# Spinel Materials for High Power Batteries

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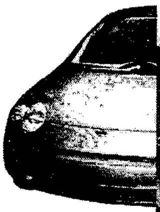
## Electric Vehicle & Hybrid Electric Vehicle



*Nissan & Sony Ene*
*Lithium Ion Te*

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## Technical Approach: Hybrid Electric Vehicle

- Partnership for a New Generation of Vehicles (PNGV) Program is working with the U.S. auto industry to develop high-power lithium-ion batteries for hybrid electric vehicles.
- Lithium-ion batteries need to overcome the key barriers of calendar life, safety, and cost.
- The approach is;
  1. to develop high-power materials,
  2. incorporate them into sealed cells,
  3. conduct well-defined thermal abuse and accelerated aging tests on the cells, and
  4. then employ a suite of diagnostic tools and techniques to identify the main factors that control their life and abuse tolerance.

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## Strategies

- **Developing Electrode Materials in high Power Application.**
- A material should have following properties;
  - high rate capability
  - long cycle life
  - safety improvement
  - cost effective
  - high reversible capacity

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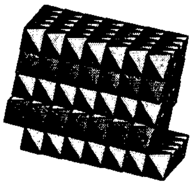
## *Choices for the Cathode Materials*

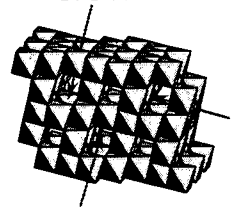
LAYERED



### $LiCoO_2$, $LiNiO_2$

Easy to synthesize
About 120-140 mAh/g useable capacity
4V system
$Li_{1-x}Co(Ni)O_2$ releases O when heated
Expensive and toxic materials
Used in almost all Li-ion products made today

SPINEL



### $LiMn_2O_4$

Tricky to synthesize good material
Cheapest raw materials
Environmentally benign
About 120 mAh/g useable capacity
Most thermally stable with Li removed
4V system

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## *Technical Approach: Hybrid Electric Vehicle*

- The layer compounds are favorable for high rate capability with their better electrical and ionic conductivity.
- The amount of cobalt should be minimized or eliminated for cost concern.
- The structural instability of lithium nickel compound drives searching for suitable metal ions to substitute.
- Our effort to develop these substitution includes Ca, Mg, Cu, Al, Co, Mn, Ti, Si, etc.

  >> nano-scale structural engineering is needed!!

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## *Why Titanium?*

- Assume $Ni^{2.9+}$ presents, stoichiometric amounts of Li and Ni are reacted.
  - $Li_{1.00}Ni_{1.00}^{2.9+}O_{1.95} = Li_{1.03}Ni_{1.03}^{2.9+}O_{2.00}$
  - $(Li_{0.97}Ni_{0.03}^{2.9+})_{3a}(Ni_{1.00}^{2.9+})_{3b}O_{2.00}$ + 0.03($Li_2O$, as impurity)

- Assume $Ni^{2.9+}$ presents and substituting 10% of $Ni^{2.9+}$ by $Ti^{4.0+}$,
  - $Li_{1.00}Ni_{0.90}^{2.9+}Ti_{0.10}^{4.0+}O_{2.00}$
  - $(Li_{1.00})_{3a}(Ni_{0.90}^{2.9+}Ti_{0.10}^{4.0+})_{3b}O_{2.00}$ + no $Li_2O$

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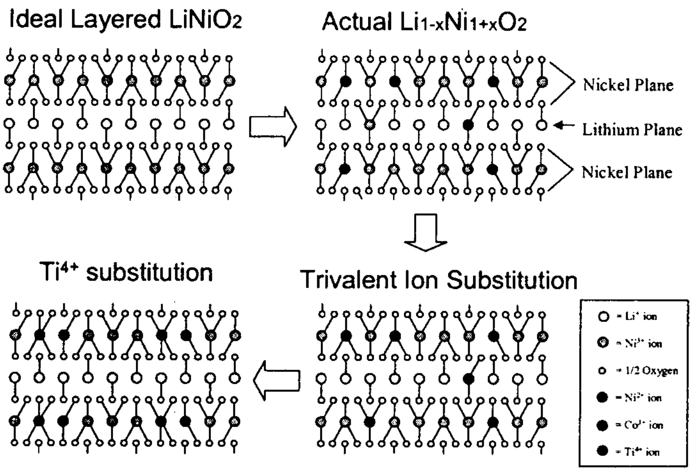
## *Nano-scale structural Engineering*

