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**“ $\mu$  -Thin Film Battery”**

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**조 원 일**

(한국과학기술연구원)



# $\mu$ -Thin Film Battery

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조원일, 윤영수, 남상철\*

나노환경/박막기술, 한국과학기술연구원

\*Microcell Center, (주) 누리셀



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# Introduction

새로운 밀레니엄 시대를 살아가고 있는 오늘, 각 분야별로 전 세계를 휩쓸고 있는 몇가지 현상이 있는데, 과학기술분야에서 나타나고 있는 현상 가운데 하나가 신형 이차전지의 개발 붐을 들 수 있다. 성능 면이나 제조방법에서 좋은 장점을 가지고 있는 Ni-Cd 전지는 환경상의 문제로 인하여 점차 그 자리를 다른 전지에 내어주고 있으며, Ni-MH 전지를 필두로 하여 리튬이온전지, 리튬폴리머전지가 속속 개발되어 상품화되었거나 진행 중에 있다. 이러한 신형 이차전지의 개발러시 현상은 전자 및 반도체분야의 급속한 발전에 기인하며, 특히 셀룰러폰, 노트북 PC, EV(electric vehicle) 등의 개발과 크게 결부되고 있다.

고체상 배터리는 납축전지 또는 Ni-Cd 전지와 같은 기존의 전지에서 나타나는 많은 문제점을 피할 수 있는 매력적인 전지이다. 빠른 이온전도체를 전해질로 하고 인터칼레이션이 가능한 화합물을 양극으로 하면 높은 이론 에너지 밀도를 갖게 할 수 있으며, 특히 높은 셀 전압을 나타내는 알칼리-금속 전극을 사용하면 더욱 높게 된다. 그러나, 이러한 전고상 계에서는, 높은 가역성과 밀접한 관계에 있는, 낮은 계면저항을 갖는 양호한 고체-고체 계면을 유지하기가 매우 어려우며, 이러한 점이 배터리의 동작을 제한하는 변수로 작용한다.

최근 반도체 산업의 고도화 및 미세화 및 미세화에 따라서 이를 기본으로 한 초소형 정밀 기계 부품 소자와 같은 미세 소자의 제작을 위한 마이크로 공정 기술 개발이 세계적으로 급격하게 진행되고 있다. 이러한 마이크로 공정 기술을 이용한 초소형 정밀 기계 부품 소자는 메모리 소자를 주축으로 해오던 반도체 분야에 버금갈 것으로 예상되며, 2000년대의 성장산업으로 미개척 분야인 통시에, 선진국이 독점하고 있는 고부가가치 기술종의 하나이다. 특히 메모리 소자용 반도체 일변의 국내 부품 산업의 다각화와 고 부가가치의 소자 개발 및 생산에 대한 관심이 고조되고 있는 시점에서 마이크로 공정을 이용한 초소형 정밀 기계 부품 소자의 개발은 필수적이다.

