고출력 리튬이차전지용 양극재료

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2004년 11월 5일

한양대학교

선양국 교수

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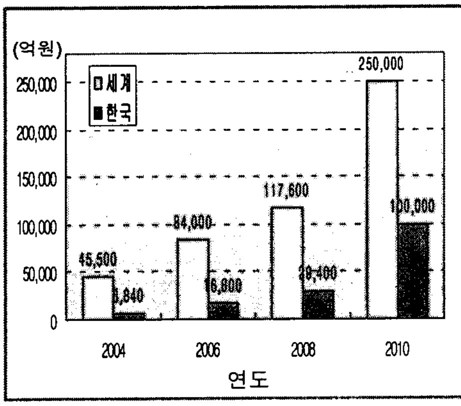
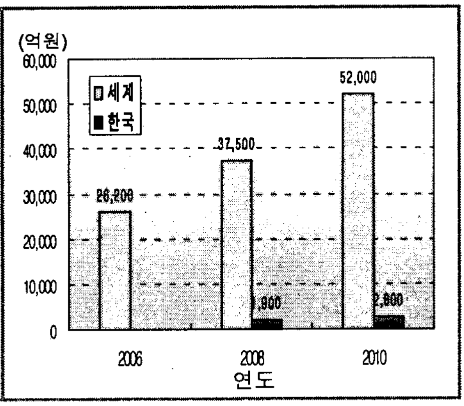
2차 전지산업의 시장 전망

❑ 소형 전지



❑ HEV 전지



ㅇ 출처
▪ 2004,2006년 Yano Report 참조

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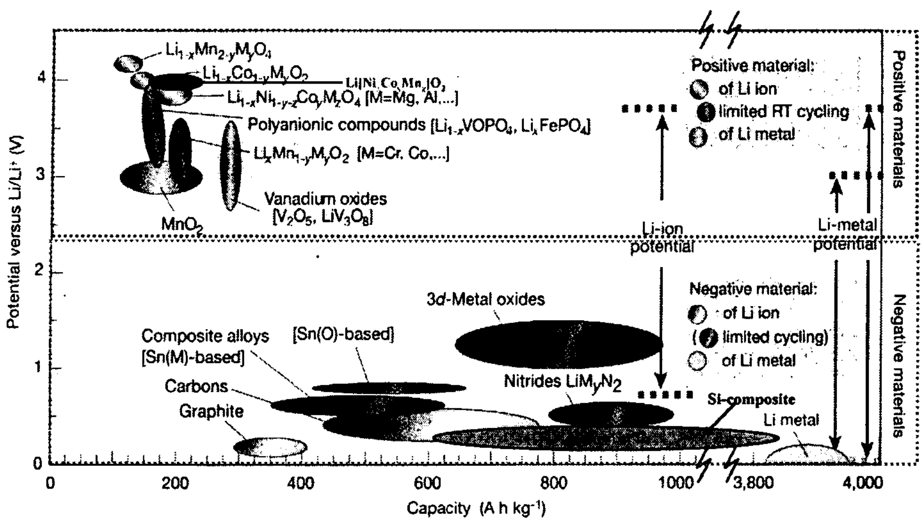
Materials for Lithium Secondary Batteries



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Positive Materials for Lithium Secondary Batteries

	$LiCoO_2$	$LiNiO_2$	$LiMn_2O_4$	$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$	$Li[Ni_{1/2}Mn_{1/2}]O_2$	$LiFePO_4$
Structure	Layered	Layered	Spinel	Layered	Layered	Olivine
Theoretical capacity	274 mAh/g	275 mAh/g	148 mAh/g	285 mAh/g	285 mAh/g	170 mAh/g
Available Capacity	145 mAh/g	1850 mAh/g	120 mAh/g	170 mAh/g	170 mAh/g	150 mAh/g
Voltage	3.7 V	3.6 V	3.8 V	3.7 V	3.7 V	3.4 5V
Advantage	-High conductivity - Easy synthesis	- High capacity - Stability of electrolyte	-Low price -Non-toxic	-High capacity -Low price -Good thermal stability	-High capacity -Low price -Good thermal stability	-Lowest Price -Environment friend
Disadvantage	-High cost -Toxic	-Difficult synthesis -Thermal instability	-Capacity fading @ High Temp	-Lower Tap density compared to $LiCoO_2$	-Low conductivity	-Lowest Conductivity