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## *Experimental Procedures*

- Materials Preparation (solid-state reaction)
  - Mixing required amounts of hydroxides using ball-mill.
  - Heating at 750 °C for 30 hours in oxygen or air stream.
- Materials Characterization
  - TG-DTA, XRD, SEM, EDX, ICP, PSA, TG-DTA, XPS, etc.
- Electrochemical Characterization
  - Forming laminate on Al foil. Li or C/LiPF6 in EC:DEC/materials
  - GC, CV, Pulse power testing, AC impedence, etc.

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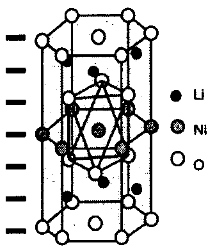
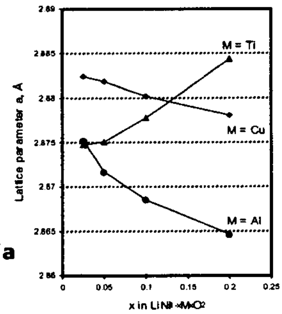
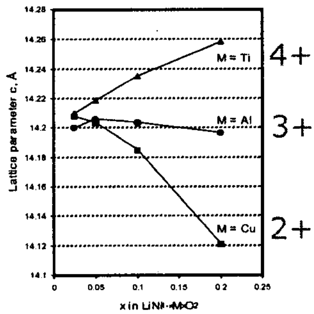
## *Crystalline Structure Stabilities*



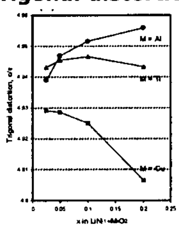

**Lattice parameter a**




**Lattice parameter c**




**Trigonal distortion c/a**



***Strongly depends on the degree of ionicity of $(Ni_{1-x}M_xO_2)_n$ sheets***

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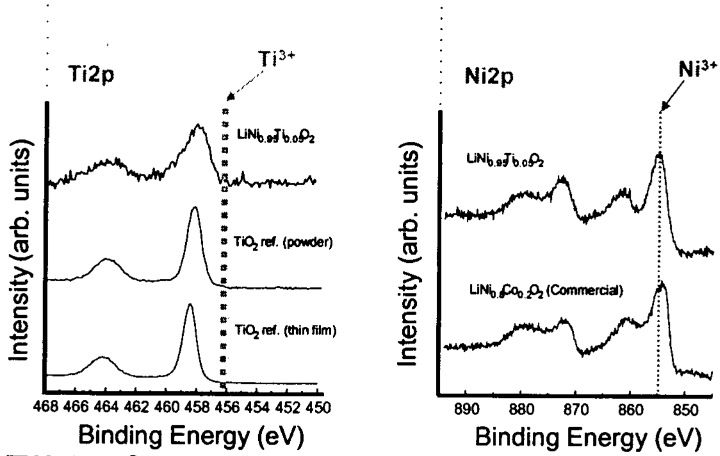
## *X-ray Photoelectron Spectroscopy Results*

