Progress in rechargeable Li ion batteries.

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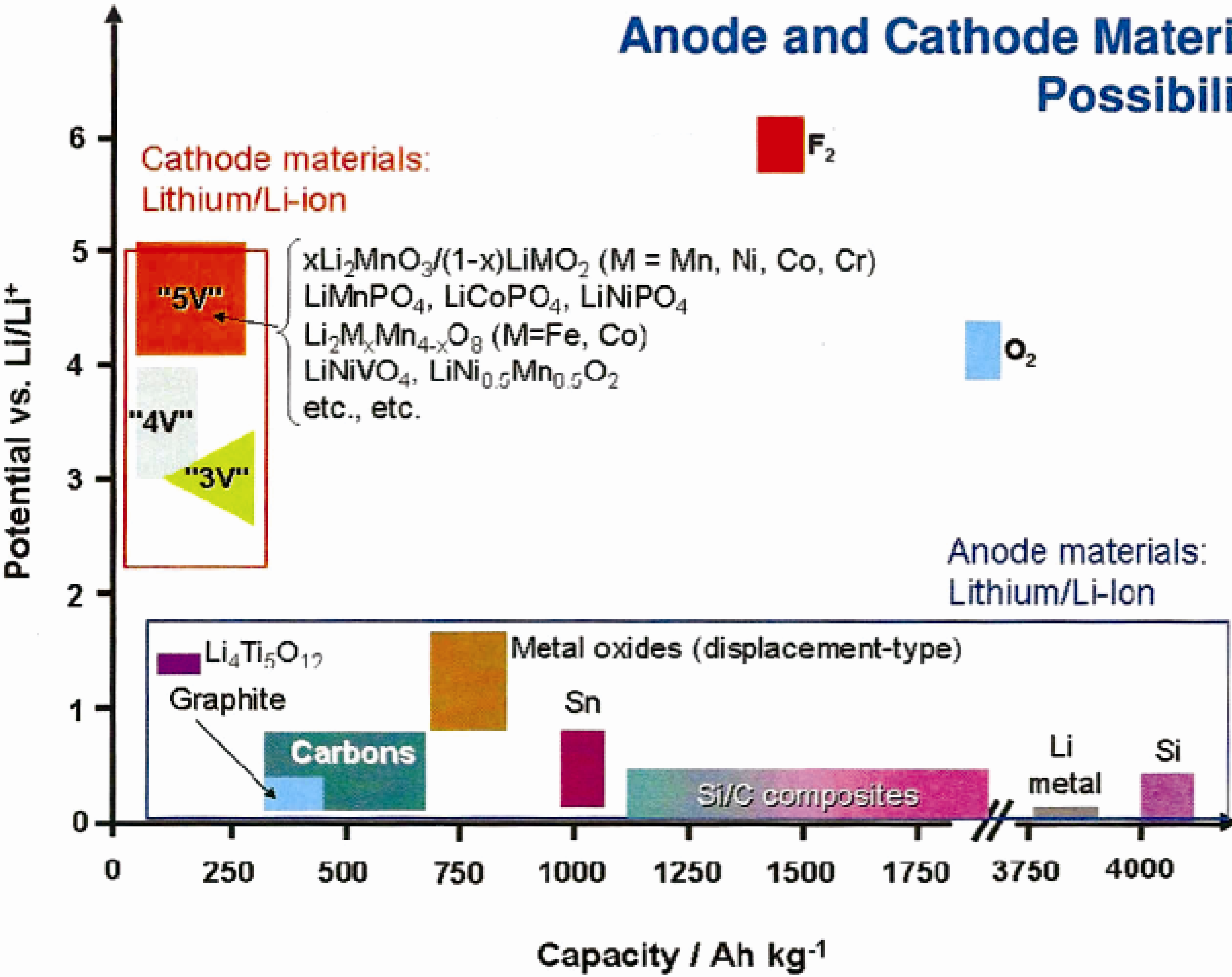
GM, Sion Power (USA).

In collaboration with UBE Industries, Japan.

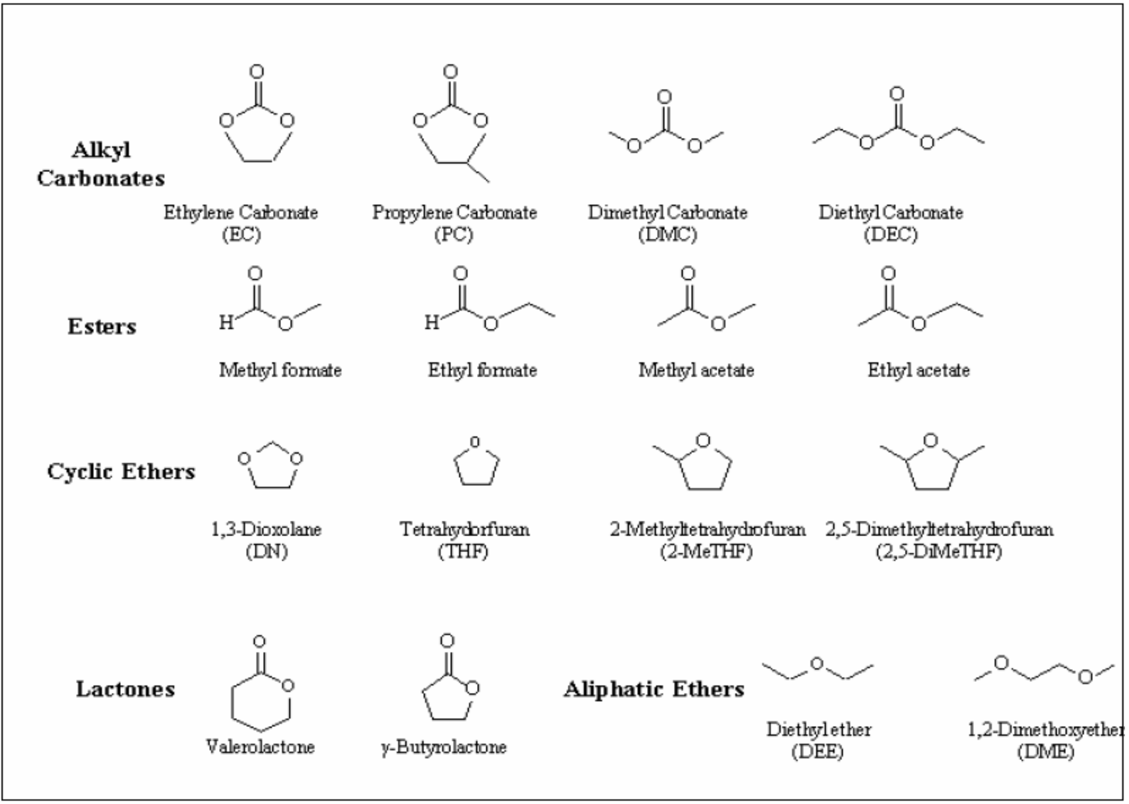
Anode and Cathode Materials: Possibilities



Outline

- Introductory remarks.
- On polar aprotic solutions for Li ion batteries.
- On the use of ionic liquids for rechargeable Li electrodes: 5 V cathodes, Li-Graphite, Li-Si.
- Comparative study of cathode materials:
  - $LiMn_{1.5}Ni_{0.5}O_4$ spinel
  - $LiNi_{0.5}Mn_{0.5}O_2$
  - $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$
  - $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
  - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
  - $LiMnPO_4$ two generations.
- Aging, stability, rate capability, cycle life and surface chemistry.
- Conclusion.

Solvents for Li batteries



Choice of salts →

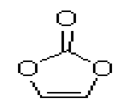
- $LiAsF_6$ toxic
- $LiClO_4$ explosive
- $LiBF_4$ *poor* passivation
- LiBOB limited anodic stability
- $Li(NSO_2CF_3)_2$ poor passivation
- $LiPF_6$ **The best compromise**

Side products: LiF, PF_5, HF, POF_3

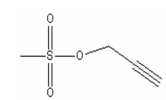
$$LiPF_6 \leftrightarrow LiF + PF_5$$
$$PF_5 + H_2O \rightarrow 2HF + PF_3O$$

Interesting additives (UBE Industries)
Surface reactive compounds that polymerize on both anodes and cathodes

VC



PMS



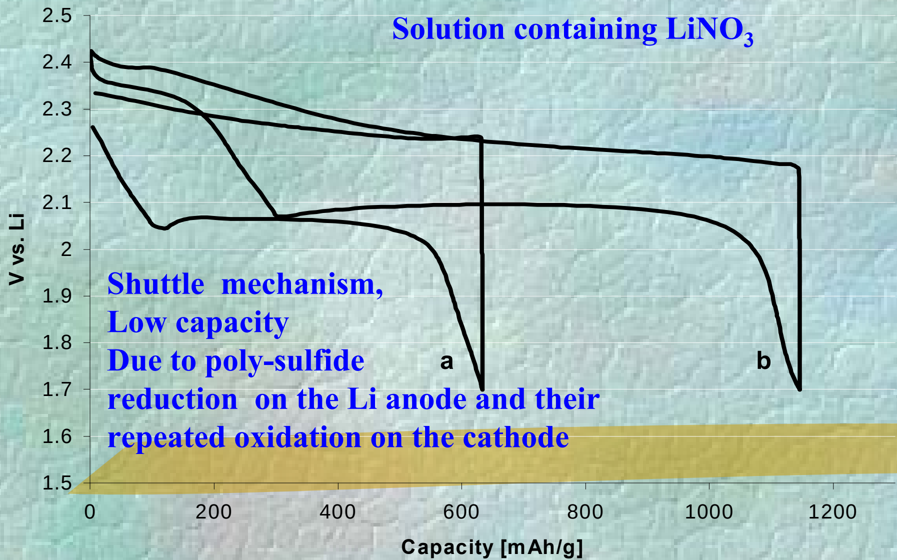
Donor #	density gr/cc	viscosity C_p (γ)	Dielectric ε	b.p . °C	m.p. °C	Mw [g/mol]	Solution
16.4	1.3218	1.86	(40C°) 89.6	243	36.4	88.06	EC
15.1	1.19	2.53	64.4	241	-49		PC
-	1.0636	0.57-0.58	3.12	90.5	3	90.08	DMC
15.1	0.9692		2.82	126	-43	118.13	DEC
	0.88	0.46	7.39	65	-108.5		THF
-	1.012		2.96	107.5	-14	104.11	EMC

Rechargeable Li sulfur cells: The highest energy density due to the high electrodes capacity

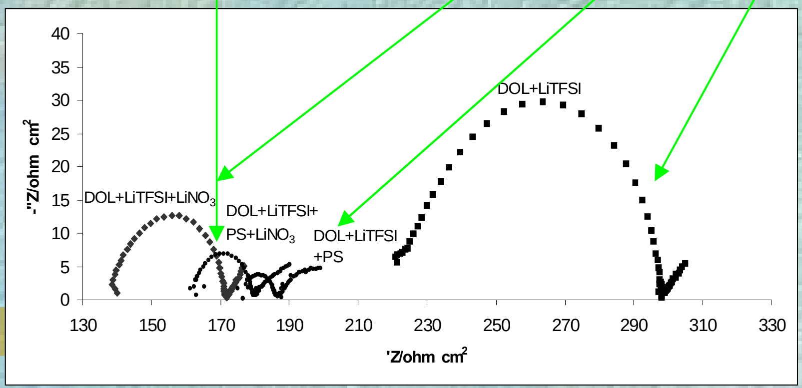
Ethereal solvents such as 1-3 Dioxolane + an electrolyte such as $LiN(SO_2CF_3)_2$

A major problem: limited capacity of the sulfur cathode due to shuttle mechanism.