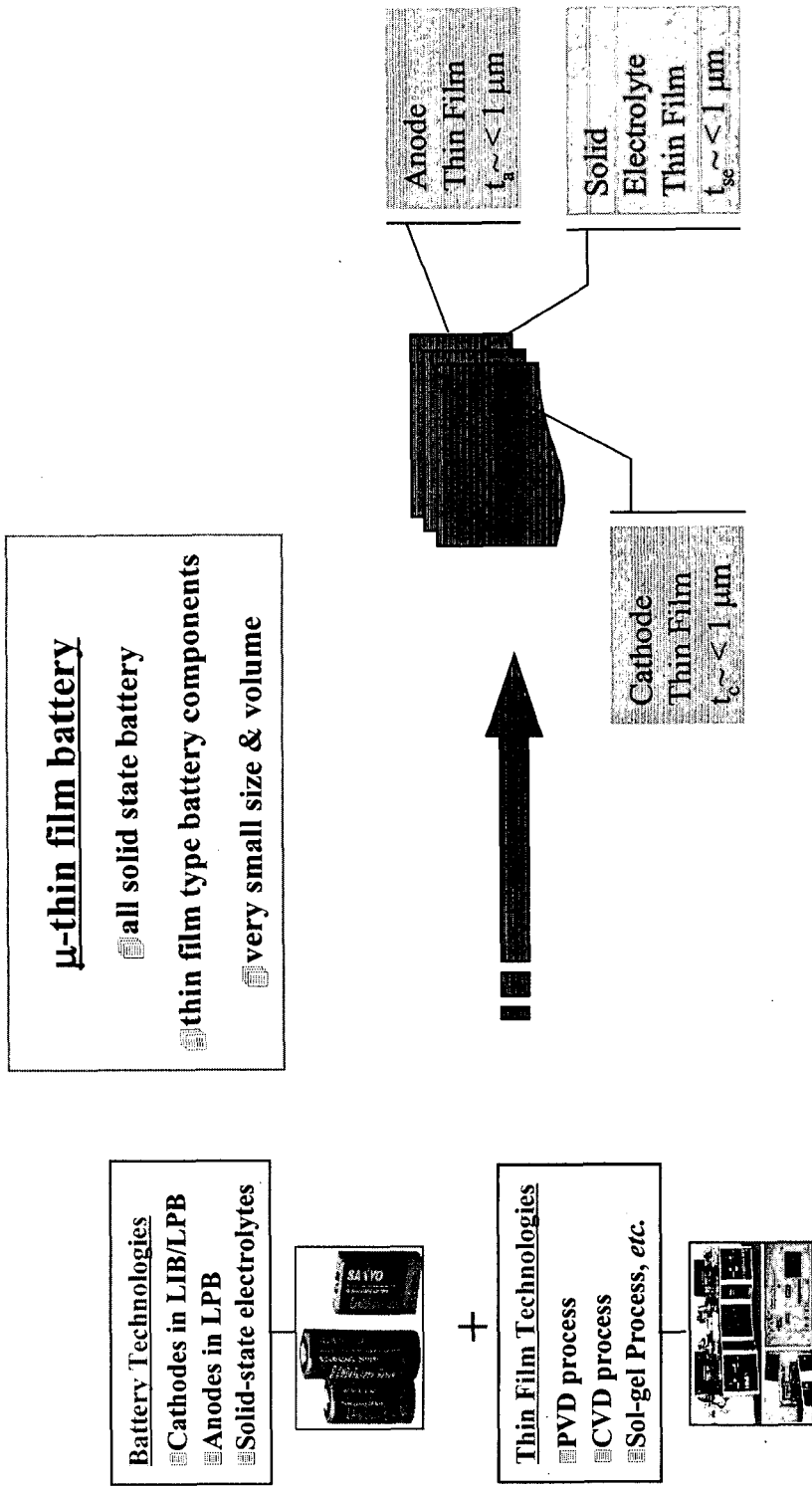


마이크로 공정을 이용한 초소형 정밀 기계는 공정 기술과 재료 기술의 발전에 의하여 더욱 소형화되고 있으며, 특히 기능을 갖는 부분과 이 부분을 제어하는 주변회로의 on-chip화의 요구가 증가되기 시작하였다. 이와 같은 추세에 있어서의 문제점은 초소형 정밀 기계 부품 소자의 구동을 위한 에너지원의 개발이다. 즉, 소자의 크기가 작아진 것에 부합되는 초소형의 전지가 필요하게 된 것이다. 따라서 보다 완전한 초소형 정밀 기계 및 마이크로 소자의 구현을 위하여 마이크로 소자와 혼성(hybrid)되어 이용될 수 있는 고성능 및 초소형의 전지의 개발이 필수적이다.

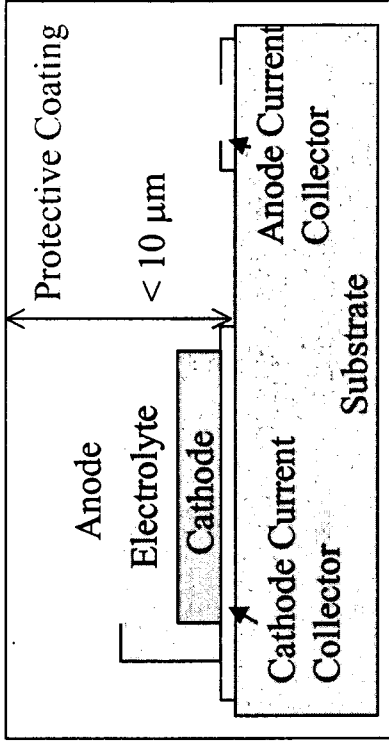
본고에서 다루고자 하는 마이크로 배터리, 또는 박막전지라고 불리는 신형 이차전지는 박막 셀에 의해 구성되며, 기본적인 구조는 일반 이차전지와 동일한데, 요구되는 전지성능에 맞는 유사한 양극과 음극을 사용할 수 있으나 박막 상으로 형성되어야 하므로, PVD(physical vapor deposition), CVD(chemical vapor deposition) 및 졸겔과 같은 박막제조기술을 이용한 박막 제조가능성 여부와 적합한 전해질이 고체상으로서 또한 박막형성이 가능한지의 여부가 마이크로 배터리의 가능성을 부여하게 된다. 본고에서는 이러한 마이크로 배터리의 구성 시스템에 대한 각론과 함께 설계와 종류 및 응용을 다루었다.



