전 고상박막전지의 개발 및 응용

남 상 철 연구소장

(㈜ 누리셀 마이크로셀 센터)

전 고상박막전지의 개발 및 응용

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㈜ 누리셀 마이크로셀 센터

남상철, 박호영

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What is Thin Film Battery?

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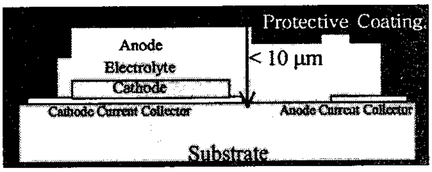
- ***All solid state*** **components**
- ***Thin film*** **fabrication of all battery components**



Schematic cross section

Advantages

- possible to make flexible & nude
- variety of shapes and size
- absence of possible pollution
- thermal stability (wide working temp.)
- low self-discharge
- easy to mass-production
- combine with imbedded devices
- Good cyclability

Disadvantages

- The current densities are limited because of the high internal resistance
- Low ionic conductivity of the electrolyte
- Low capacity because of small mass of active materials

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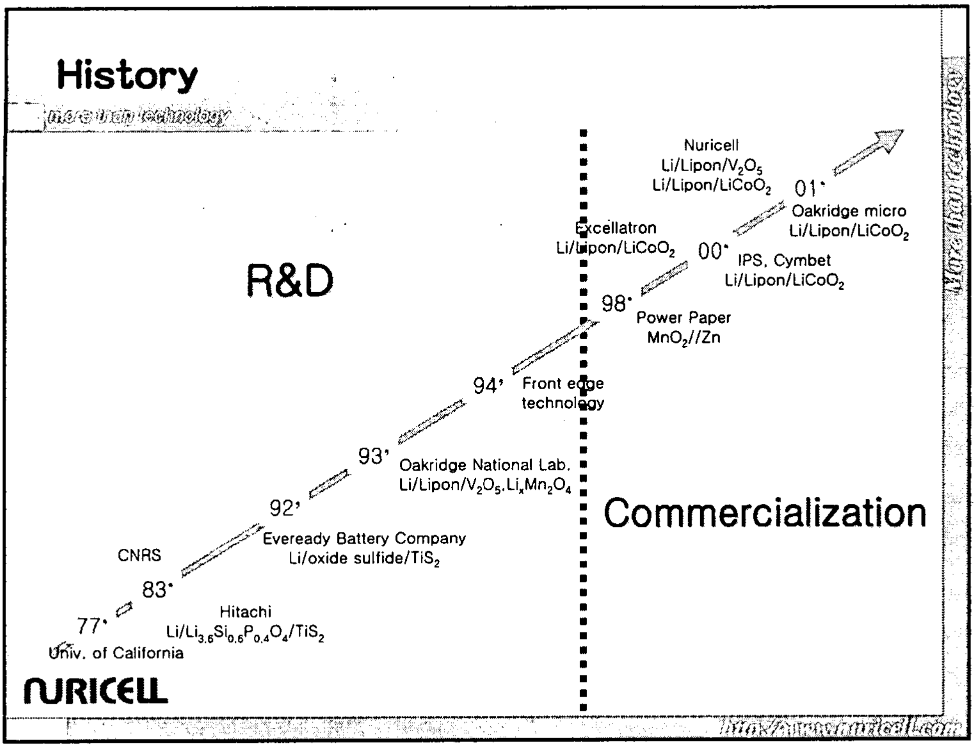