Voltage profiles of Li-S cells based on dioxolane & $LiN(SO_2CF_3)_2$ solutions

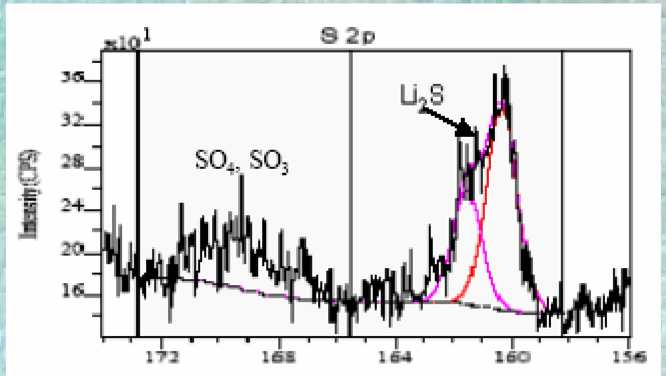


Impedance spectra of Li electrodes prepared fresh in dioxolane LiTFSI solutions : with no additives ; with $LiNO_3$; with Li_2S_6 and with $LiNO_3$ + Li_2S_6

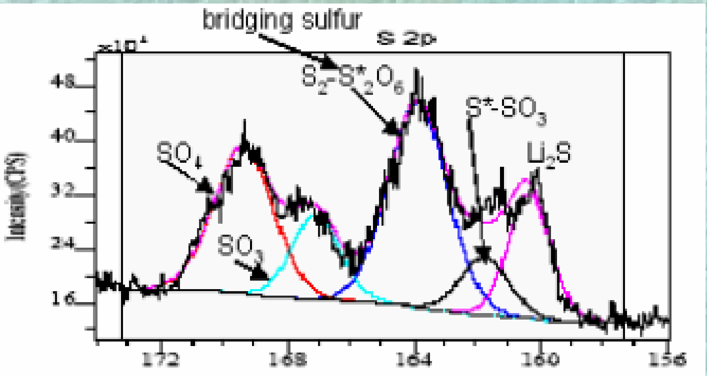


Sulfur XPS spectra of Li electrodes prepared and stored in 1,3-dioxolane solutions

Solution containing only Li_2S_6



Solution containing both Li_2S_6 and $LiNO_3$

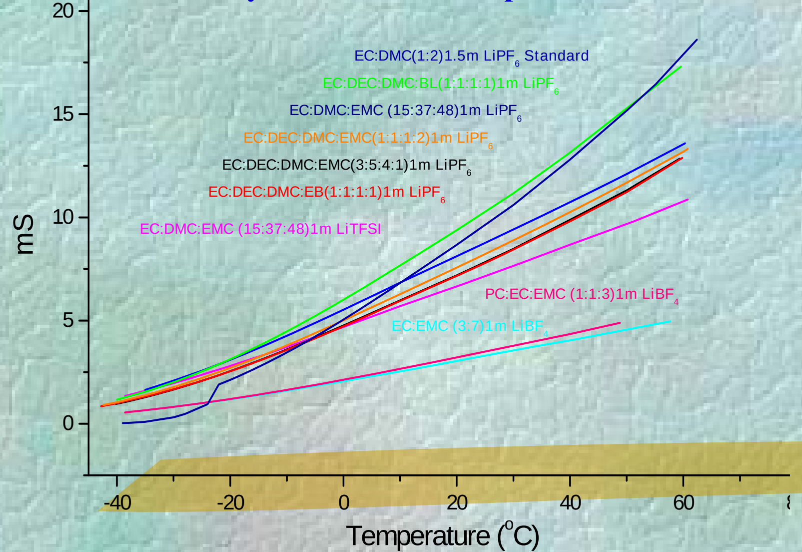


Note the high oxidation state of Li surface sulfur due to the presence of $LiNO_3$

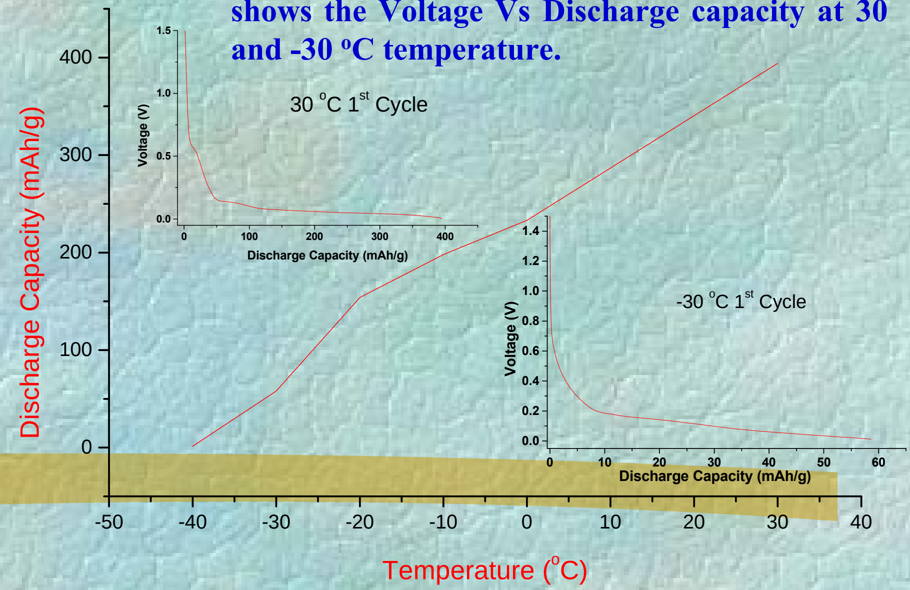
The passivation of Li is due to the formation of various Li-S-O compounds

Low-temperature electrolytes for Li-batteries

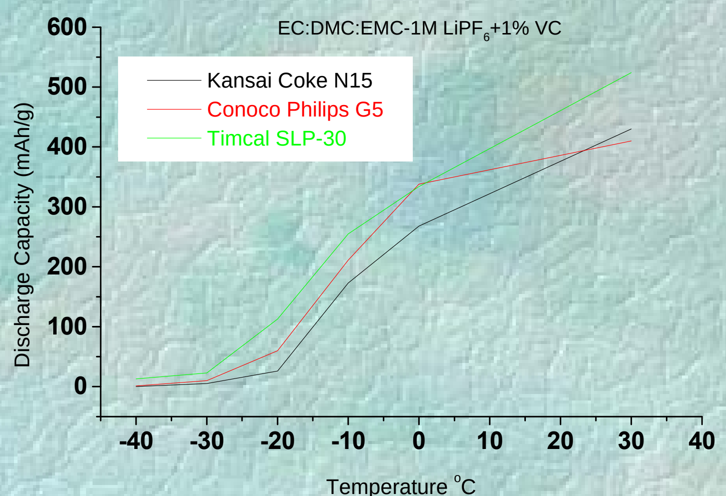
Conductivity results obtained for different electrolytes at various temperatures.

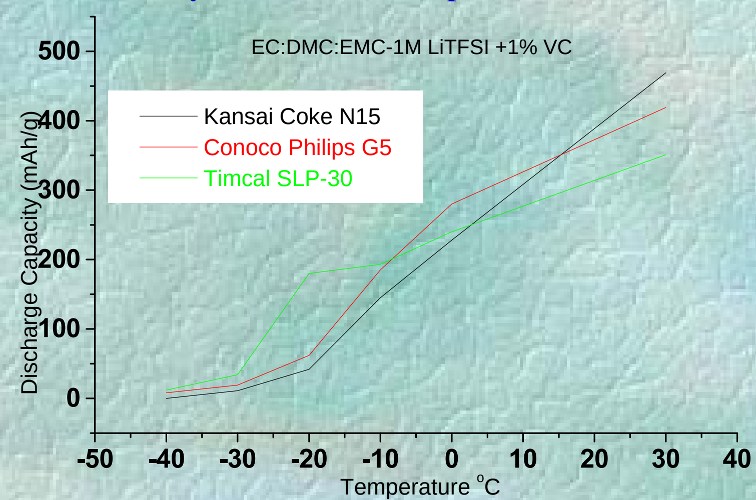


Kansai coke graphite NG15 in standard electrolyte EC:DMC 1.5M $LiPF_6$. Inset graph shows the Voltage Vs Discharge capacity at 30 and -30 °C temperature.



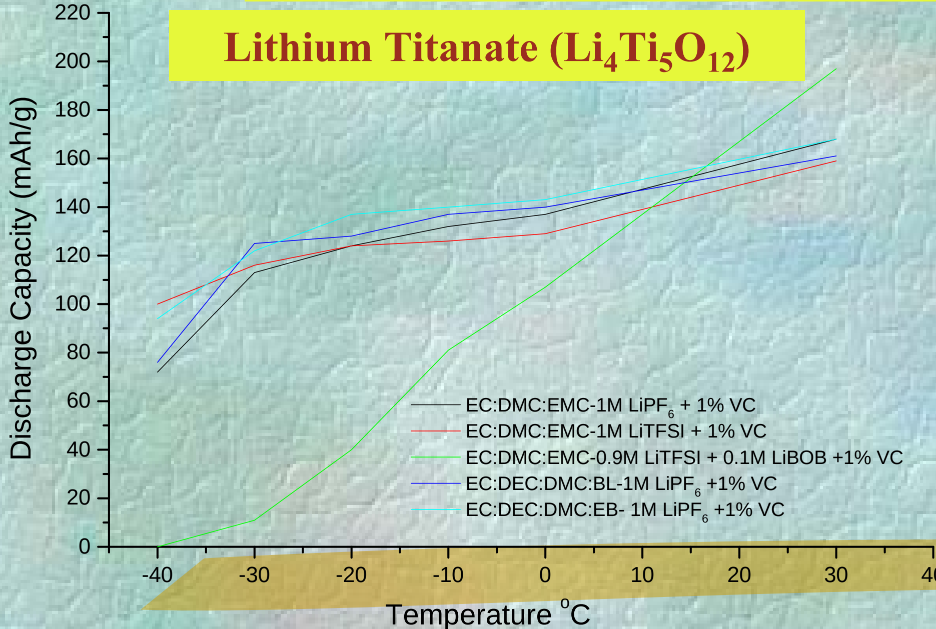
Performance of different graphite materials in two different electrolytes at various temperatures.



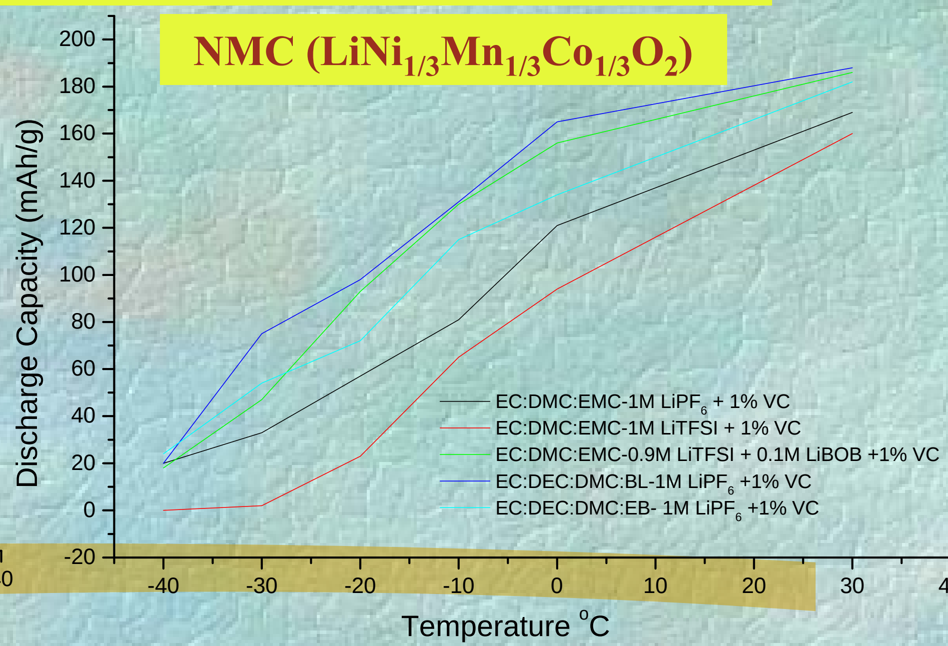


Low temperature performance of different cathode and anode materials in various electrolytes

Lithium Titanate ($Li_4Ti_5O_{12}$)

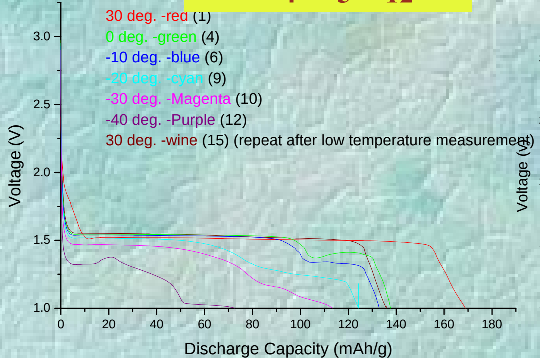


NMC ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$)

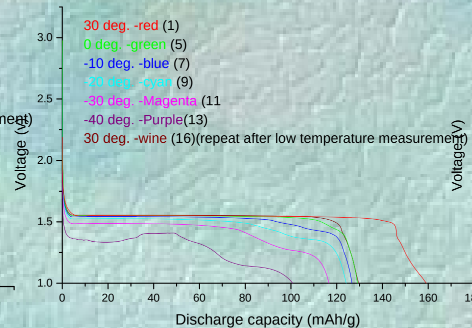


Voltage Vs Discharge capacity curve of $Li_4Ti_5O_{12}$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ at various temperature in different electrolytes.