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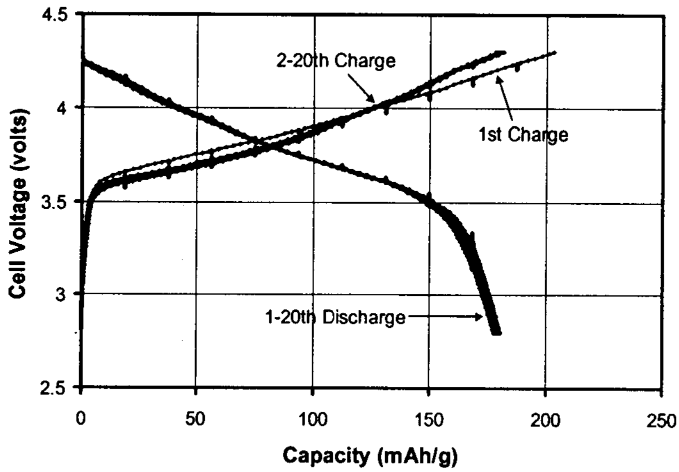
## *The Galvanostatic Cycling Results of $LiNi_{0.9}Ti_{0.1}O_2$ Sample*

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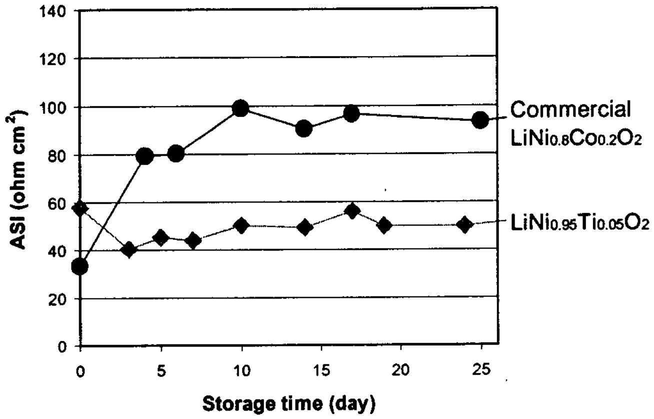
## ASI Test Results as a Function of Storage Time at 50 ºC

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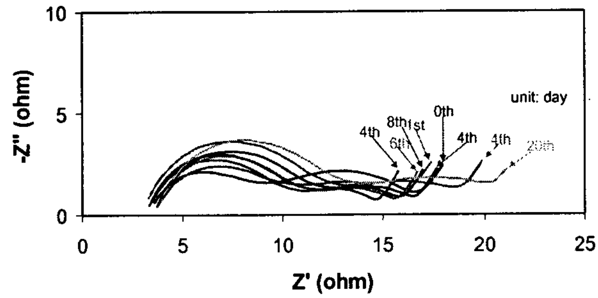
## AC Impedence Test Results as a Function of Storage Time at 50 ºC

AC Impedence of Tetravalent Titanium Substituted Lithium Nickel Oxide.

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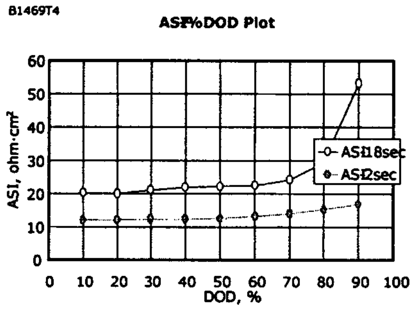
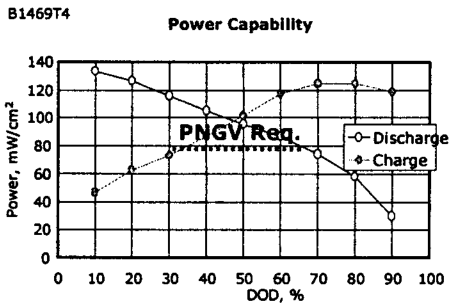
## *HPPC Result of Materials of $LiNi_{0.95}Ti_{0.05}O_2$*




➢ ***ASI(Area Specific Impedance) and power capability value shows 22 Ohm.cm², which exceed well the PNGV requirement.***

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## *Problem in Spinel:*

***Is Jahn-Teller distortion the only problem in manganese spinel ?***

- lattice distortion at discharged state
- Jahn-Teller effect occurs at $x \geq 1.08$($V_{oc}$ = 2.96 V vs. $Li/Li^+$) in $Li_xMn_2O_4$

Cubic phase (c/a = 1.0)

↓ Jahn-Teller distortion

Tetragonal phase (c/a = 1.16)

-c axis; 12 % increased
-a axis; 3 % decreased
=> volume; 5.38 % increased

➡ **Could be managed by careful control of chemistry, morphology and voltage control**

- The instability of manganese depending on its valence states in organic electrolyte causes manganese dissolution.
- It results in the deterioration especially at high temperature.