History
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R&D
Commercialization
77' Univ. of California
83' Hitachi
Li/$Li_{3.6}Si_{0.6}P_{0.4}O_4$/$TiS_2$
CNRS
92' Eveready Battery Company
Li/oxide sulfide/TiS_2
93' Oakridge National Lab.
Li/Lipon/V_2O_5,$Li_xMn_2O_4$
94' Front edge technology
98' Power Paper
MnO_2//Zn
Excellatron
Li/Lipon/$LiCoO_2$
00' IPS, Cymbet
Li/Lipon/$LiCoO_2$
01' Oakridge micro
Li/Lipon/$LiCoO_2$
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Li/Lipon/V_2O_5
Li/Lipon/$LiCoO_2$
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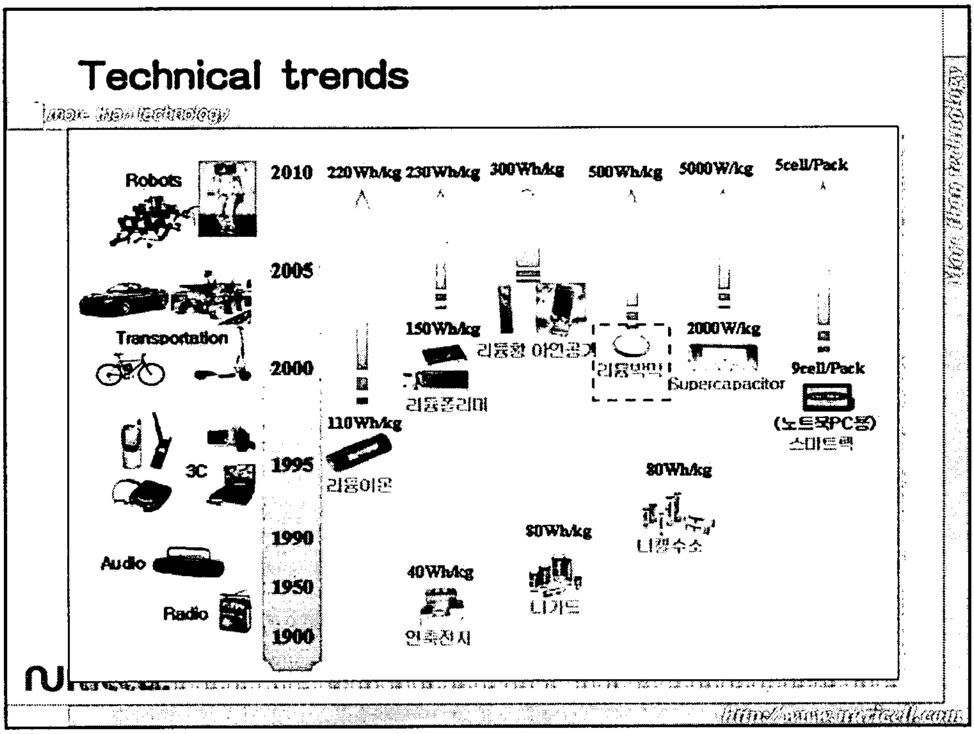
Technical trends
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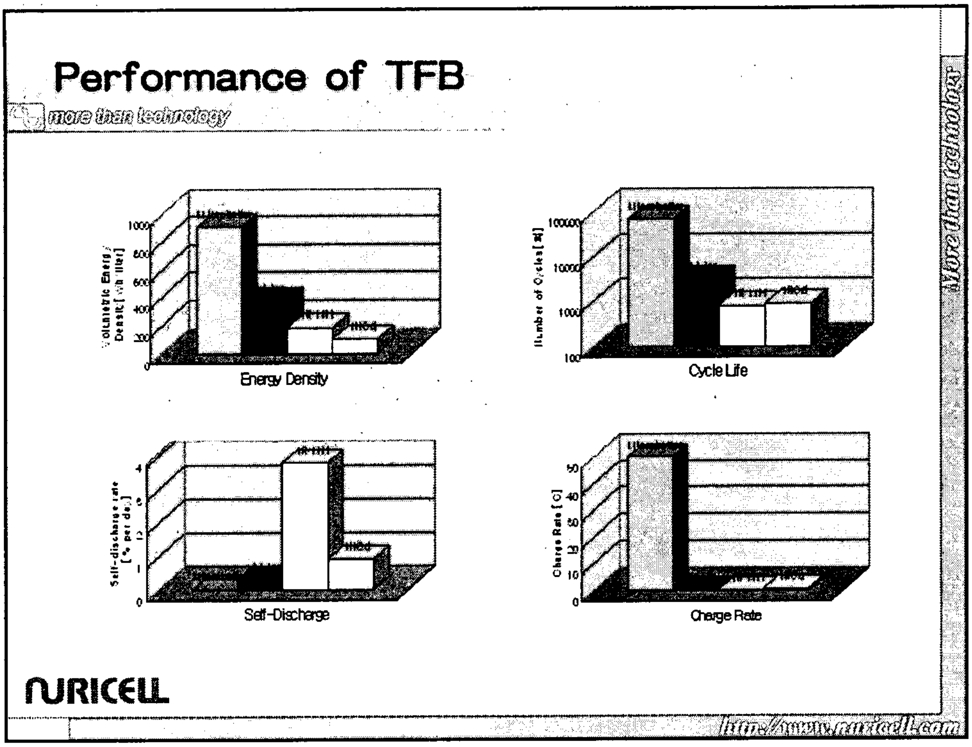
Robots
Transportation
3C
Audio
Radio
2010
2005
2000
1995
1990
1950
1900
220Wh/kg
230Wh/kg
300Wh/kg
500Wh/kg
5000W/kg
5cell/Pack
150Wh/kg
2000W/kg
Supercapacitor
9cell/Pack
(노트북PC용)
110Wh/kg
리튬이온
리튬폴리머
80Wh/kg
니켈수소
50Wh/kg
니카드
40Wh/kg
연축전지