$Li_4Ti_5O_{12}$

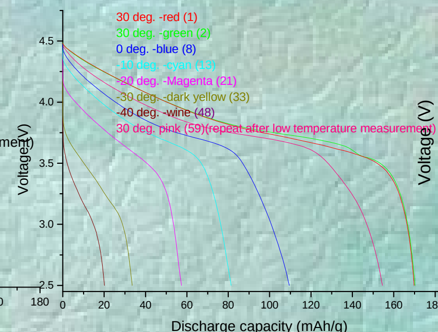


EC:DMC:EMC-1mLiPF$_6$+1%VC

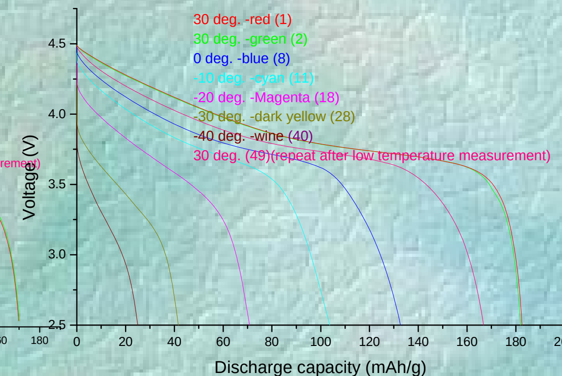


EC:DMC:EMC-1mLiTFSI +1%VC

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$



EC:DMC:EMC-1mLiPF$_6$+1%VC

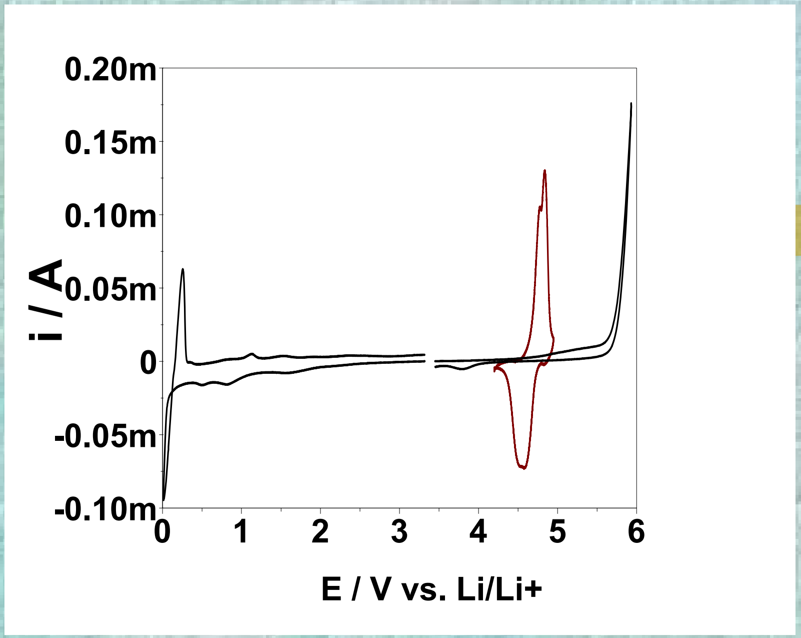


EC:DEC:DMC:EB- 1mLiPF$_6$+1%VC

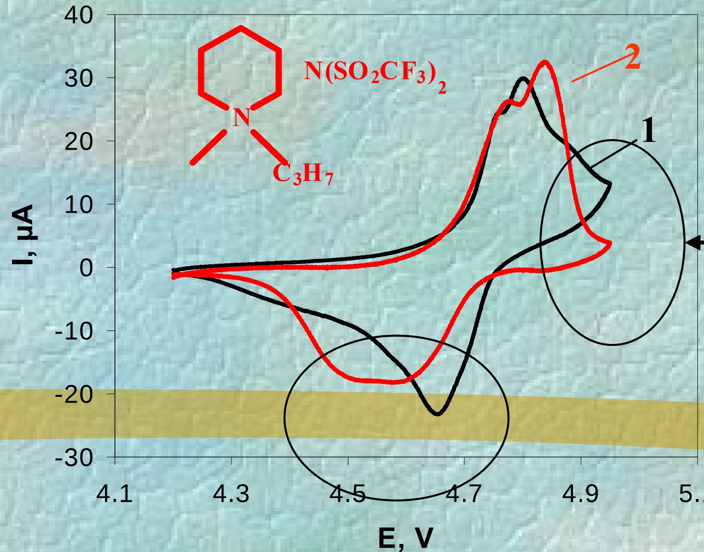
Why Ionic Liquids (Ils)?

Wide electrochemical window
Safety

The electrochemical stability window of LiTFSI in MPPpTFSI electrolyte Pt and $LiNi_{0.5}Mn_{1.5}O_2$ electrodes



$LiNi_{0.5}Mn_{1.5}O_2$ electrodes in 1.5M $LiPF_6$ EC/EMC 1:2 and in IL solution 0.5M LiTFSI in MPPpTFSI

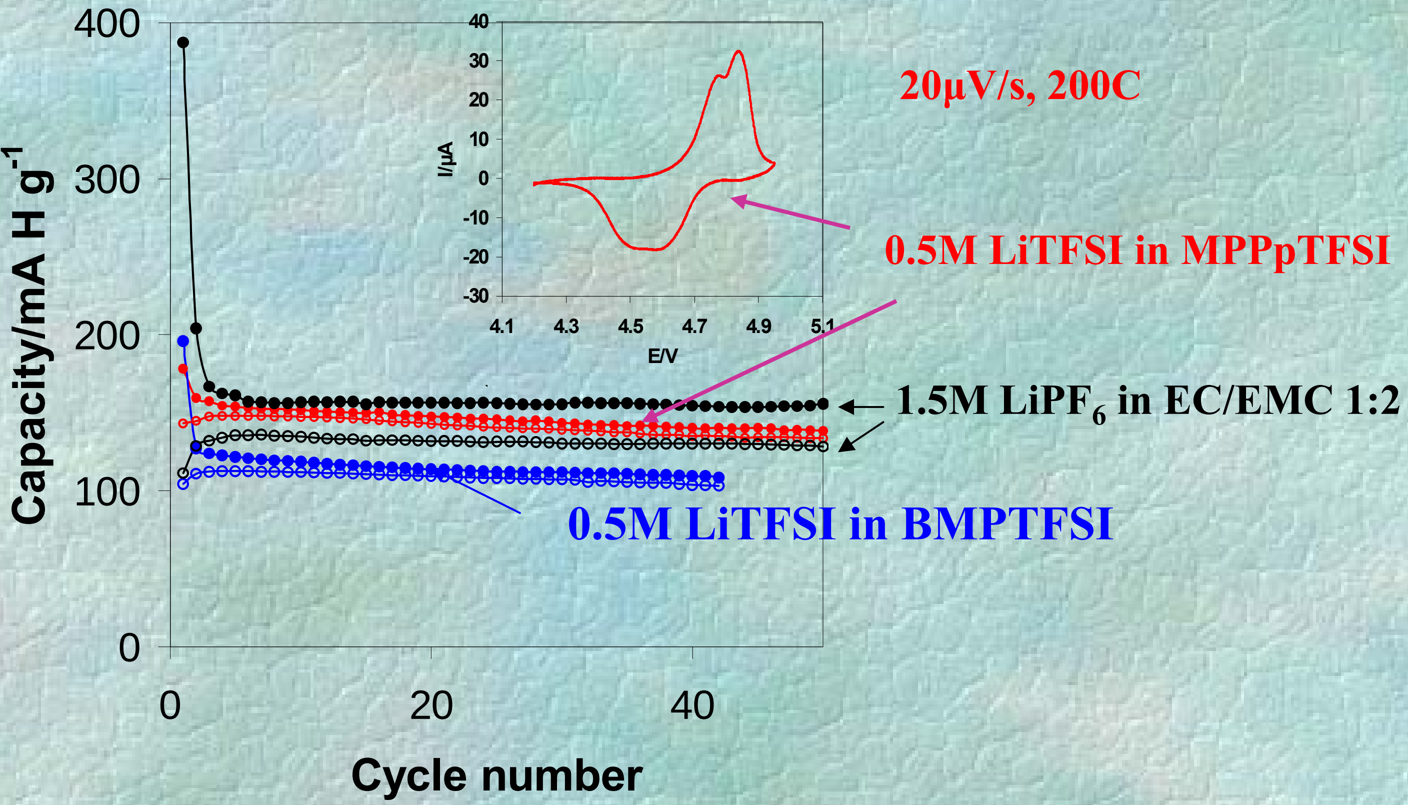


side parasitic oxidation processes in standard electrolytes not in Ils

Kinetics is slower in the ionic liquid electrolyte

$LiNi_{0.5}Mn_{1.5}O_2$ /Li "5V" cells demonstrate stable cycling with IL electrolyte solutions : elaboration of real "5V" rechargeable Li batteries may be feasible.

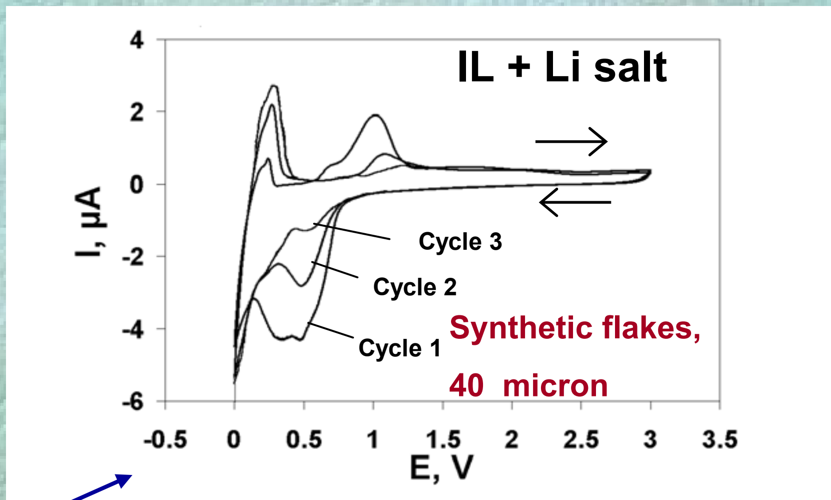
$LiNi_{0.5}Mn_{1.5}O_4$ electrodes in standard & IL solutions

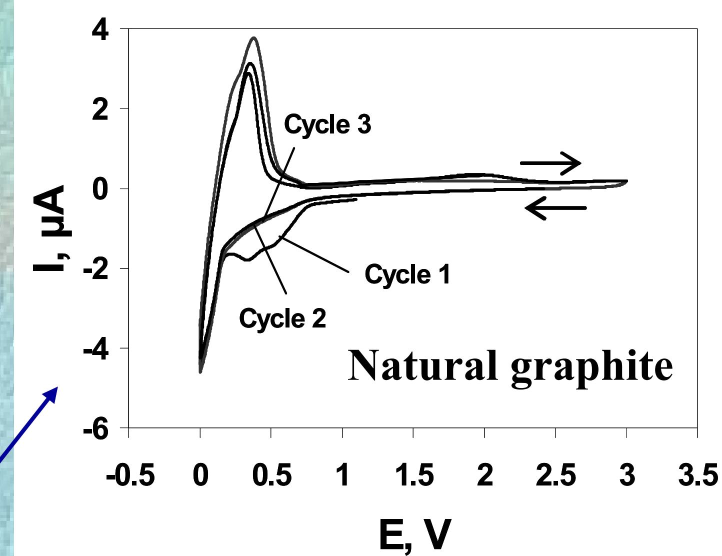


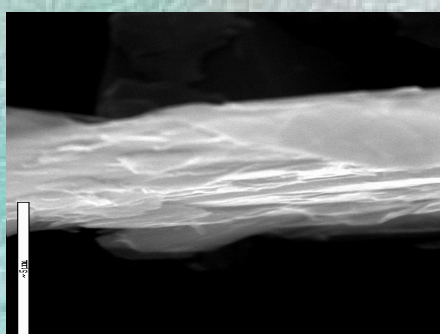
Charge and discharge capacity obtained for the galvanostatic cycling of $LiNi_{0.5}Mn_{1.5}O_2$electrodes (C/16). Upper curves are discharge proesses and the lower curves are the charging processes.
Note the much lower irreversible capacity obtained with the ILs electrolytes.