# Definition



# Characteristics of $\mu$ -Thin Film Battery



- possible to be miniaturized
- variety of shapes and size
- resistance to shocks
- absence of possible pollution
- thermal stability
- no self-discharge

## Schematic cross section

### **Disadvantages** compared to batteries using a liquid electrolyte

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





# Background

USA	Eveready Battery Company	Cathode : $TiS_2$ (RF sputtering) Electrolyte : $6LiI-4Li_3PO_4-P_2S_5$ (RF sputtering)
	Bellcore	Cathode : $LiMn_2O_4$ (Evaporation) Liquid electrolyte
	Oak Ridge National Laboratory	Cathode : $LiMn_2O_4$ , $LiCoO_2$ , $V_2O_5$ (RF sputtering) Electrolyte : Lipon (RF sputtering) Anode : Li-free, $Sn_3N_4$ , $Zn_3N_2$ (RF sputtering)
Europe	Christian-Albrechts-Univ. (Germany)	Cathode : $LiCoO_2$ , $LiMn_2O_4$ (RF sputtering) Electrolyte : Lipon (RF sputtering)
	Delft Univ. of Technology (Netherlands)	Cathode : $TiS_2$ , $LiMn_2O_4$ , $LiCoO_2$ (CVD, Electrostatic spray deposition) Liquid Electrolyte
	Tokyo Institute of Technology (Japan)	Cathode : $LiCoO_2$ (Soft Solution Processing) Liquid Electrolyte
Asia	KAIST (Korea)	Cathode : $LiMn_2O_4$ (Sol-Gel Method) Liquid Electrolyte
	Seoul National Univ. (Korea)	Cathode : $LiMn_2O_4$ (RF Sputtering) Electrolyte : Lipon (RF Sputtering), PAN
	KIST (Korea)	Cathode : $V_2O_5$ , $LiCoO_2$ , $LiNiO_2$ (DC & RF sputtering) Electrolyte : Lipon (RF sputtering)