Performance of TFB
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Energy Density
Cycle Life
Self-Discharge
Charge Rate
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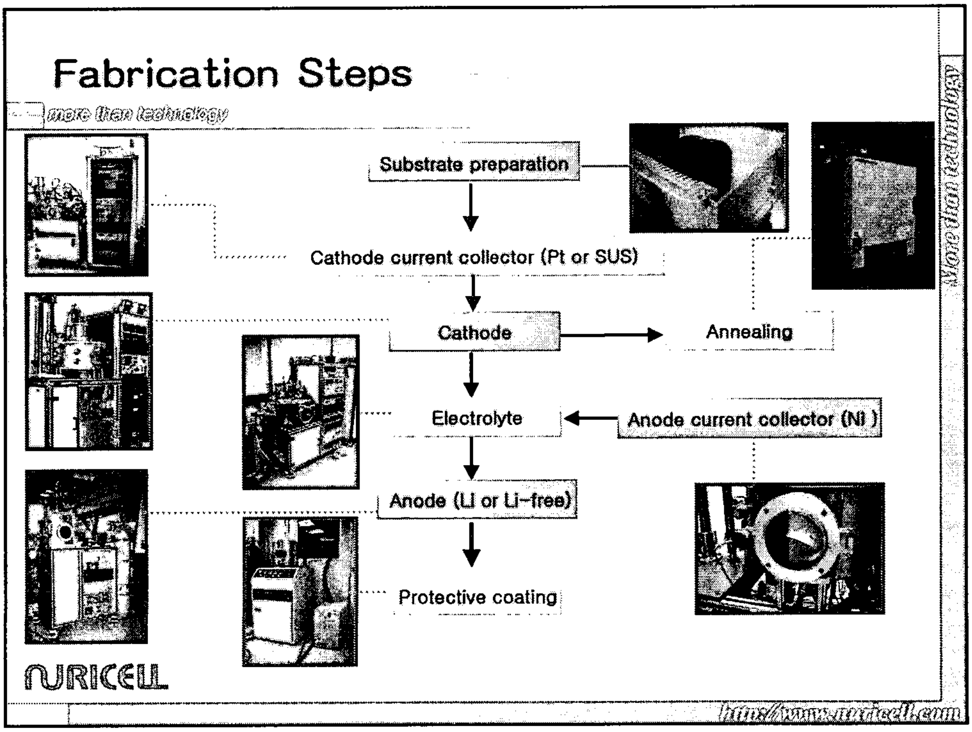
Fabrication Steps
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Substrate preparation
Cathode current collector (Pt or SUS)
Cathode
Annealing
Electrolyte
Anode current collector (Ni)
Anode (Li or Li-free)
Protective coating
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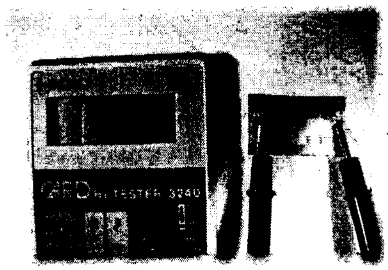
Prototype



- Prototype of Nuricell Inc. : unit cell on polymer film
- Voltage : 1.5 ~ 3.4 V
- It works a stopwatch for 2 weeks.

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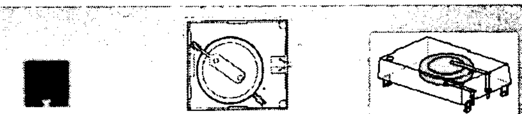
Comparison with other batteries



Parameter	Cymbet (0.25 cm^2, on silicon)	Dallas/Maxim (PowerCap)	STMicroelectronics (SNAPHAT)
Charge Capacity	90 μAh (x 10,000 cycles)	130mAh (not rechargeable)	130 mAh (not rechargeable)
Thickness (mils)	2	215	385
Price (each, in volume)	$ 0.25	$ 3.43	$ 3.55
Integration	In IC package	External circuit board	Snap-on package
Operating Temperature	-40 to +150°C	0 to +70°C	-40 to +85°C

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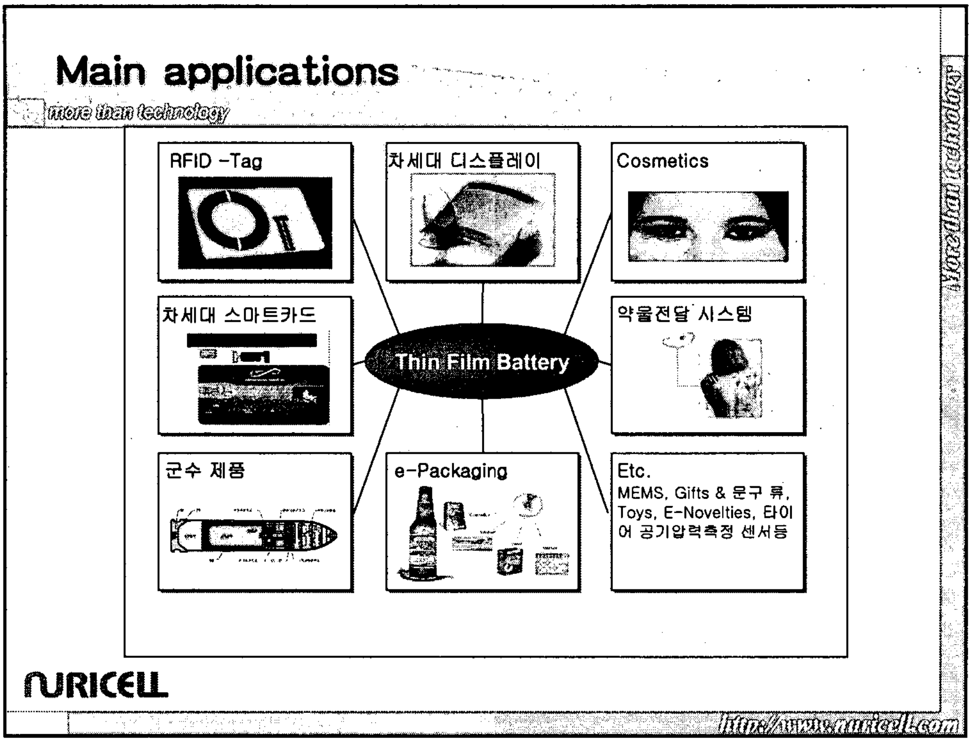