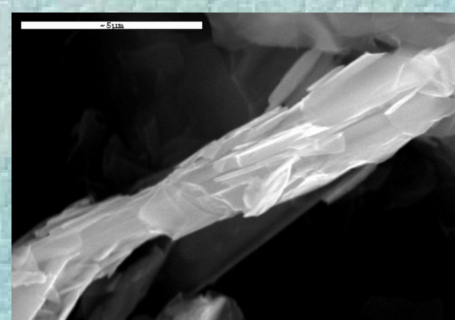
V. Burgel et Al, *J. Power Sources* (2008) In press

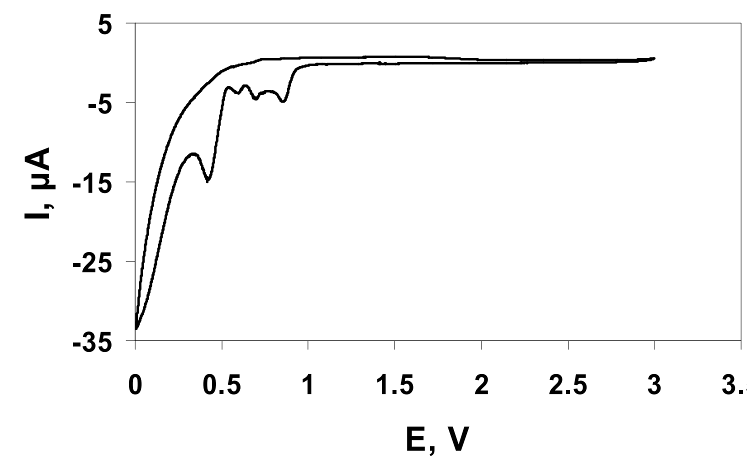
A comparative study of the behavior of different kinds of graphite electrodes in solutions based on ionic liquids

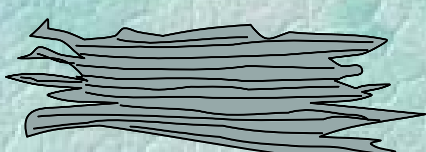


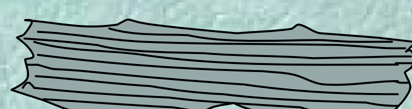










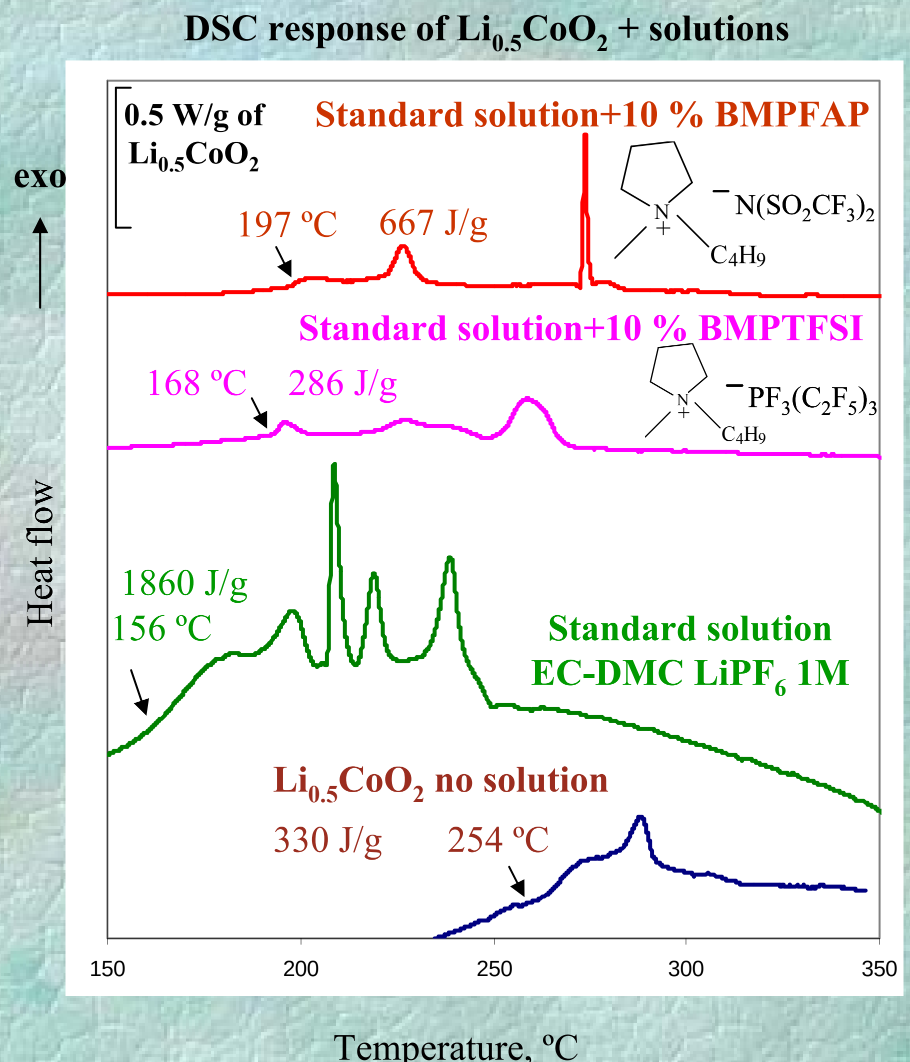


Synthetic flakes

NG

Graphite in pure IL (MPPpTFSI): no Li ions, no passivation, irreversible IL intercalation

Attenuation of thermal activity by use of ILs as additives



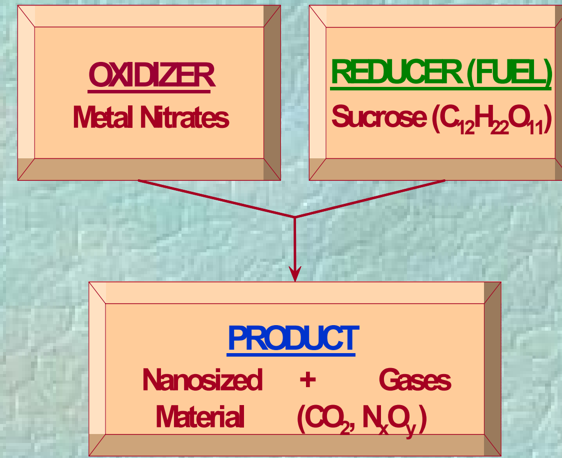
Synthesis

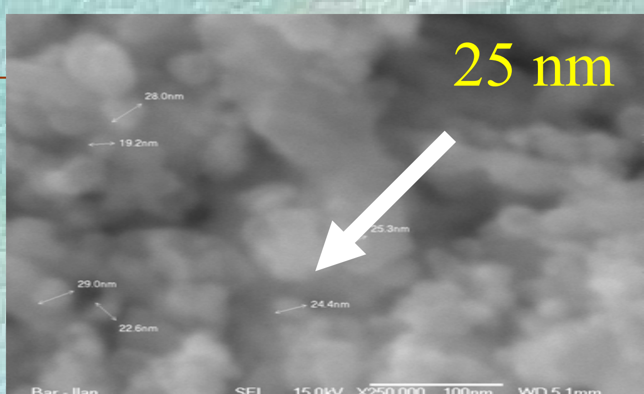
Single-step sucrose-aided Self-Combustion Reaction for production of layered compounds of nanosized lithiated oxides

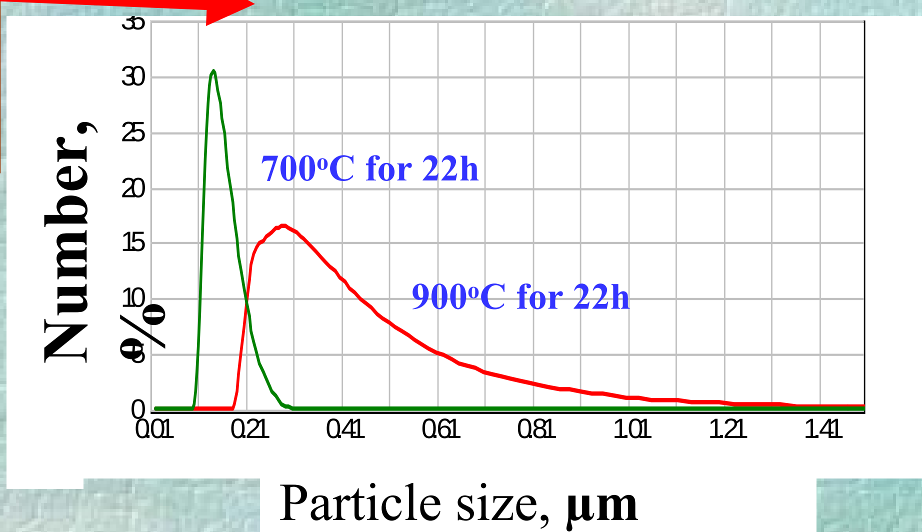
$$LiNO_3 + 0.5\ Ni(NO_3)_2.6H_2O + 0.5\ Mn(NO_3)_2.4H_2O + 0.3125\ C_{12}H_{22}O_{11} + 0.25\ O_2 \rightarrow LiNi_{0.5}Mn_{0.5}O_2 + 3.75\ CO_2 + 8.4375\ H_2O + 3\ N_2$$

Then, calcination provides the final structure.

The temp. & time of calcination determine the particle size.

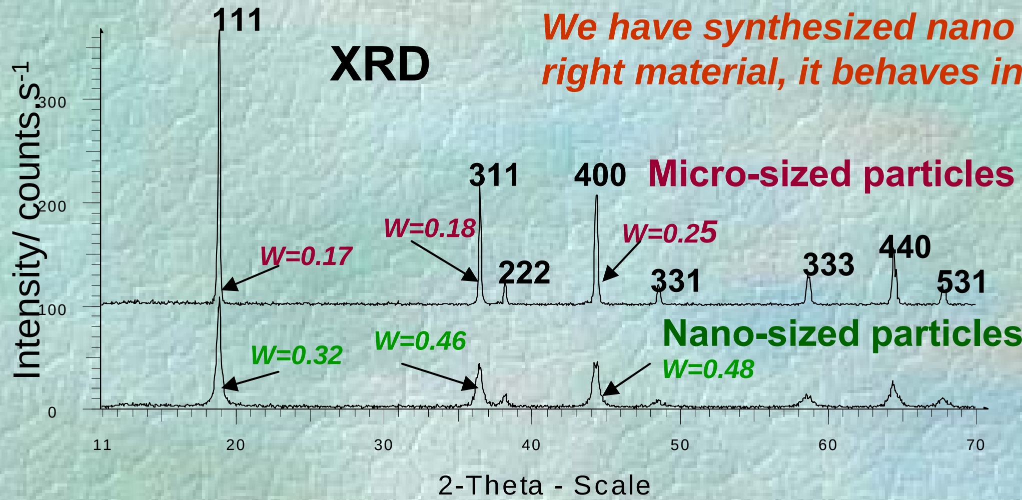


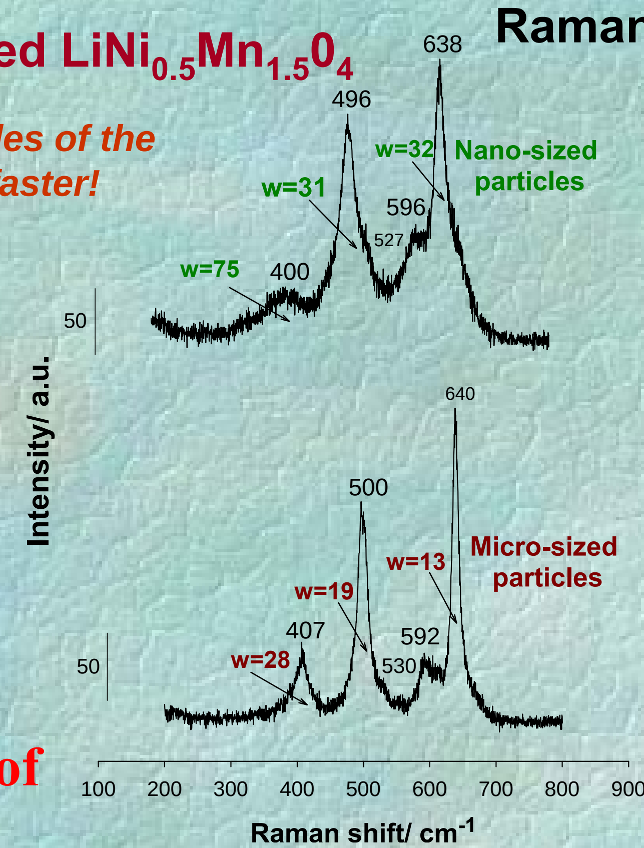


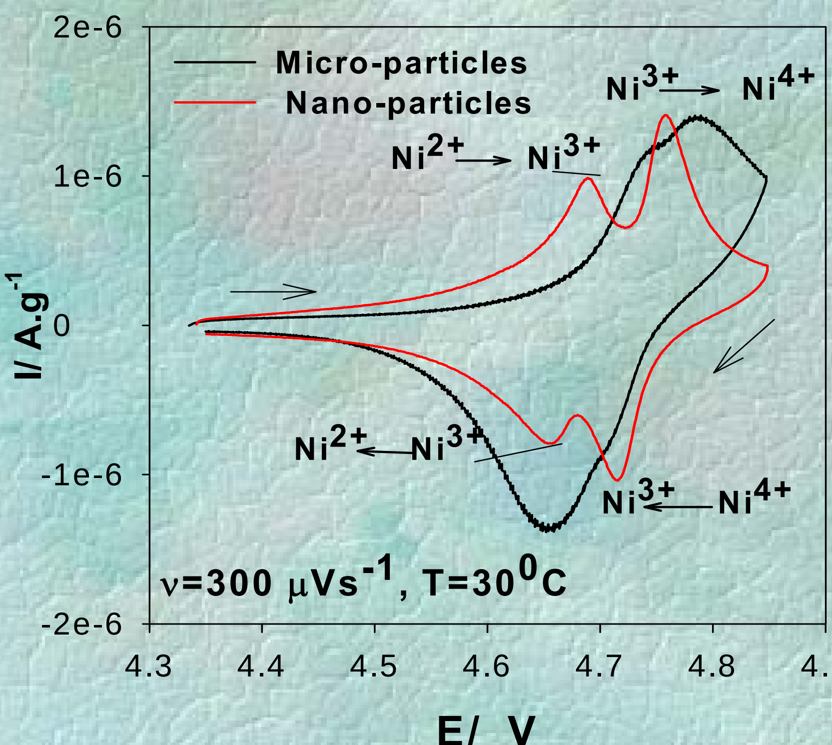


Nano-sized $LiNi_{0.5}Mn_{1.5}O_4$ *vs.* *Micro*-sized $LiNi_{0.5}Mn_{1.5}O_4$

We have synthesized nano particles of the right material, it behaves indeed faster!