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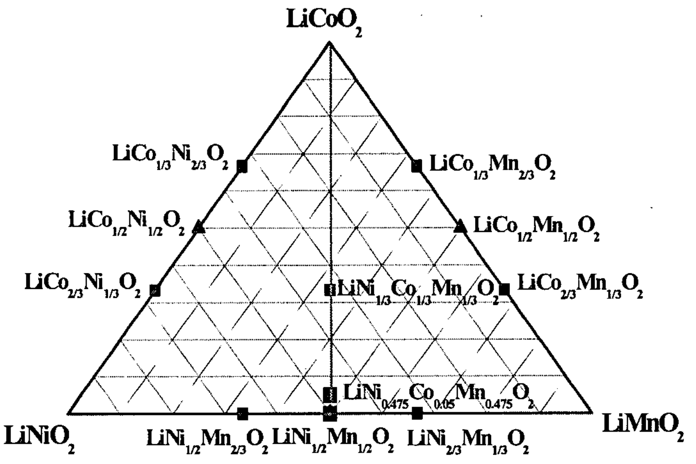
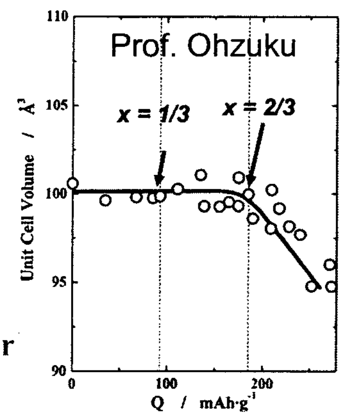
New Layered Oxide $Li[Ni_xCo_yMn_z]O_2$

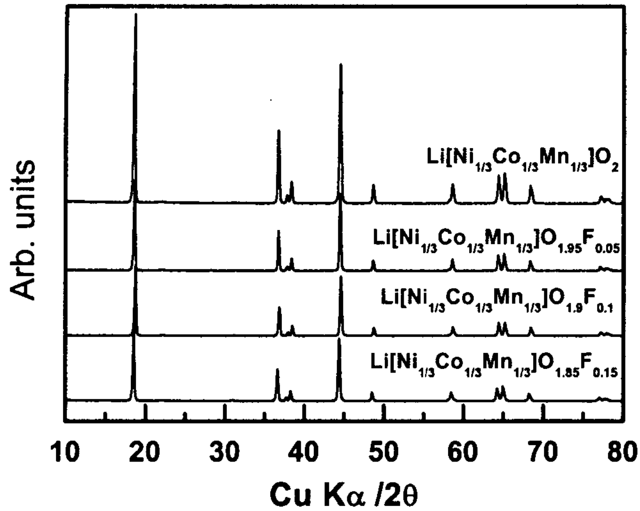


New Layered Oxide $Li[Ni_xCo_{1-2x}Mn_x]O_2$

- Ni, Co, and Mn are combined in the lithiated oxide, Ni is 2+, Co is 3+, and Mn is 4+.
- Inactive Mn^{4+} plays a major role in the stability of the materials during charge/discharge process.
- Ni^{2+} provides a two-electron redox center which oxidizes to Ni^{4+} on charge.
- Co^{3+} is oxidized to Co^{4+} during charging process.



F-doped $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$



Increase of lattice constant of *a* and *c*

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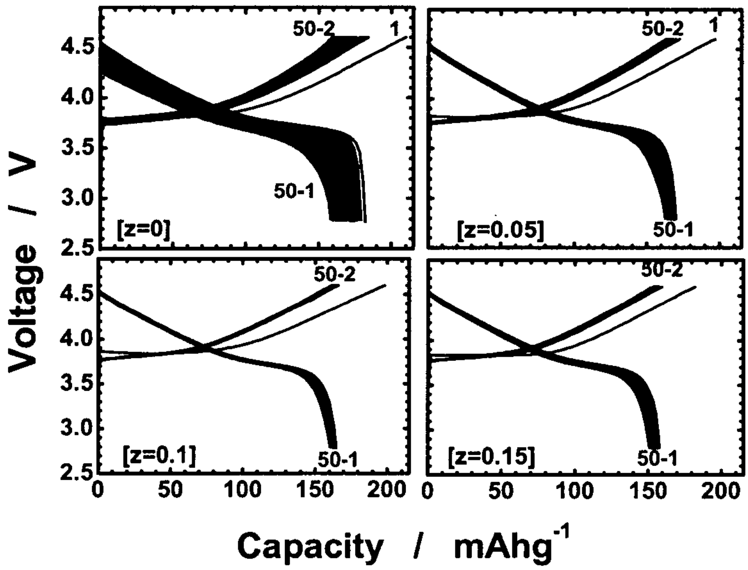
Charge and discharge curves of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-z}F_z$