Main applications
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RFID -Tag
차세대 디스플레이
Cosmetics
차세대 스마트카드
Thin Film Battery
약물전달 시스템
군수 제품
e-Packaging
Etc.
MEMS, Gifts & 문구 류,
Toys, E-Novelties, 타이
어 공기압력측정 센서등
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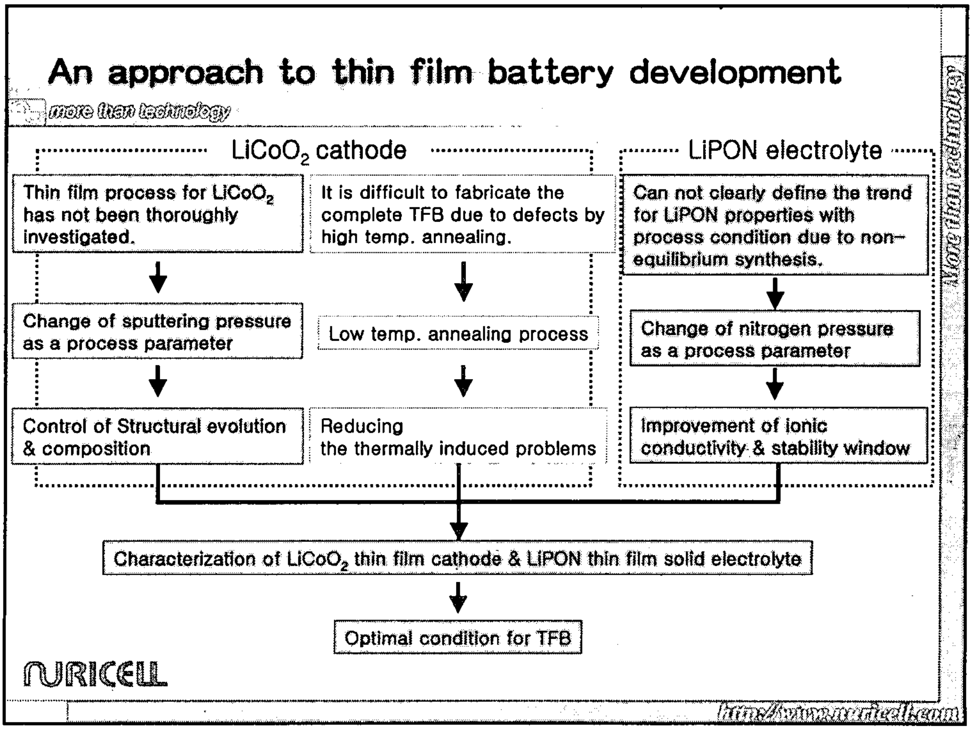

An approach to thin film battery development
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LiCoO2 cathode
LiPON electrolyte
Thin film process for LiCoO2 has not been thoroughly investigated.
It is difficult to fabricate the complete TFB due to defects by high temp. annealing.
Can not clearly define the trend for LiPON properties with process condition due to non-equilibrium synthesis.
Change of sputtering pressure as a process parameter
Low temp. annealing process
Change of nitrogen pressure as a process parameter
Control of Structural evolution & composition
Reducing the thermally induced problems
Improvement of ionic conductivity & stability window
Characterization of LiCoO2 thin film cathode & LiPON thin film solid electrolyte
Optimal condition for TFB
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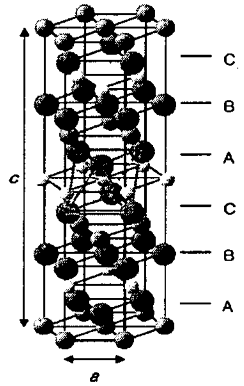
Basic properties of $LiCoO_2$ cathode



Li : 3b
Co : 3a
O : 6c

a = 2.816 Å
c = 14.051 Å

1. Reaction :

$Li_{1-x}CoO_2 + xLi^+ + xe^- = LiCoO_2$
$(0 \le x \le 0.5)$

Practical capacity : 137 mAh/g

Open circuit voltage : 4.1 V (vs. Li / Li^+)

2. Crystal Structure :

Layered metal oxide with O3 type (α-$NaFeO_2$)