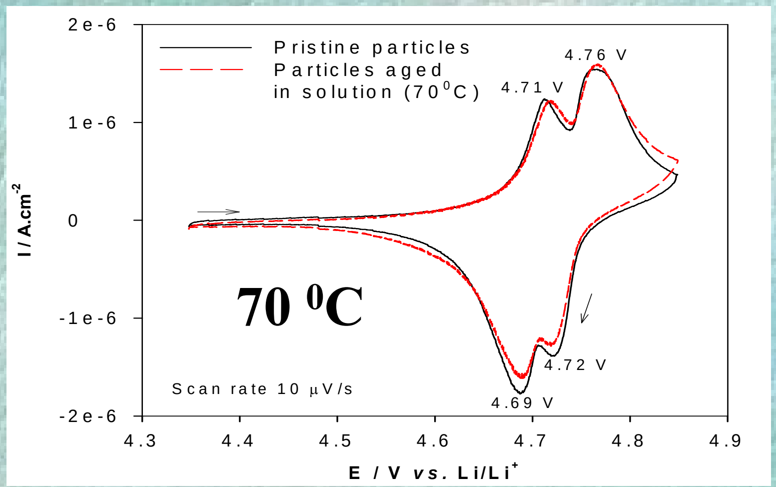






Up to 140 mAh/g

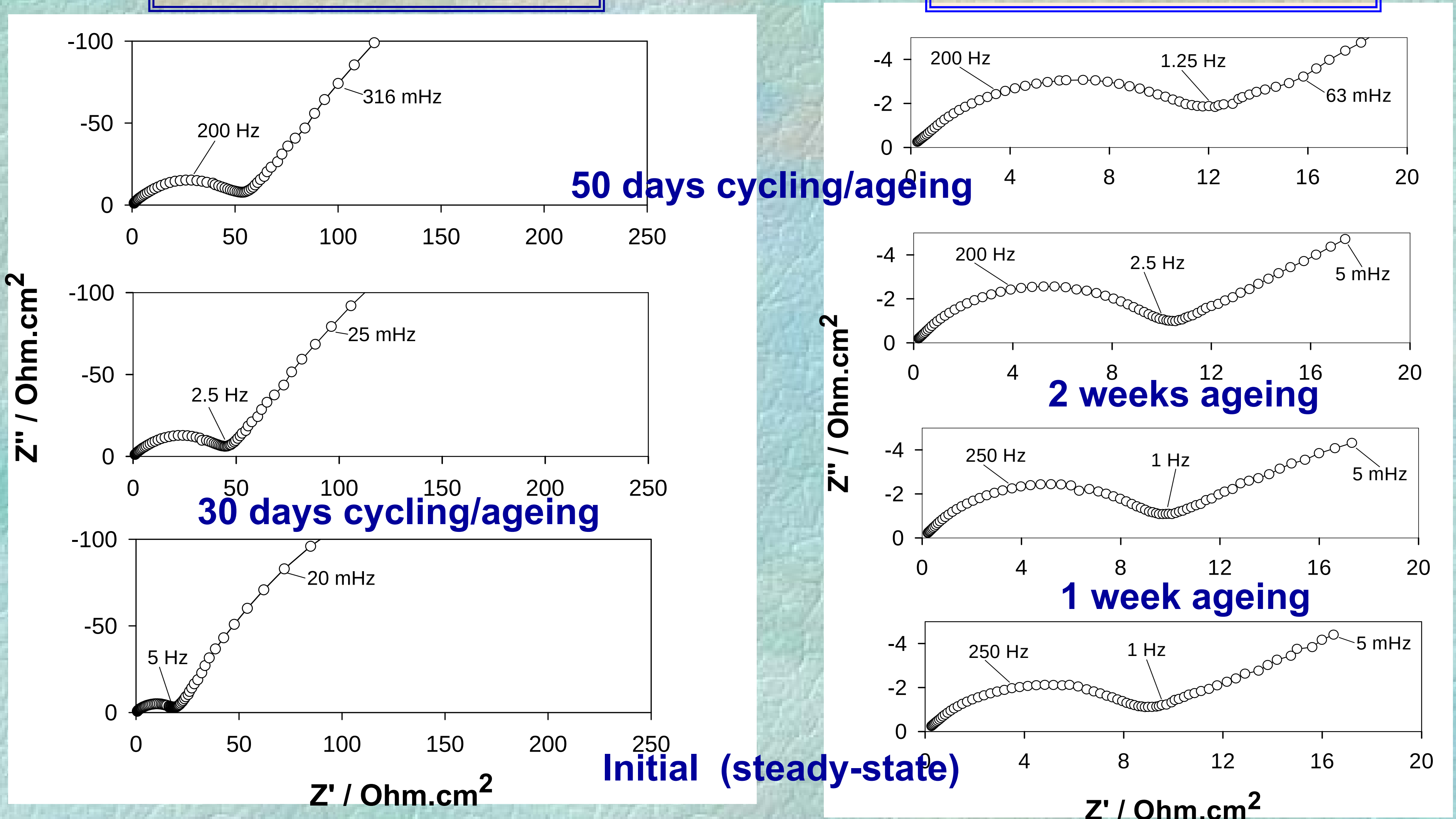
Hundreds of cycles



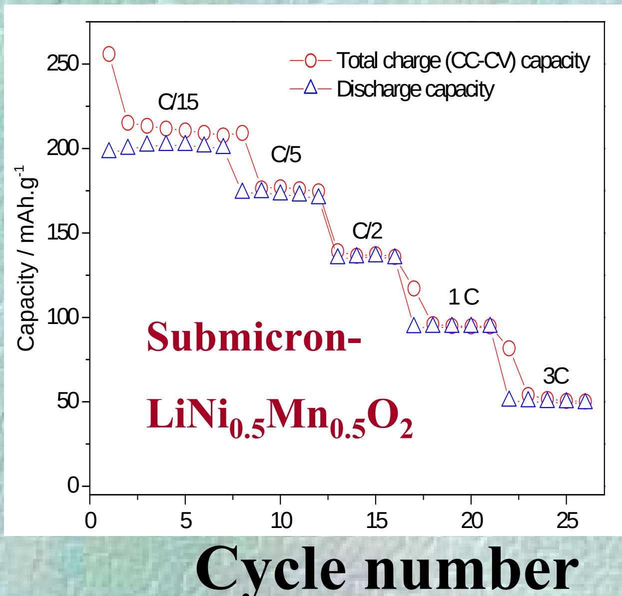
$LiNi_{0.5}Mn_{0.5}O_2$ Electrodes: 60^0C, E=3.90 V

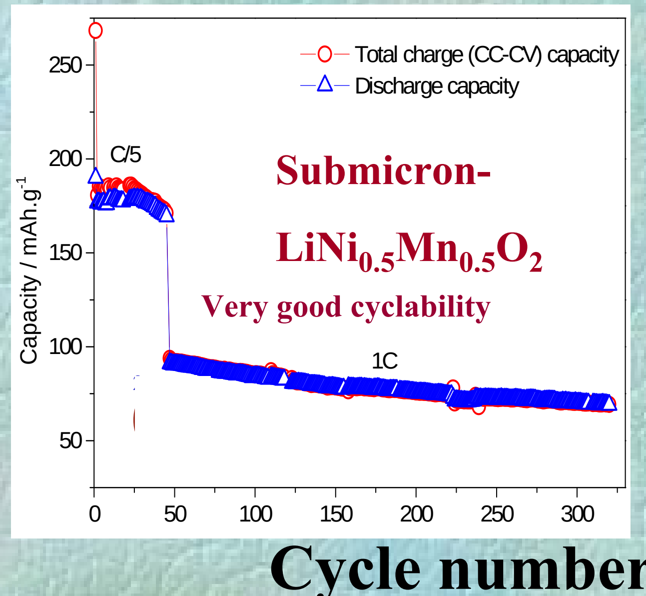
Micro-particles

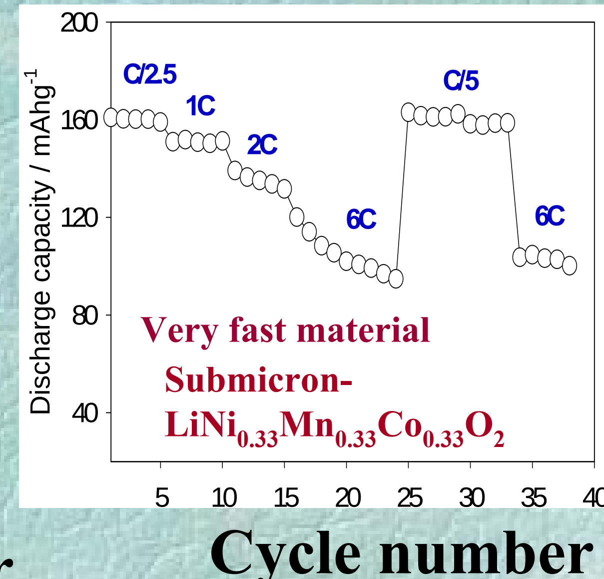
Nano-particles

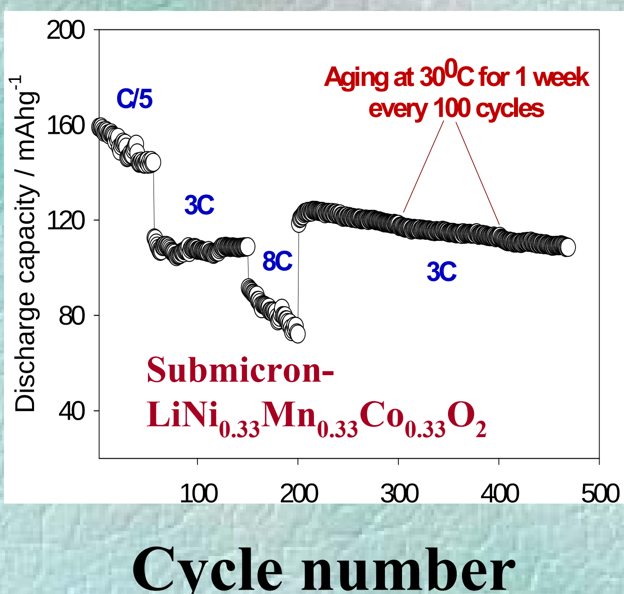


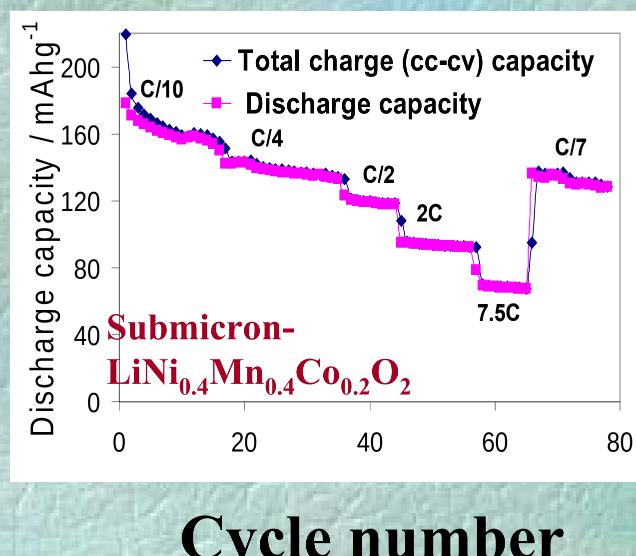
Electrochemical behavior of electrodes prepared from micro-, submicron or nano-particles in Li cells, DMC-EC/$LiPF_6$ solutions