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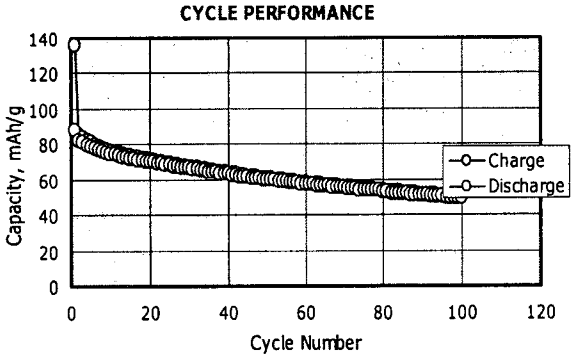
## *Cyclabilities of Spinel(+)/Carbon Gen1 (-) at 55 °C*




1st Strategies: Morphology and chemistry control.

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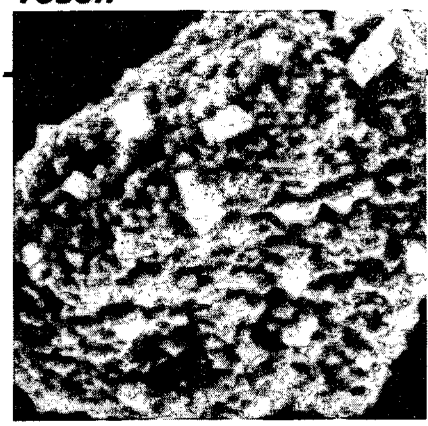
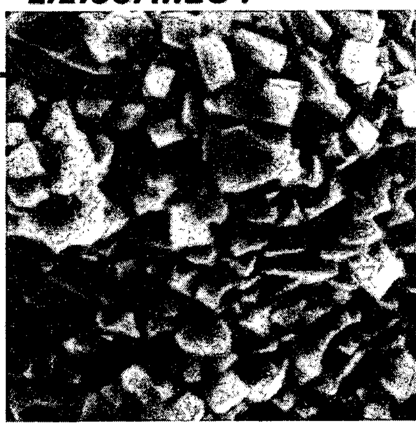
## *Comparison of Morphology:*
## *Tosoh spinel and $Li_{1.06}Mn_2O_4$*

➢ ***SEM Micrographs X2,000***

***Tosoh***



***Li1.06Mn2O4***



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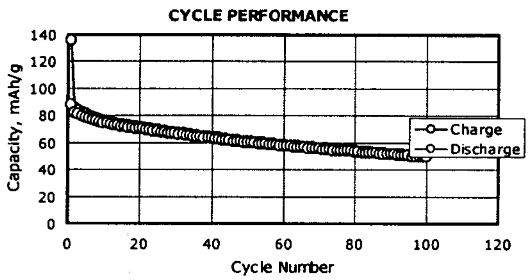
## *Strategies to obtain a stable spinel system*

Chemistry & Morphology control

-- Not effective with Carbon(-) at high temp.
exp.

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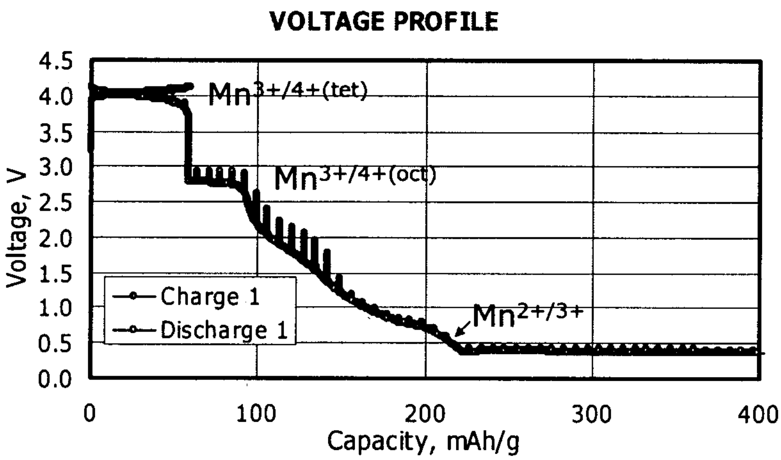
## *Voltage Profile of Tosoh(+)/Li*

