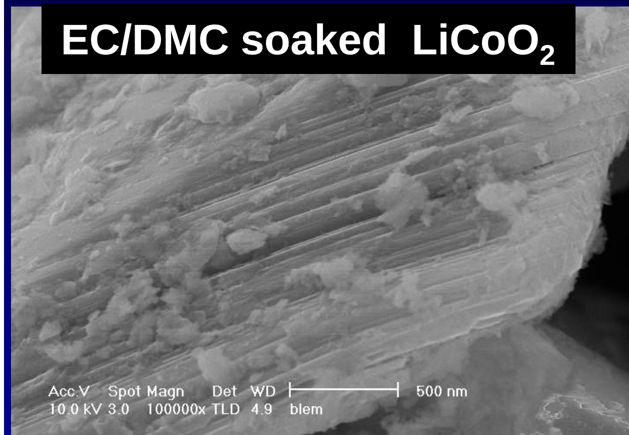
(1) No decomposition below 1.7 V

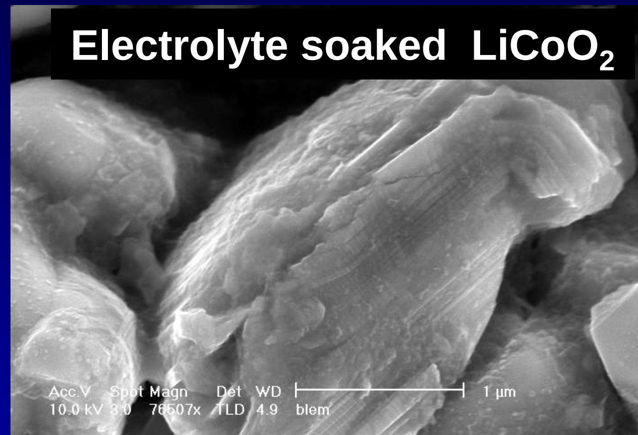
(2) SEI decomposition around 2.0 V

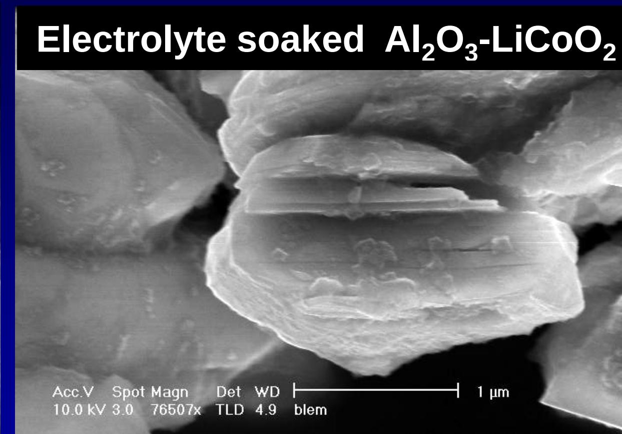
(3) Decomposition completed at 3.0V (to Li_2CO_3)

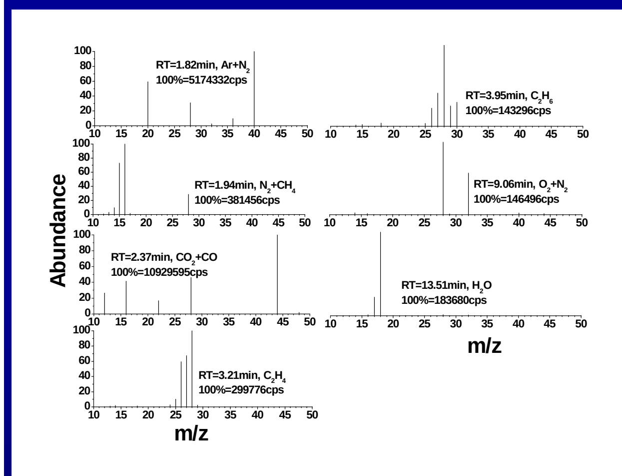
(4) Li_3PO_4 stable up to 4.2 V

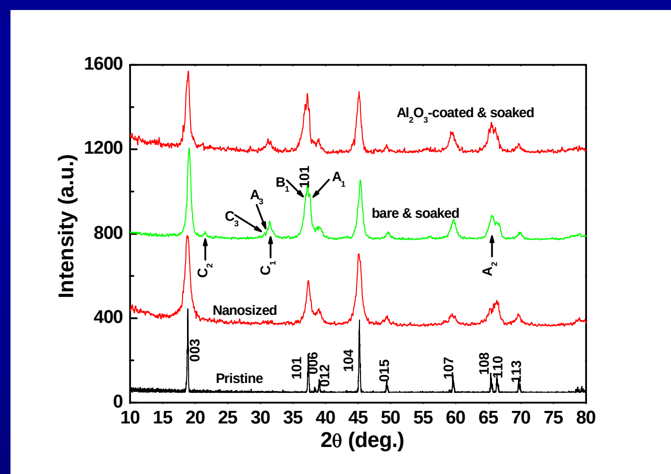
(4) Spontaneous reaction between Al_2O_3-coated $LiCoO_2$ and commercial electrolyte

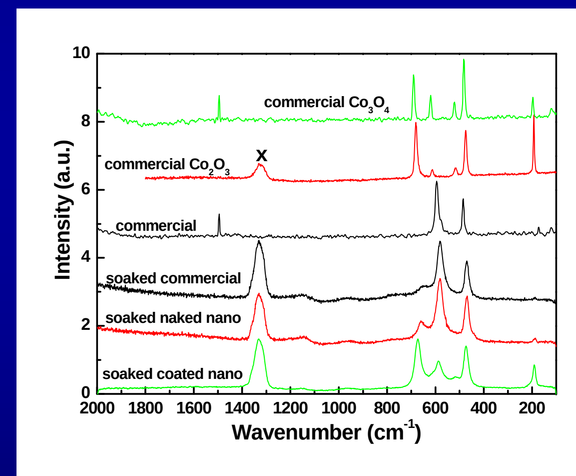












Condition	Co/Li in solid	Co/Li in liquid
Non-soaked	1:1.00	×
Bare & soaked	1:0.78	1:12.4
Coated & soaked	1:0.61	1:18.4

XRD patterns (left) indicate that storage in commercial solvent or electrolyte leads to structural degradation for naked and Al_2O_3-coated nano-$LiCoO_2$ (*A* for produced Co_3O_4, *B* for Co_2O_3 and *C* for Li_2CO_3; the number is for the order of peak intensity). Raman spectroscopic study (right) further demonstrates that $LiCoO_2$ is mainly degraded to Co_3O_4 while Al_2O_3-$LiCoO_2$ is decomposed to Co_2O_3 after storage.

Acknowledgements:

Projects supported by the MOST and NSFC of China