Space group R-3m

Oxygen stacking sequence of ABCABC……

Consist of edge-shared oxygen octahedron

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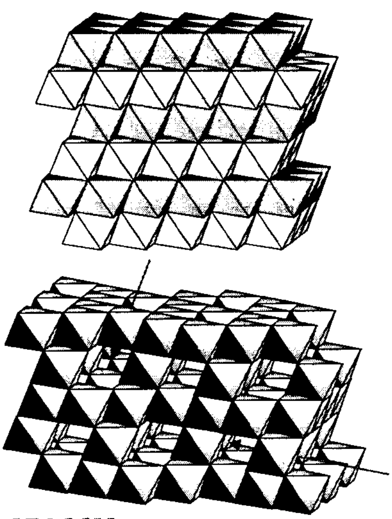
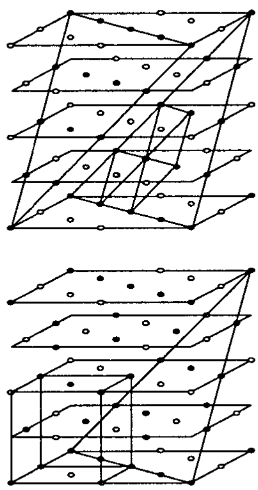
Crystal structure of $LiCoO_2$ cathode





Layered structure
of
Hexagonal symmetry
($R\bar{3}m$)
HT-$LiCoO_2$

○ Li
● Co

Spinel structure
of
Cubic symmetry
(Fd3m)
LT-$LiCoO_2$

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Defects induced by HT-annealing at 650℃

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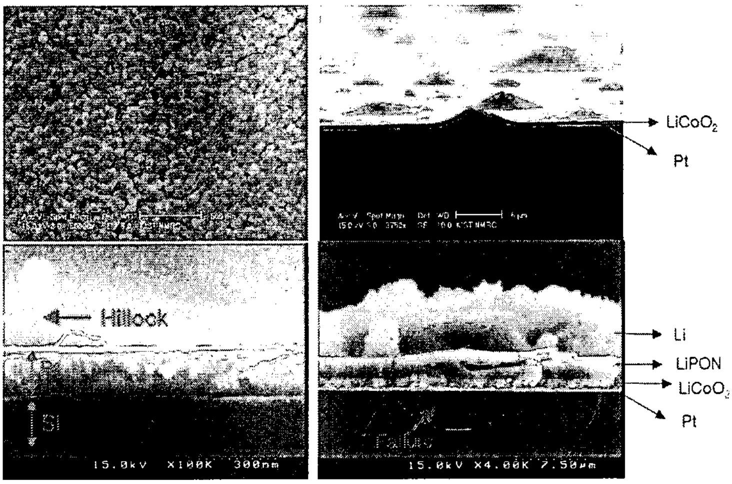
Annealing to crystallize $LiCoO_2$ cathode → Thermal Budget → Stress release → Mass transport → Hillock or Buckling of Pt → Cathode cracking → Cell failure



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SEM & XRD of $LiCoO_2$ thin films

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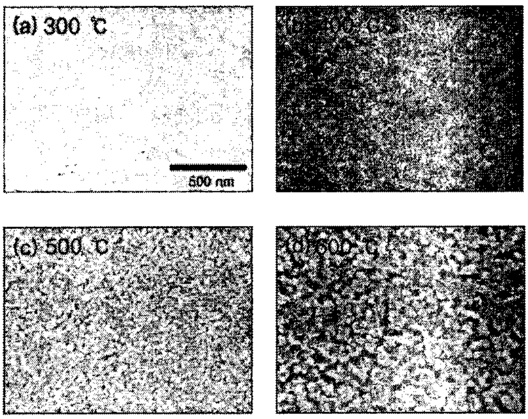
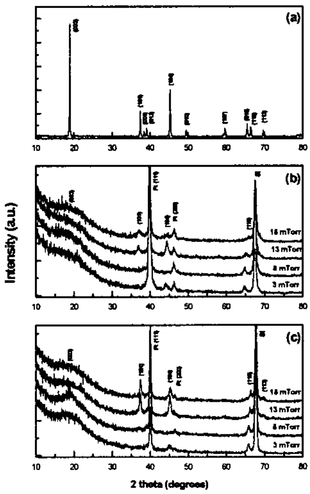


In-situ annealing by hot stage SEM



XRD Patterns

(a) Target (b) As-depo (c) 400℃

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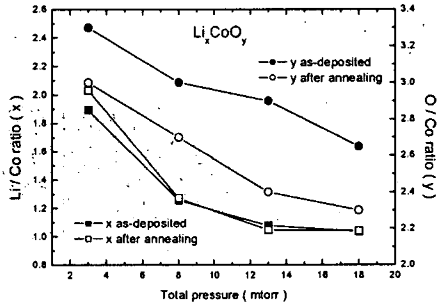
Comparison of compositions

Li : Co ratio by ICP-AES
O : Co ratio by RBS



1. Excess of Li & O, but as pressure↑, Li & O ↓
(∵ re-sputtering of Li at higher pressure, Li ∝ O)

2. Constant Li before & after annealing, but O ↓ after annealing
(∵ corner shared octahedron → edge shared octahedron by grain growth)