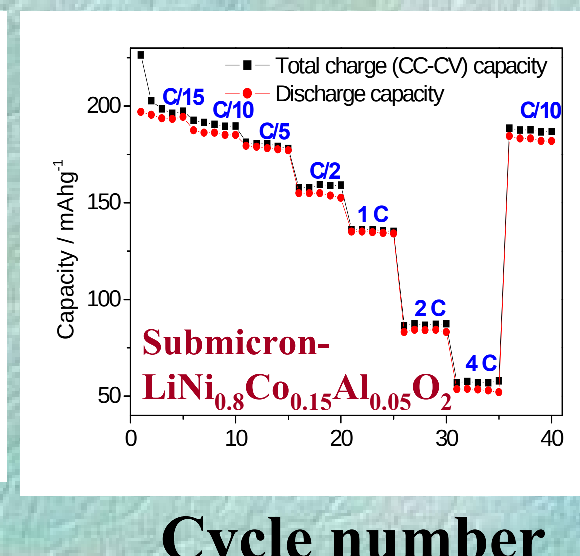




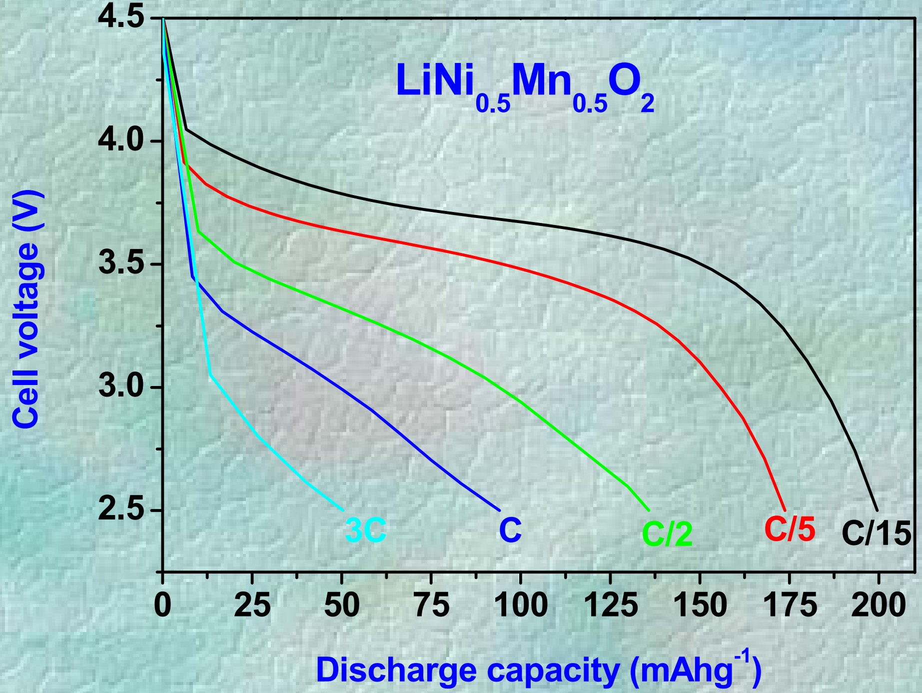


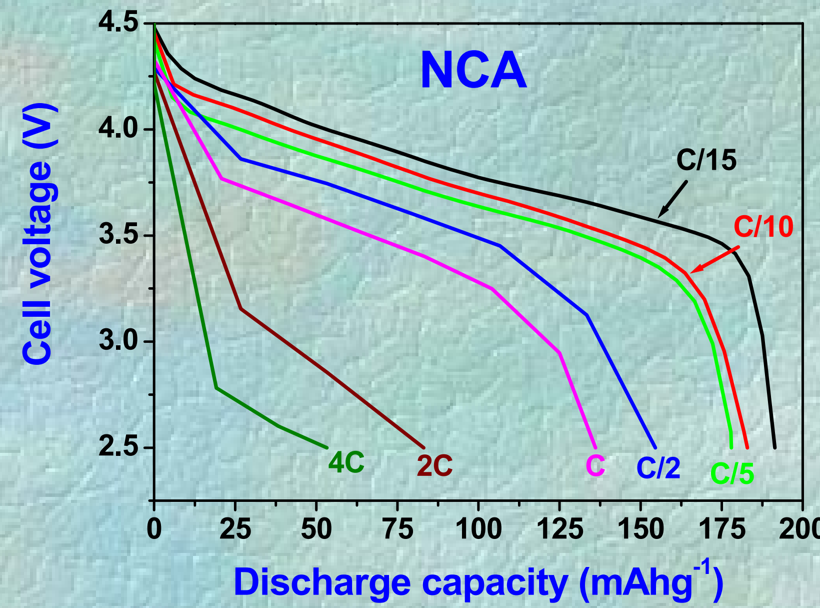


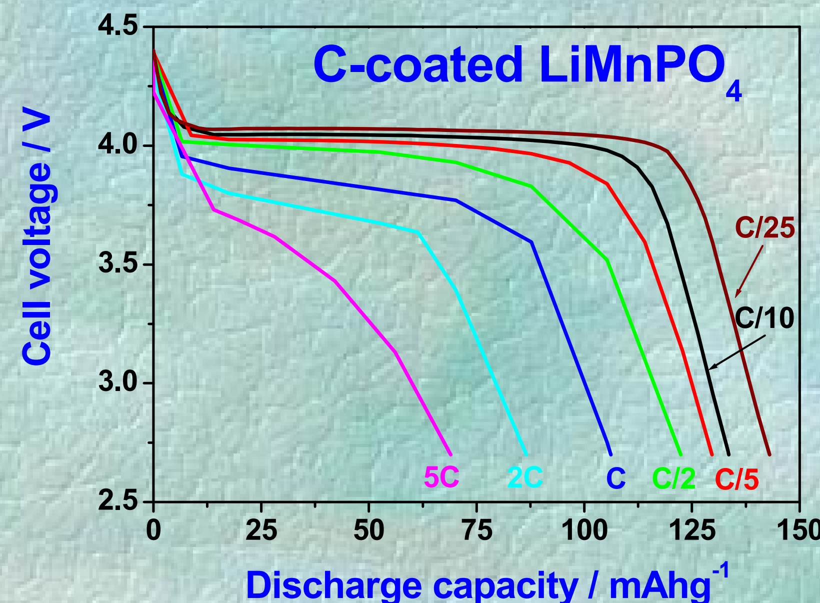




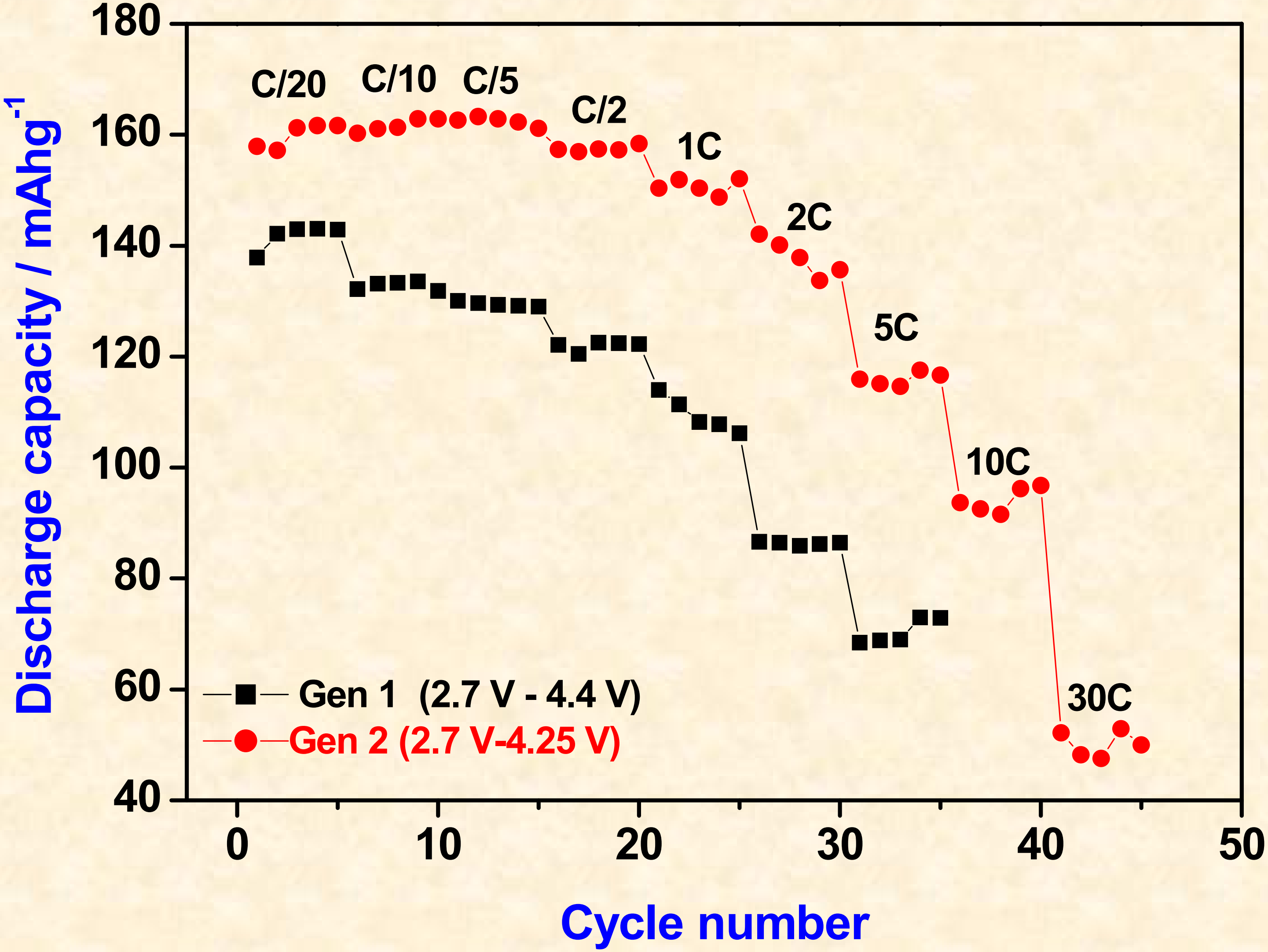
Voltage profile for $LiNi_{0.5}Mn_{0.5}O_2$, NCA and C-coated $LiMnPO_4$ composite electrodes at various discharge rates at 30°C