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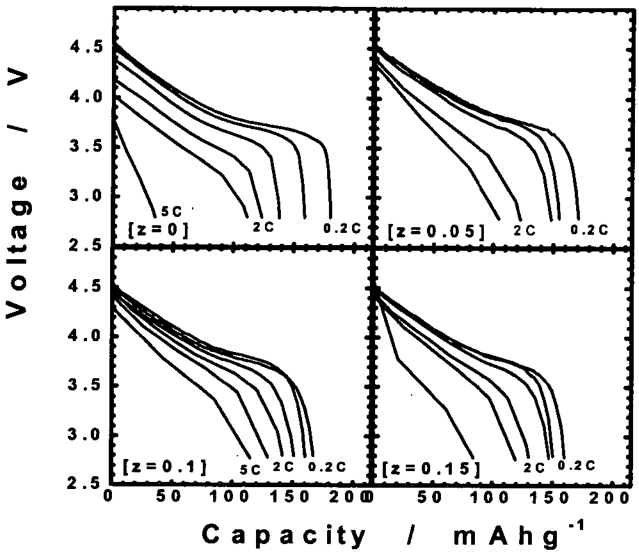
Rate Capability of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-z}F_z$



	0.2 C	2C	5C
Z=0	180	123 (68%)	35 (19%)
Z=0.05	170	122 (72%)	100 (59%)
Z=0.1	167	141 (84%)	114 (68%)
Z=0.15	160	130 (81%)	83 (52%)

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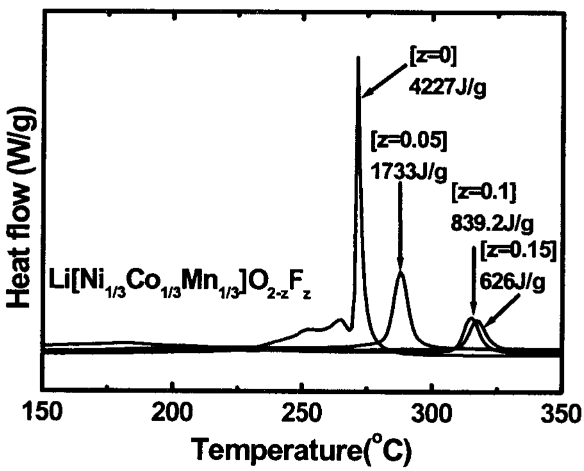
DSC of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-z}F_z$



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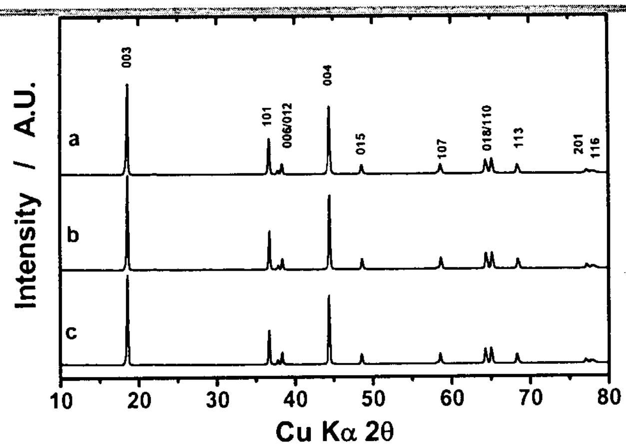
F-doped Layered Material $Li[Ni_{1/3}Co_{1/3}Mn_{(1/3-x)}Mg_x]O_{2-y}F_y$



$Mg_xO_{2-y}F_y$	*a* / Å	*c* / Å	*c*/3*a*	Volume / Å³	M in Li layer	*Rwp* / %
x = 0.00, y = 0.00	2.858	14.223	1.659	100.612	0.018(4)	11.4
x = 0.04, y = 0.00	2.864	14.252	1.659	101.233	0.011(3)	8.66
x = 0.04, y = 0.04	2.863	14.247	1.659	101.131	0.010(3)	8.94