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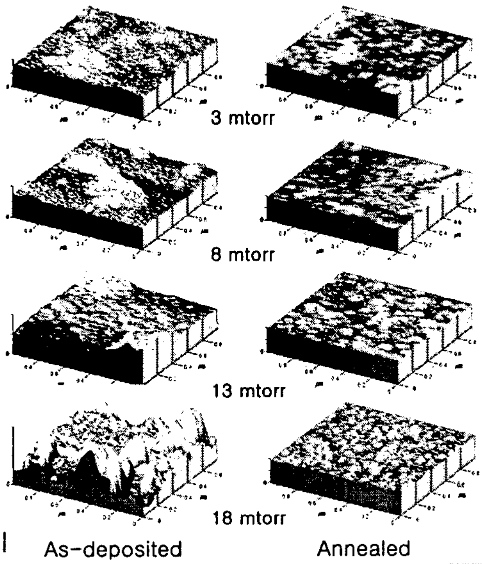
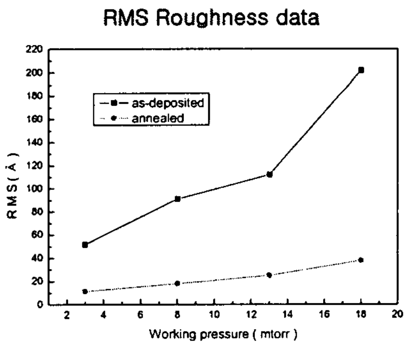
AFM micrograph & Roughness





Electrochemical properties of $LiCoO_2$ thin films

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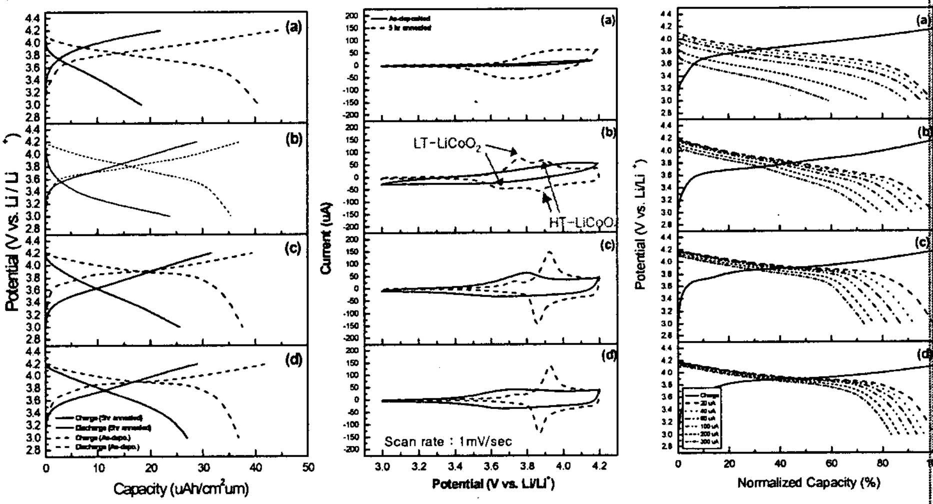

Charge-discharge characteristics | Cyclic Voltammograms | Rate capability

NURICELL Sputtering pressure : (a) 3 mtorr (b) 8 mtorr (c) 13 mtorr (d) 18 mtorr

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Electrolyte (Why LiPON ?)

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Polymer electrolyte

Difficulty to make a thin film

Inorganic crystalline materials

Need heat treatment to make a crystalline structure

Sulfide electrolyte

Environmental problems

LiPON
- **Highly stable at atmospheric condition**
- **Pretty high ionic conductivity(~ 10^{-6} S/cm)**

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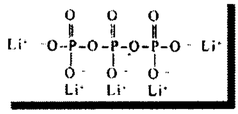
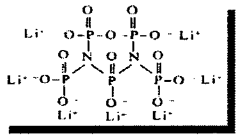
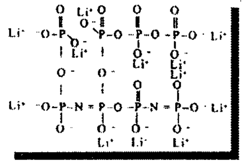
Electrolyte (Mechanism)



The structure of $LiPO_3$ glass [Substitution of O with N]



Cross linking of >N—



Cross linking of —N=

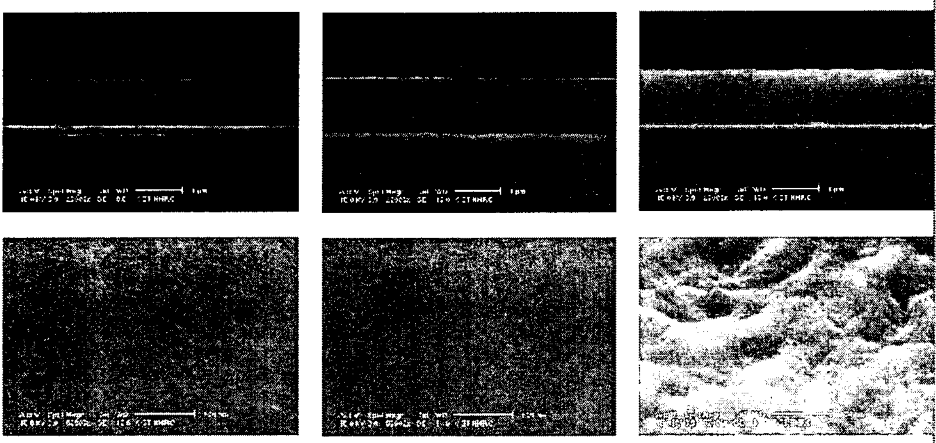
Similar effect with 'mixed former effect'