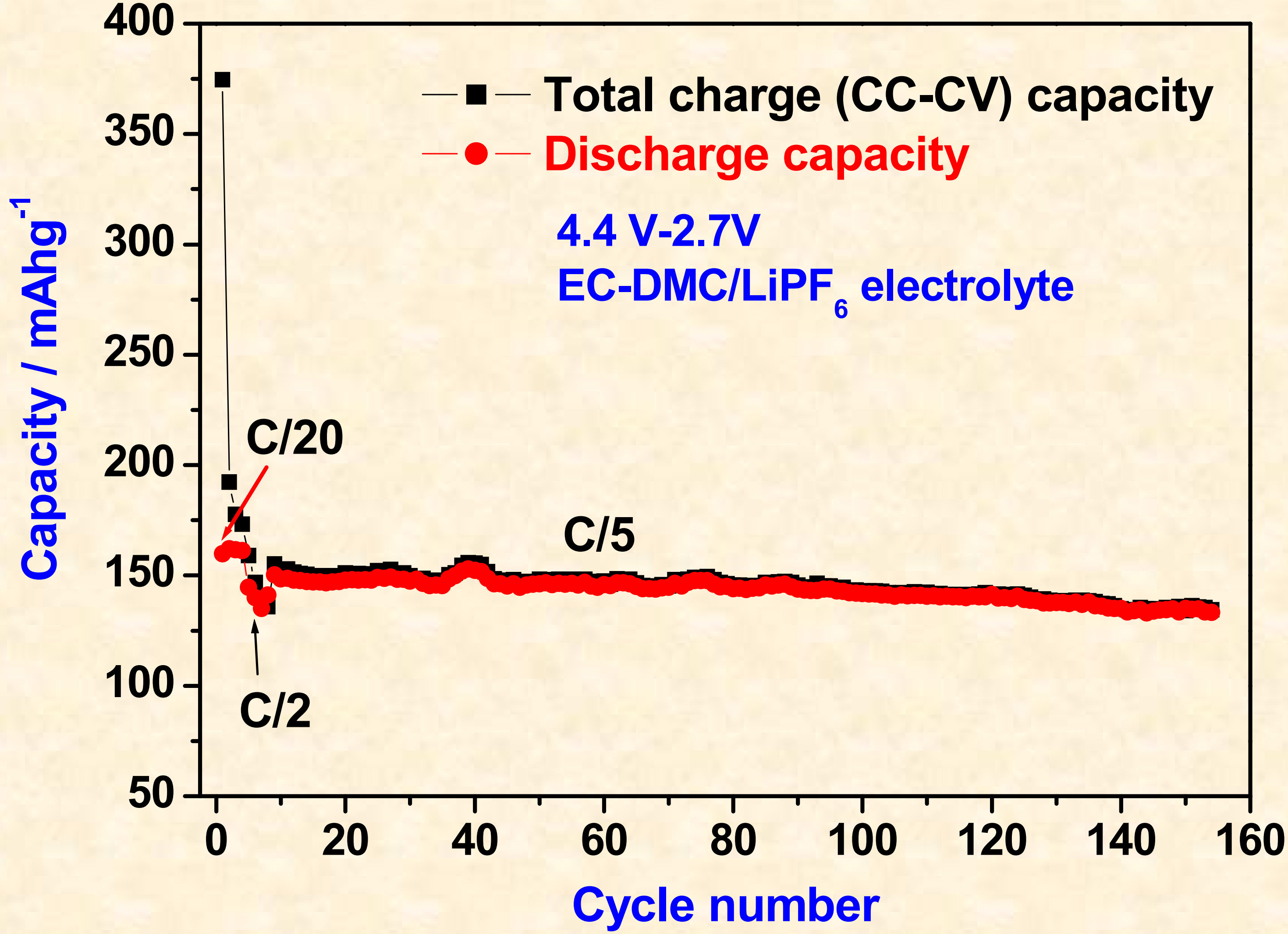




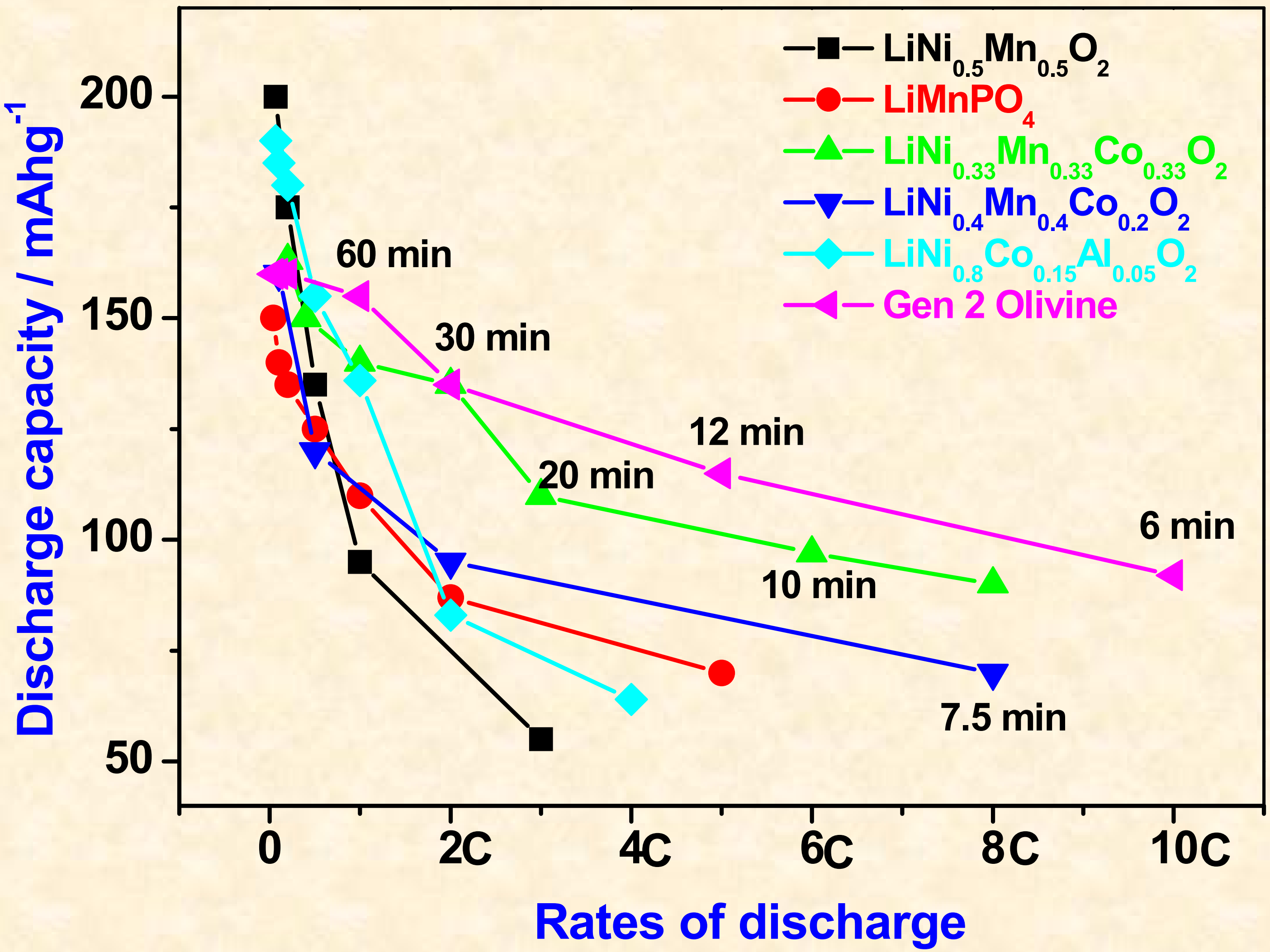
Comparison of cycling behavior at various rates of discharge for Gen 1 and Gen 2 electrodes at 30° C



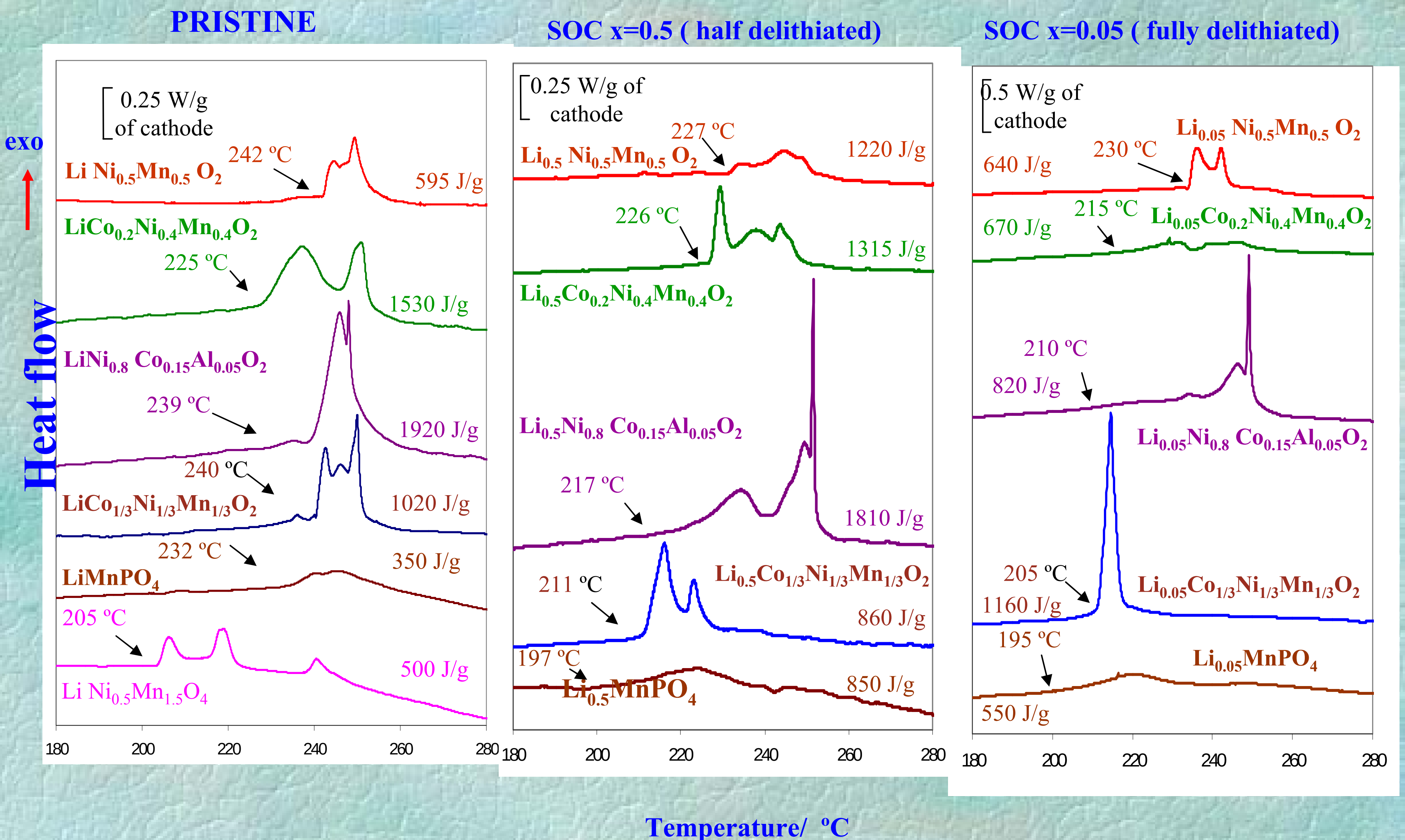
Cycling behavior at C/5 rate of discharge for Gen 2 electrodes at 30° C



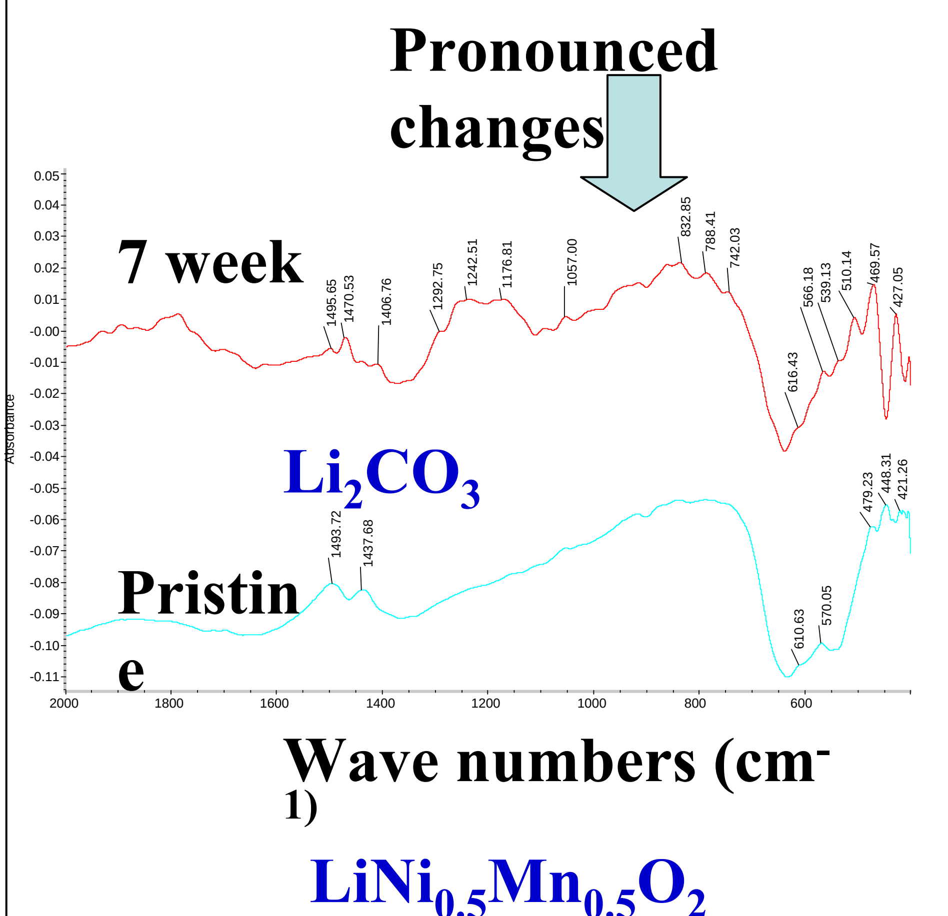
Comparison of capacity at various discharge rates for the electrodes comprising $LiNi_{0.5}Mn_{0.5}O_2$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, (NCA), $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$, $LiMnPO_4$ (Gen 1)and Gen 2 Olivine particles