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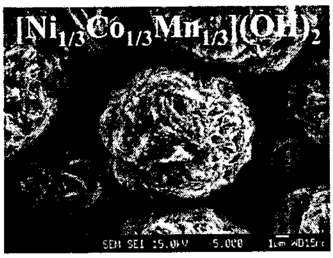
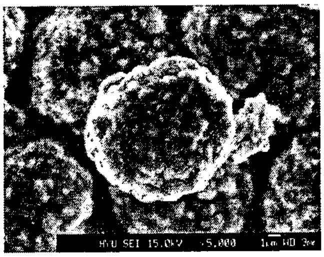
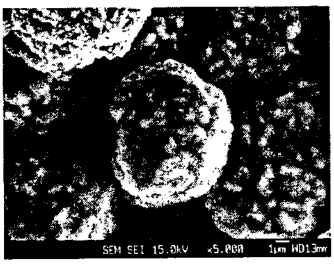
SEM Images of $Li[Ni_{1/3}Co_{1/3}Mn_{(1/3-x)}Mg_x]O_{2-y}F_y$





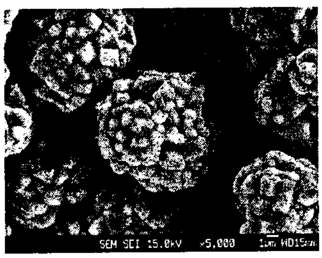
x=0

y=0



x=0.04

y=0



x=0.04

y=0.08

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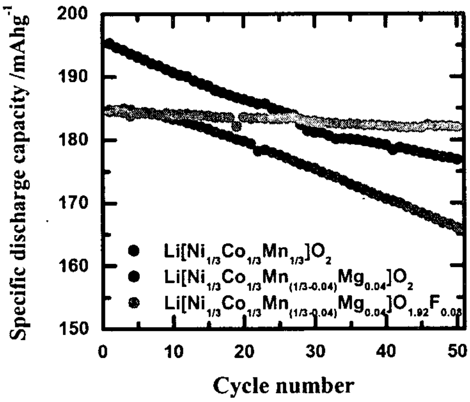
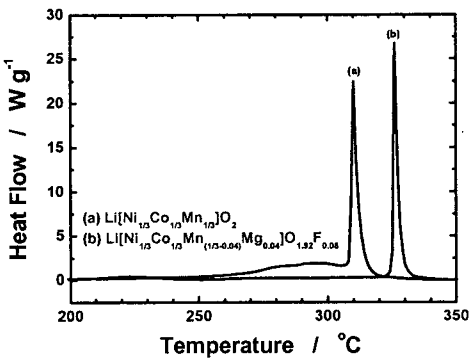
Cycleability and Thermal Stability of $Li/Li[Ni_{1/3}Co_{1/3}Mn_{(1/3-x)}Mg_x]O_{2-y}F_y$





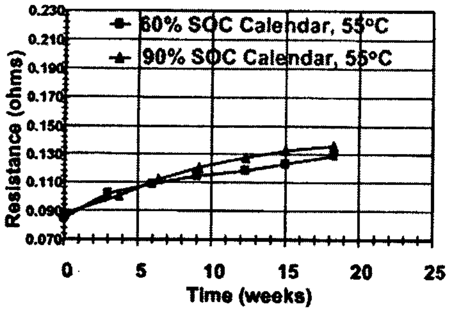
Layered $Li_{1+x}[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ as Cathode for HEV Batteries

Advantages:

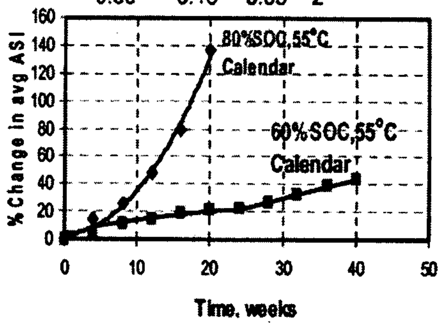
- Has a low cost compared with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes because of the very low cost of processing
- If the material is charged to 4.2V, a significant decrease in the thermal reactivity is anticipated due to very low Ni-content in the system (only small amount of Ni is oxidized to Ni^{4+})
- Operating below 4.2V will result in a significant improvement in calendar life due to a very low Ni^{4+} content in the system

Result of Calendar Life Life Test at 55°C of 18560 cells

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



$LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$/ carbon



$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ shows much better calendar life characteristics than $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ Cells both at 60% and 90%SOC