Decrease of electrostatic energy

Change of P-O bonding to stronger P-N bonding

Ionic conductivity increase

SEM images of LiPON films



(a) 5 mtorr (b) 10 mtorr (c) 20 mtorr

XRD & AFM analysis of LiPON films

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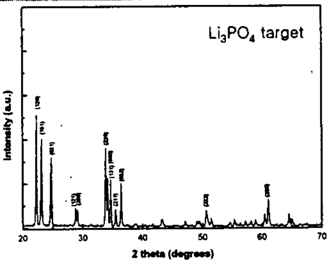
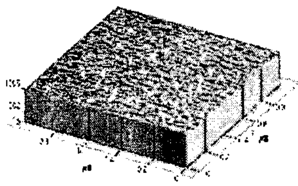
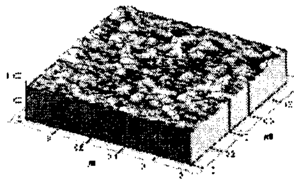
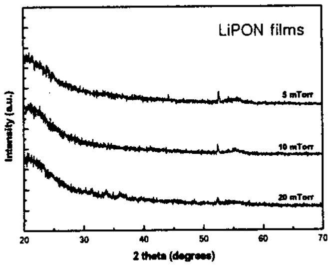


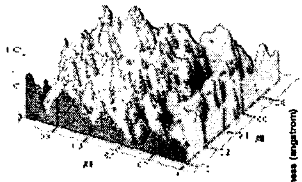


(a) 5 mtorr

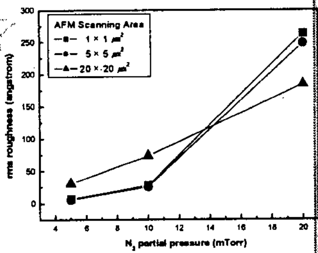


(b) 10 mtorr





(c) 20 mtorr



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EIS analysis of Pt / LiPON / Pt blocking elctrodes

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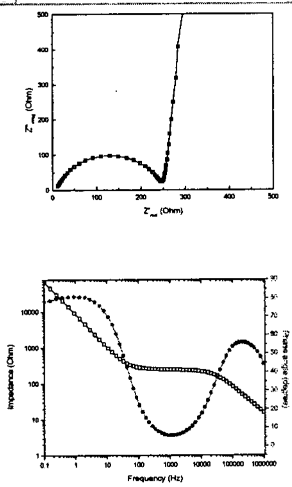
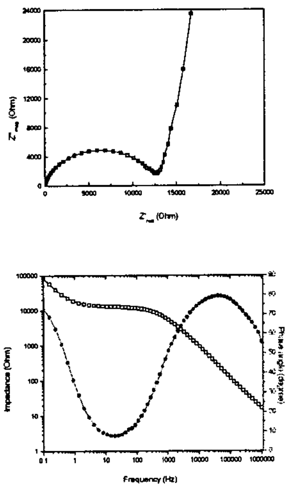
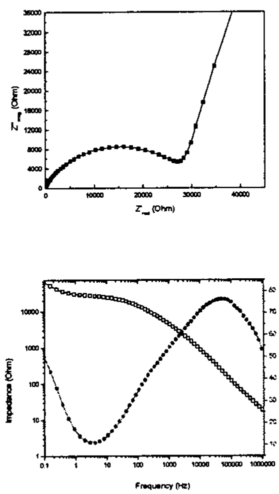


(a) 5 mtorr



(b) 10 mtorr



(c) 20 mtorr

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Properties of LiPON electrolyte with N_2 pressure

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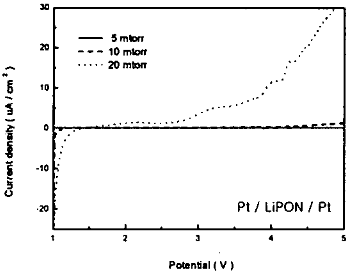
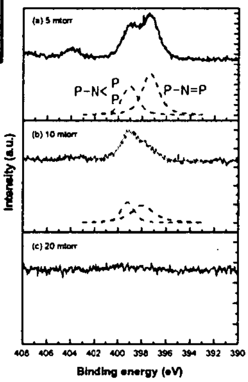
Composition & Ion conductivity

$P(N_2)$	5 mtorr	10 mtorr	20 mtorr
Li / P ratio	2.697	3.056	3.493
σ (S/cm)	8.8×10^{-7}	1.7×10^{-8}	7.2×10^{-9}