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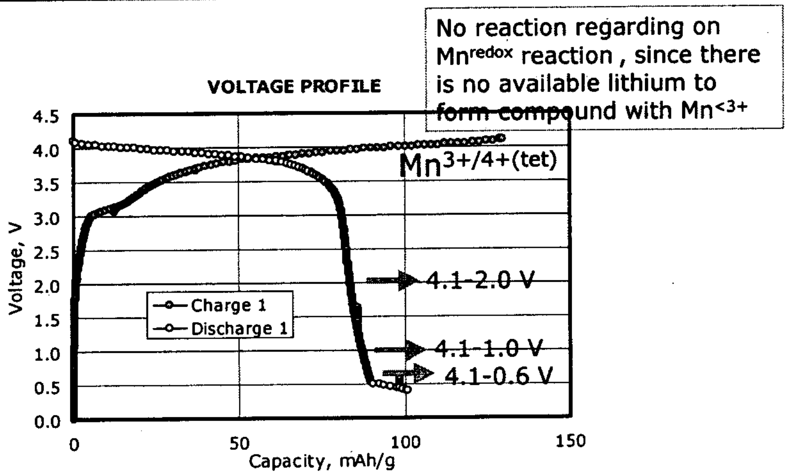
## *Voltage Profile of Tosoh(+)/Gen1(-)*

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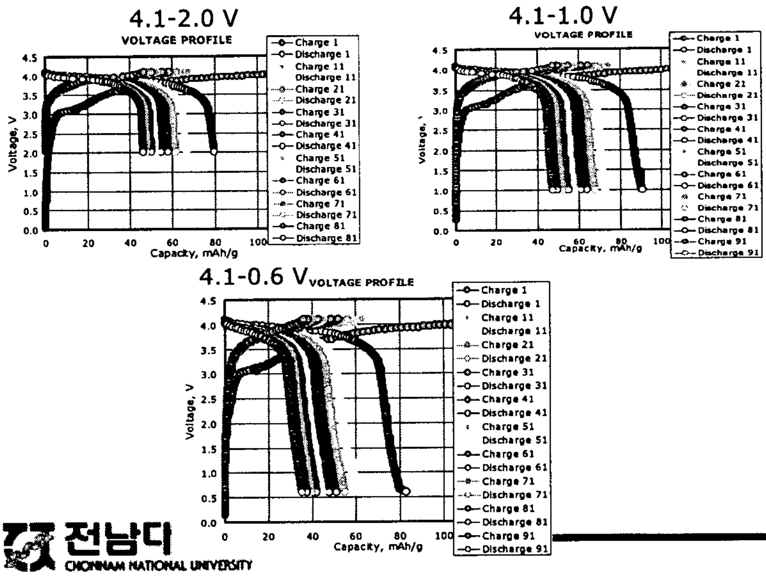
## *Cyclabilities of Tosoh(+)/Gen1(-)*

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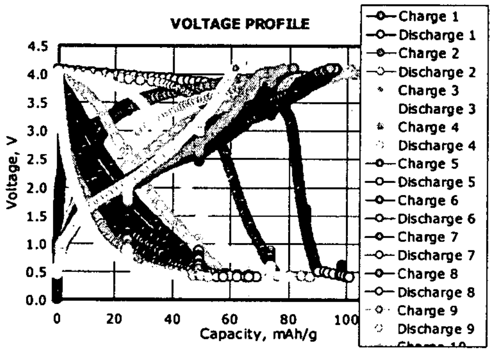
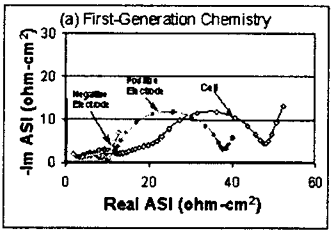
## *Cyclabilities of Tosoh(+)/Gen1(-)*