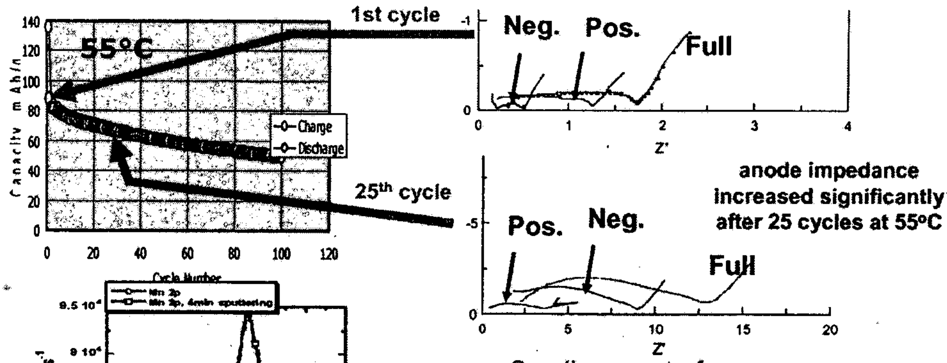
Why spinel is very attractive for the HEV battery

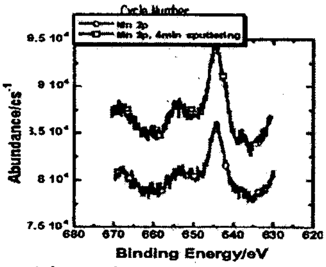
- Very low cost
- Much safer than nickel oxide system
- Could provide long calendar life (Mn^{4+} is a more stable ion than Ni^{4+})
- Excellent rate capabilities
- 6-8 Ah battery based on spinel could provide same power as 12-16 Ah battery based on nickel system (significant cost reduction at the cell chemistry level)

Materials Cost: $415	Materials Cost: $238 **(- 43%)**
$LiNi_{0.8}Co_{15}Al_{0.05}O_2$ Cell capacity 16Ah	$Li_{1+X}Mn_{2-X}O_2$ Cell capacity : 8.5Ah

Material cost for spinel and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ system based on ANL cost modeling

Issue of spinel/carbon system during cycling at 55°C





Mn-metal was observed at the carbon surface bv XPS

Small amount of manganese dissolution (5ppm) was reduced at the carbon and played a catalytic role in forming a film at the carbon surface that leads to interfacial impedance increase at the carbon

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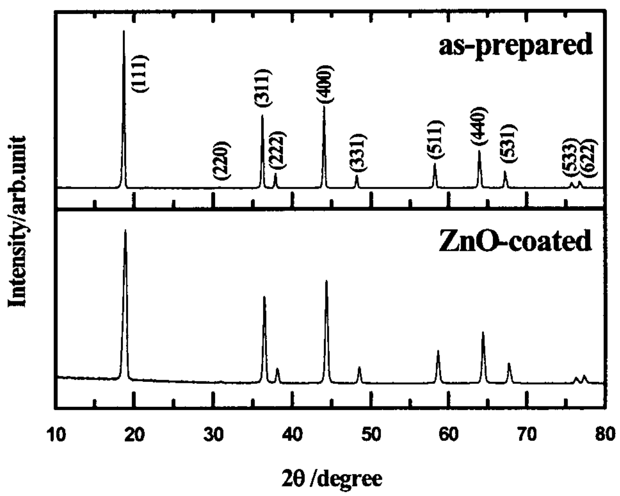
ZnO-coated Spinel $LiMn_2O_4$ (XRD)



a = 8.2318 Å

for both electrodes

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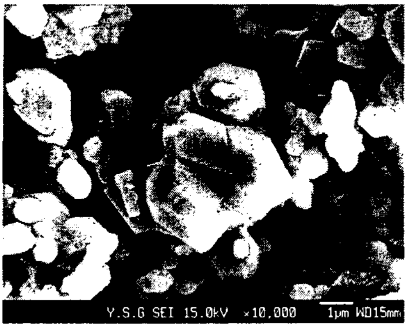
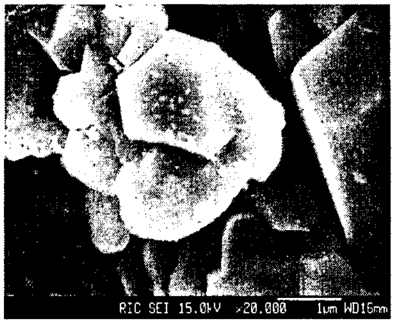
SEM of as-prepared and ZnO-coated $LiMn_2O_4$