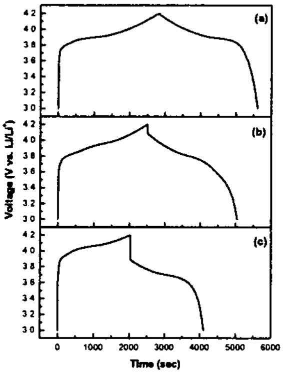
Stability window measured by LSV



N 1s spectrum by XPS analysis



Charge-discharge characteristics of Li / LiPON / $LiCoO_2$ thin film battery



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High power property of complete thin film battery

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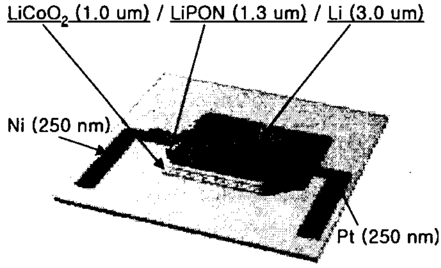
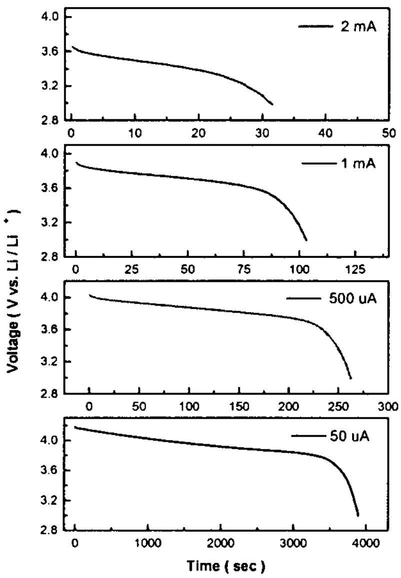


Electrode area : 0.8 × 0.8 cm²

Parallel connection of 2 cells

Unit cell capacity : 66 uAh / cm² um
(~ 97% of theoretical capacity)



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Conclusions

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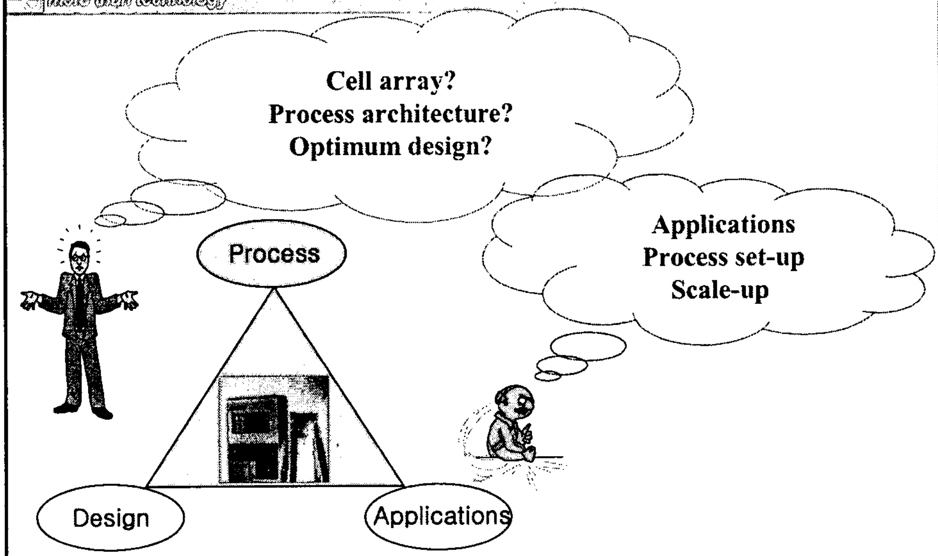

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Foreign activities

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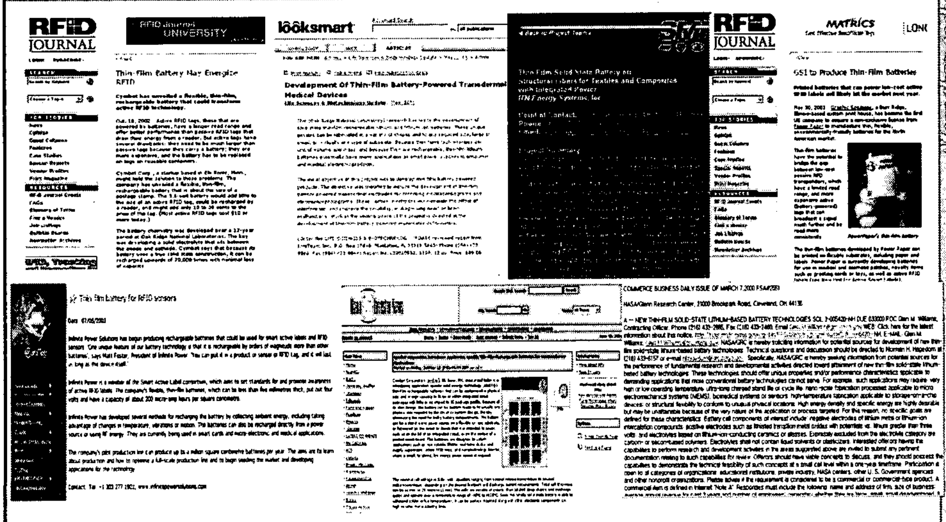

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