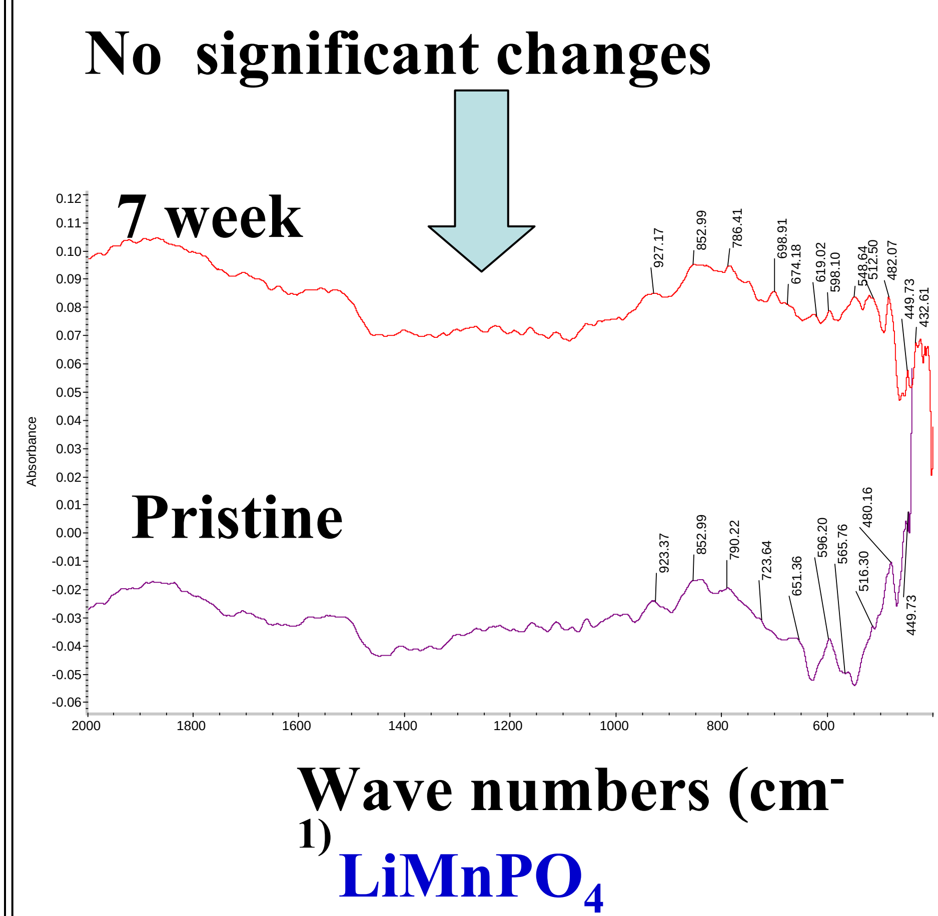


DSC response for different cathodes in EC-DMC/ $LiPF_6$ Solution

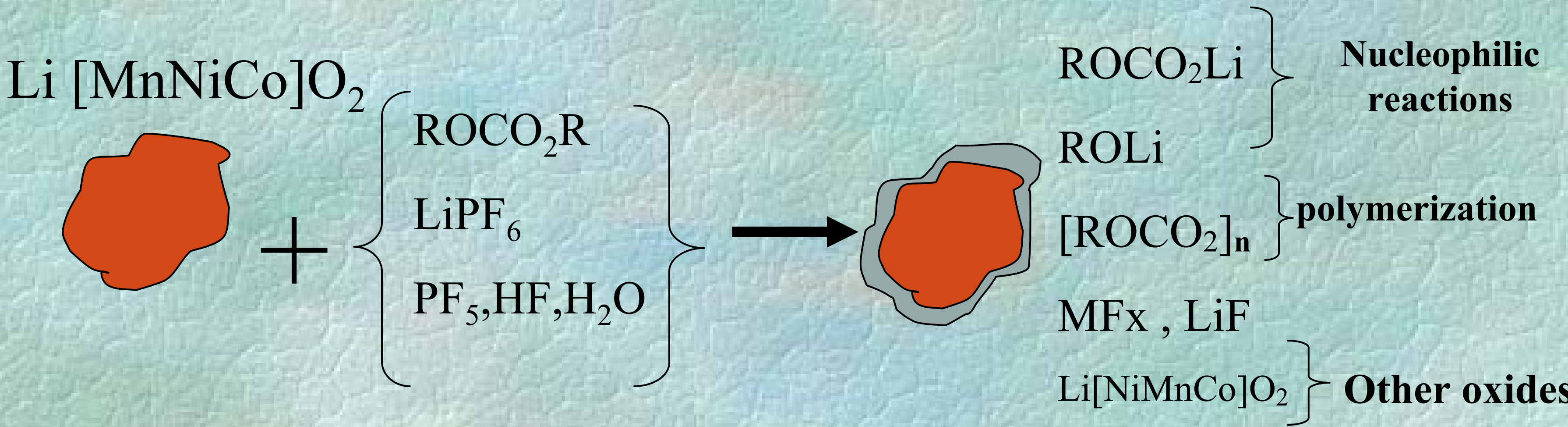


Comparison between surface active and non active cathode materials





Surface chemistry

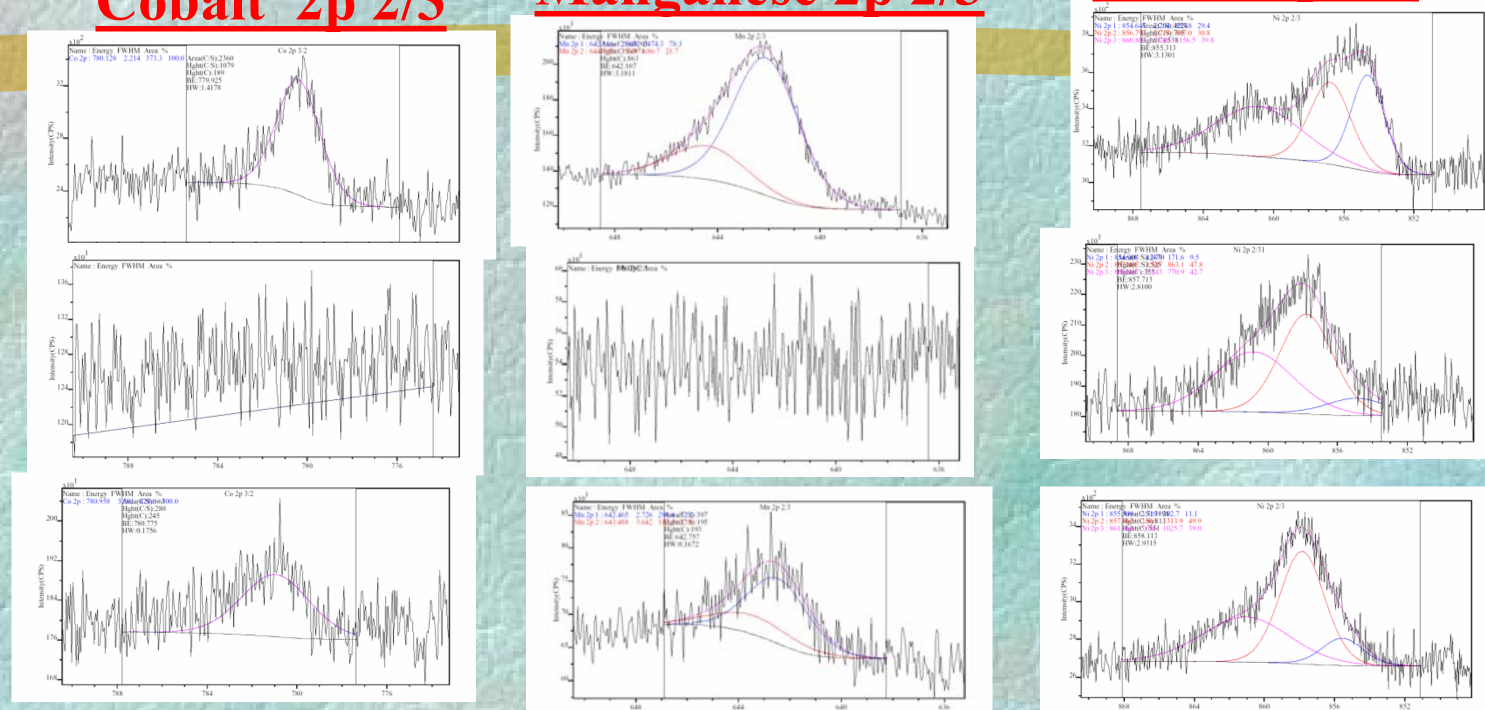


Cobalt 2p 2/3 | **Manganese 2p 2/3** | **Nickel 2p 2/3**

Pristine powder

$Li[NiMnCo]O_2$ Powder aged

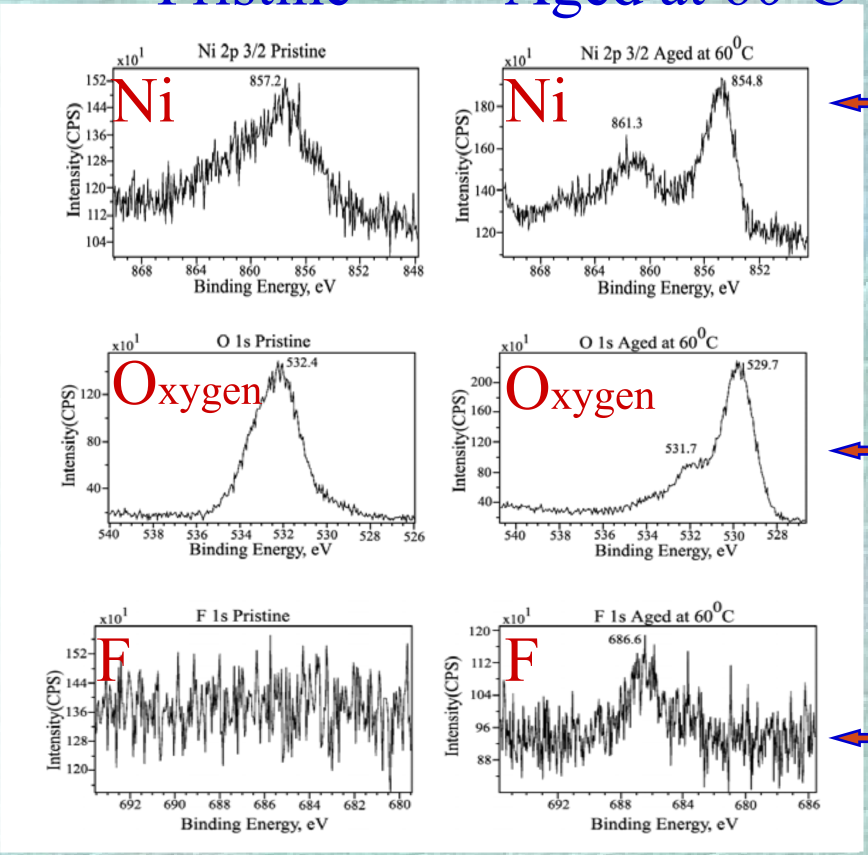
$Li_x[NiMnCo]O_2$ Electrode charged



Surface chemistry

XPS spectra of nano-$LiNi_{0.5}Mn_{0.5}O_2$ particles

Pristine | Aged at 60^0C



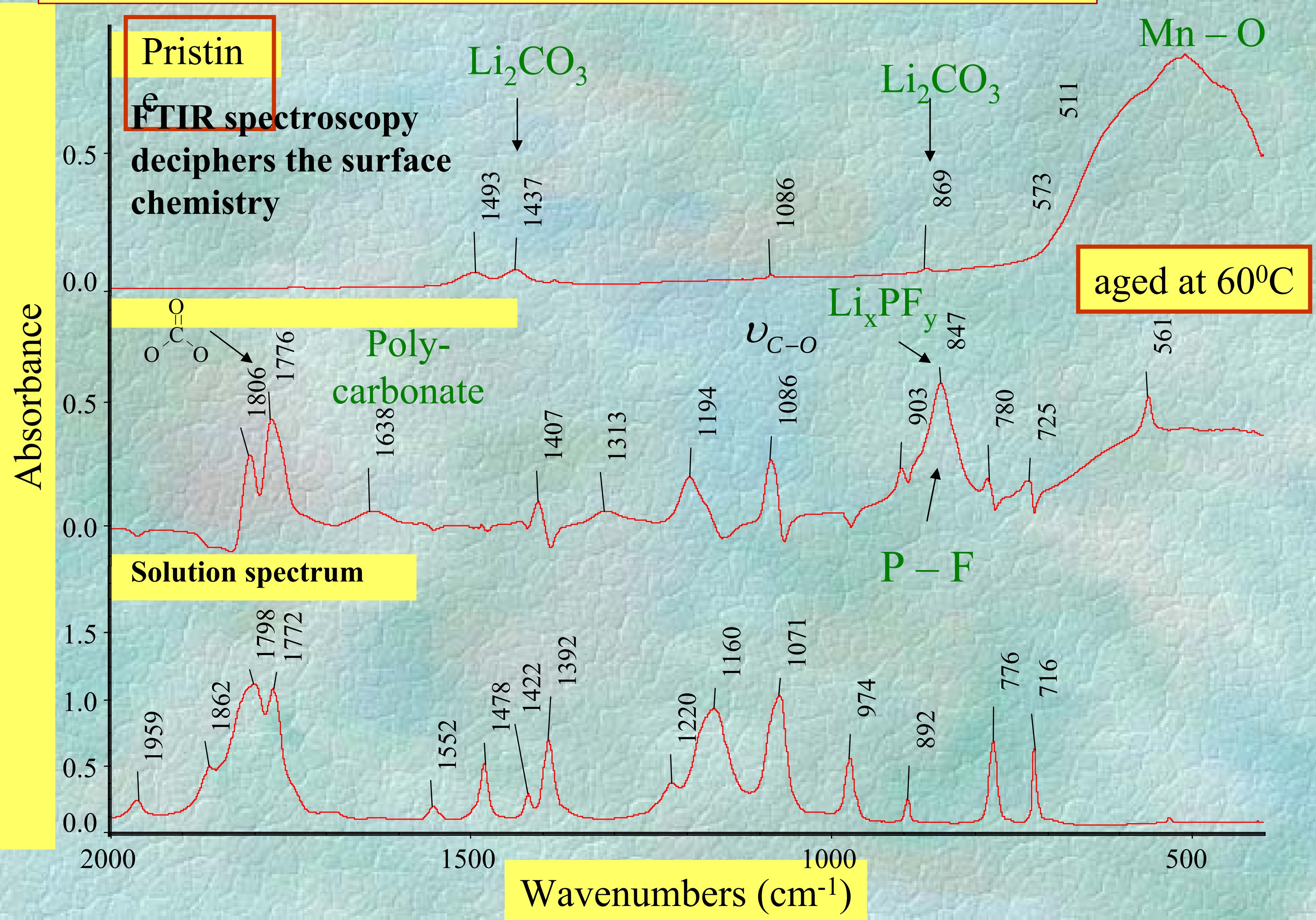
peaks at 855 eV and at 861.3 eV : formation of surface species containing Ni of higher oxidation state than 2^+.

peak at 529.7 eV: nickel (III) oxide and manganese oxides.
a satellite peak at 531.7 eV: organic species with carbonyl groups

peak at 686 eV: LiF, MnF_2, NiF_2

Ageing in solution → **Changes in surface chemistry and passivation**

Nano-$LiNi_{0.5}Mn_{0.5}O_2$ EC-DMC (1:2)/1.5 M $LiPF_6$



Summary: Main Demonstrations

1. Ionic liquids can work well with all relevant electrodes materials. The anodes passivation can be controlled by additives.

2. $LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{0.5}O_2$ and $Li[NiMnCo]O_2$ nano-materials can be apparently chemically stable in standard electrolyte solutions, even at high temperatures.

3. These materials develop unique surface chemistry in standard solutions that leads to their efficient passivation.

4. A maximal practical capacity up to 200 mAh/g can be from both $LiNi_{0.5}Mn_{0.5}O_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$.The former one is a slow material.

5. The fastest material is $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ however the practical capacity is around 160 mAh/g .

6. $LiMnPO_4$ produced by HPL is the least surface reactive of all the cathode materials studied, what is well expressed in very good cycleability. Its rate capability is better than that of $LiNi_{0.5}Mn_{0.5}O_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$