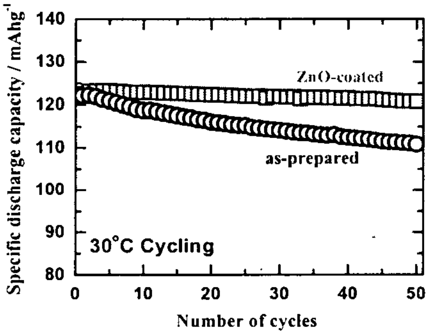


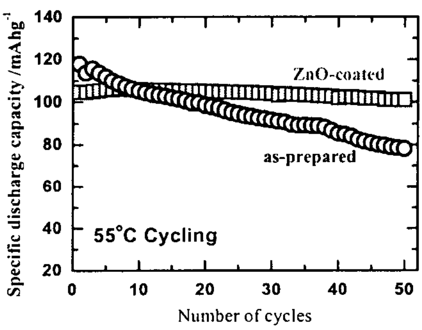
As-prepared



ZnO-coated

Cycling behavior at 30 and 55°C





Capacity retention

100% for ZnO-coated

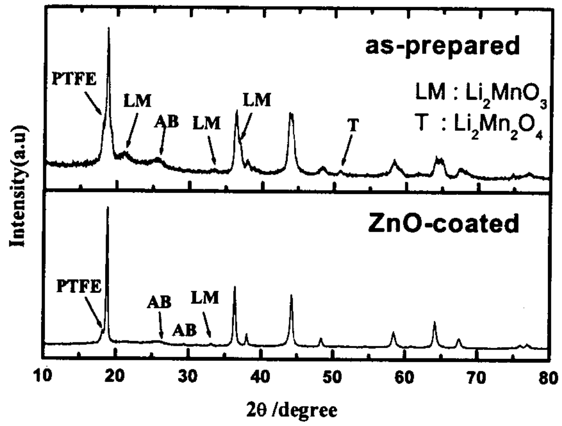
90% for as-prepared

Capacity retention

97% for ZnO-coated

57% for as-prepared

XRD after cycling at 55°C



Dissolution Mechanism (Y.-K. Sun et al. J. Mat. Chem., 11, 2519(2001))

$LiMn_2O_4 \rightarrow Li_2Mn_2O_4 \rightarrow Li_2MnO_3 + MnO$

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HF contents in the 1 M LiPF6 in EC/DMC (1:1) after treated various samples for 1 week at 30 and 55℃

Temperature(℃)	Samples	Residual HF(ppm)
30	Bulk electrolyte (1M $LiPF_6$ in EC/DMC)	80
	As-prepared $LiMn_2O_4$ powders	80
	2wt% ZnO-coated $LiMn_2O_4$ powders	49
	Only ZnO powders	0
55	Bulk electrolyte (1M $LiPF_6$ in EC/DMC)	123
	As-prepared $LiMn_2O_4$ powders	123
	2wt% ZnO-coated $LiMn_2O_4$ powders	66
	Only ZnO powders	0

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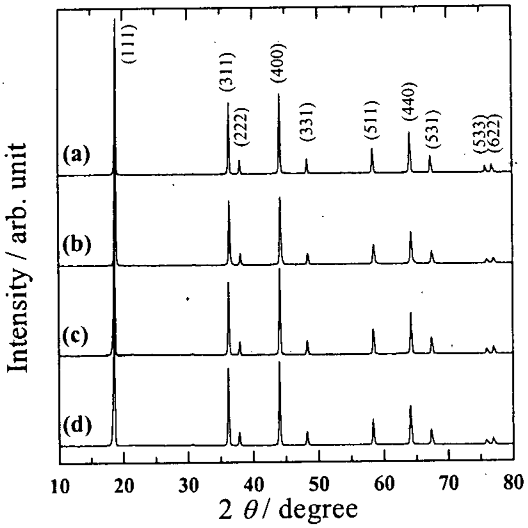
F-doped Spinel (XRD)



$Li[Li_xAl_yMn_{2-x-y}]O_{4-z}F_z$

(a) x = 0, y = 0, z = 0,

(b) x = 0, y = 0.1, z = 0,

(c) x = 0.05, y = 0.1, z = 0,

(d) x = 0.05, y = 0.1, z = 0.2.