4.1-0.4 V




**Micro electrode Exp.**

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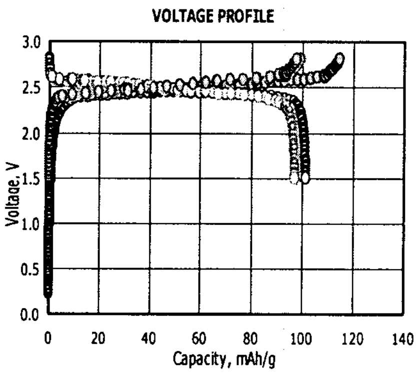
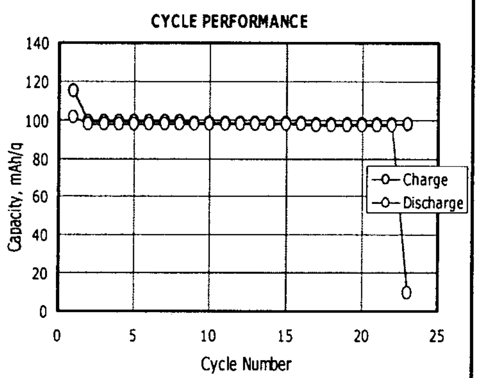
## *Tosoh Spinel(+) / LP40 / $Li_4Ti_5O_{12}$(-) at 55 °C*

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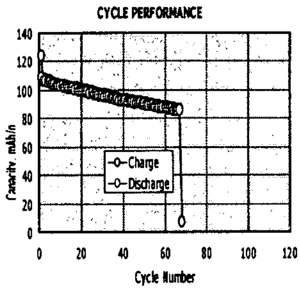
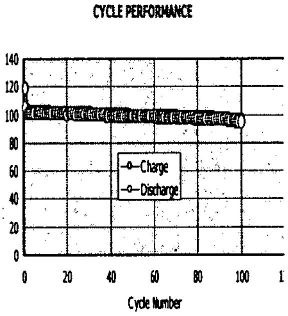
## *Comparison Cyclabilities of Spinel(+)/$Li_4Ti_5O_{12}$(-), Carbon Coated $Li_4Ti_5O_{12}$(-), and Carbon Gen1 (-) at 55 °C*

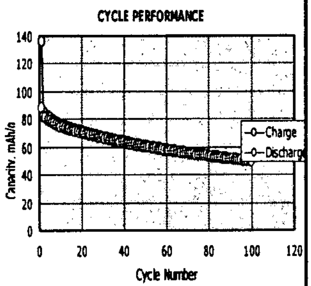
Carbon Coated $Li_4Ti_5O_{12}$(-)




$Li_4Ti_5O_{12}$(-)




Carbon Gen1 (-)

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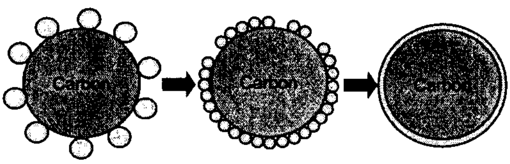
## Strategies to obtain a stable spinel system

Surface modification of carbon electrode
(ex. Alumina, Zirconia, Silver, etc)
!! Not effective for stabilizing spinel(+)/carbon(-) system




Polymer Film?

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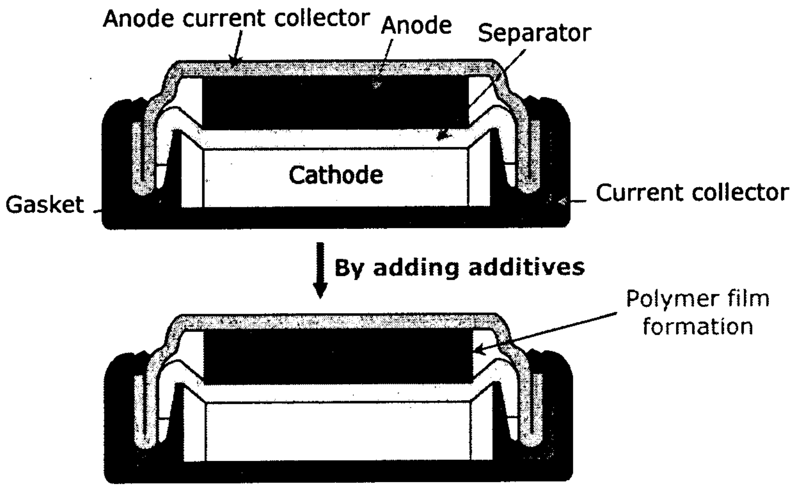
## *Way to work*

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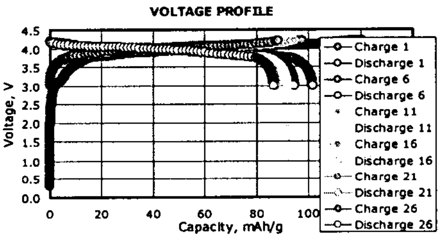
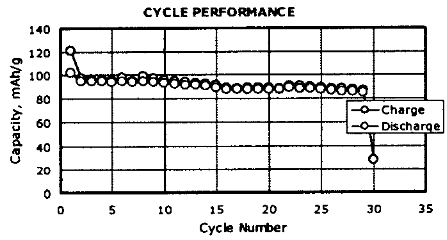
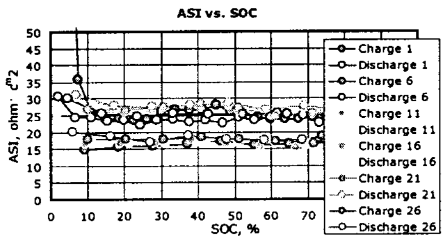
## *Example of optimized system*

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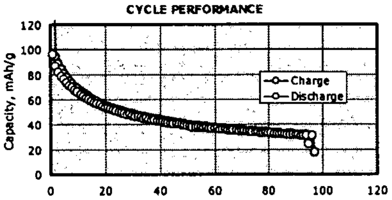
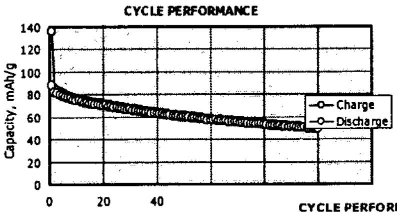
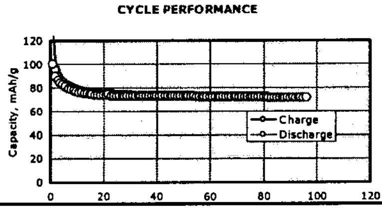
## *Effect of multiple additives*




LiPF$_6$ EC/DEC electrolyte at 55 °C




LiPF$_6$ EC/DEC electrolyte with additives at 55 °C




LiPF$_6$ EC/DEC electrolyte with double additives at 55 °C

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## *Summary for stabilization of spinel*

- The additives with specific structure in electrolyte react with anode at very low voltage range to form a thin polymer film on anode surface while battery is being charged.
- The polymer film thus provides a lithium-ion battery having not only improved electrochemical performance, but also improved calendar life and safety.
- It is also found that the addition can give improved stability in electrochemical performance in an amount of about 2% to a 0.001% by weight.

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## Summary

- Technology-driven new needs
  - Various kinds of requirement depend on environments.

- Science-driven design and synthesis

***Roles;***
***Identify target materials,Characterize virtually,***
***Develop and optimize synthesis routes.***

- Who should do it?

~~Electrochemists, Materials scientist, University, Institute,~~ etc.

*Multidisciplinary !!*

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