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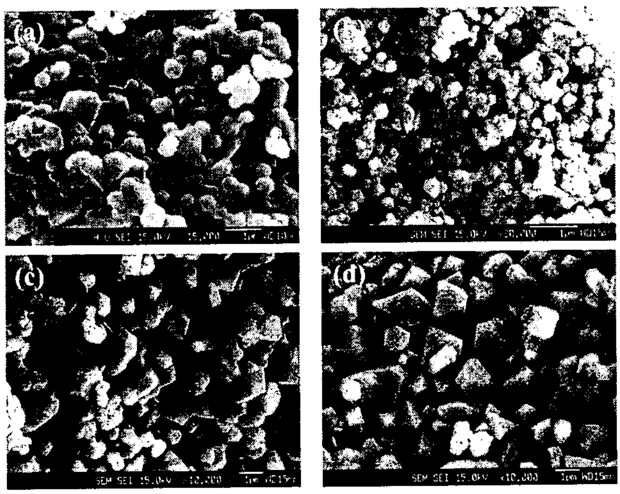
SEM Image of $Li[Li_xAl_yMn_{2-x-y}]O_{4-z}F_z$



(a) x = 0, y = 0, z = 0

(b) x = 0, y = 0.1, z = 0

(c) x = 0.05, y = 0.1, z = 0

(d) x = 0.05, y = 0.1, z = 0.1

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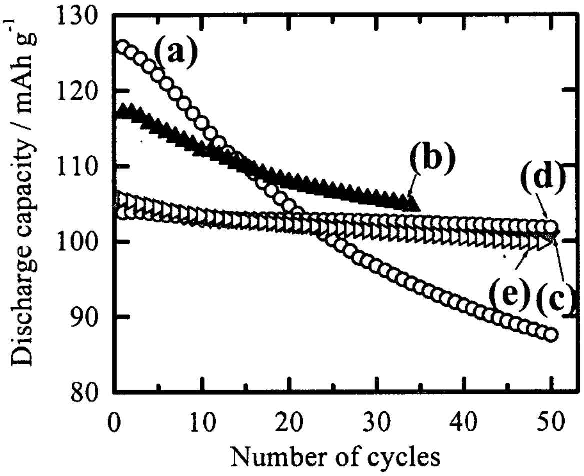
Cycleability of $Li[Li_xAl_yMn_{2-x-y}]O_{4-z}F_z$



$Li[Li_xAl_yMn_{2-x-y}]O_{4-z}F_z$

(a) x = 0, y = 0, z = 0

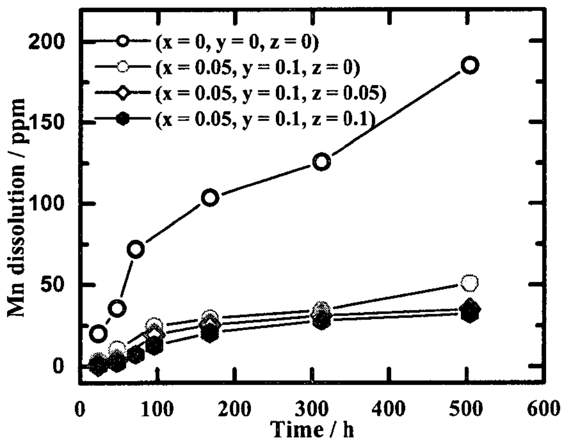
(b) x = 0, y = 0.1, z = 0

(c) x = 0.05, y = 0.1, z = 0

(d) x = 0.05, y = 0.1, z = 0.1

(e) x = 0.05, y = 0.1, z = 0.2

Mn dissolution for $Li[Li_xAl_yMn_{2-x-y}]O_{4-z}F_z$



전망

❖ 소형전지

- $Li[Ni_xCo_{1-2x}Mn_x]O_2$ with high tap density
- Mixture of $LiCoO_2$ and $Li[Ni_xCo_{1-2x}Mn_x]O_2$

❖ HEV

- $Li[Ni_xCo_{1-2x}Mn_x]O_2$ with high rate capability
- Mixture of $LiMn_2O_4$ compound and $Li[Ni_xCo_{1-2x}Mn_x]O_2$
- $LiMn_2O_4$ compounds having no Mn dissolution @ >60°C

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