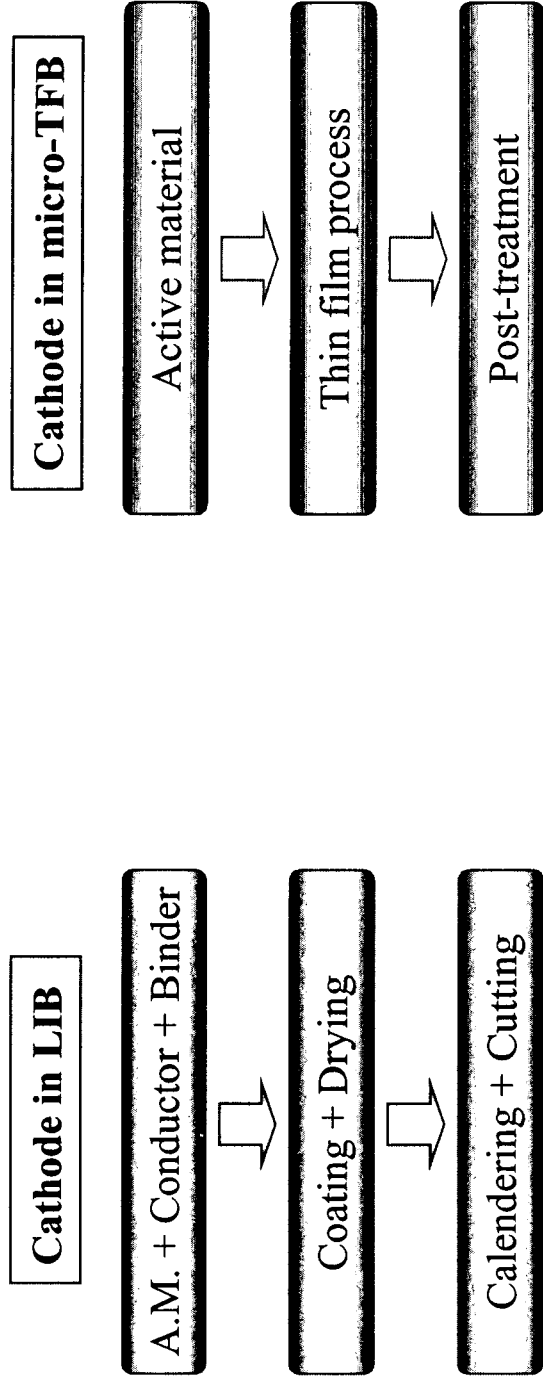


# Cathode-I

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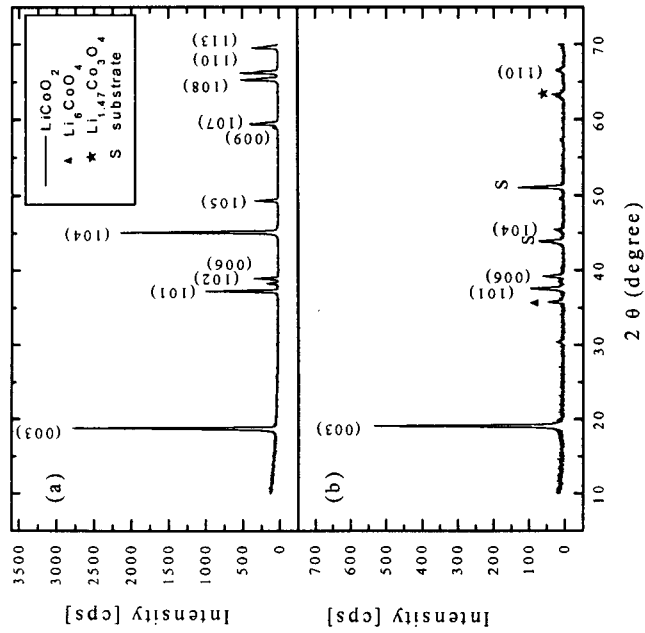
- ◆ Cathode materials ;  
☒  $\text{TiS}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ , *etc.*

- ◆ Fabrication process ;



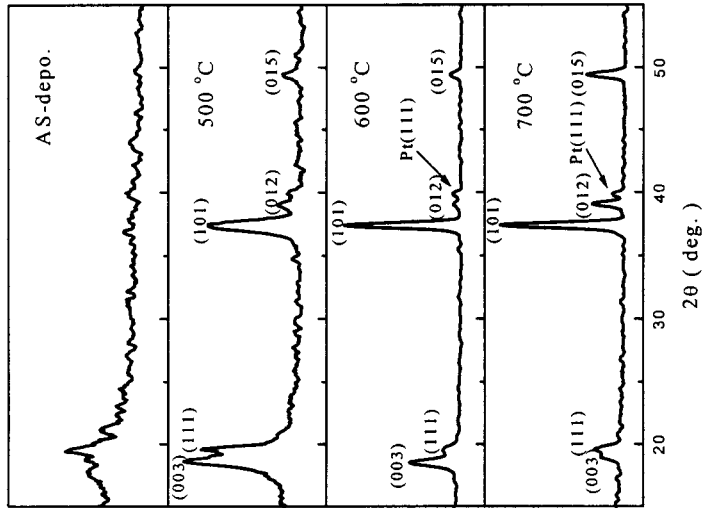
# Cathode-II(LiCoO<sub>2</sub>, crystal structure)

## E-beam evaporated LiCoO<sub>2</sub>



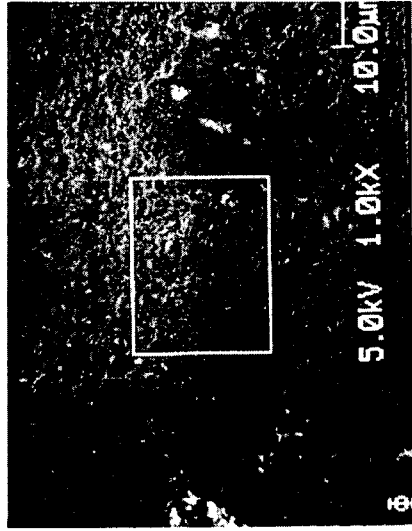
(a) LiCoO<sub>2</sub> powder as a source material (cyprus), (b) LiCoO<sub>2</sub> thin film (t = 1 mm) annealed at 700°C, 10 min

## Sputter coated LiCoO<sub>2</sub>



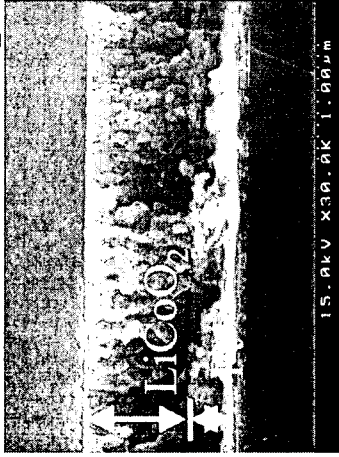
# Cathode-III(LiCoO<sub>2</sub>, surface morphology)

E-beam evaporated LiCoO<sub>2</sub>

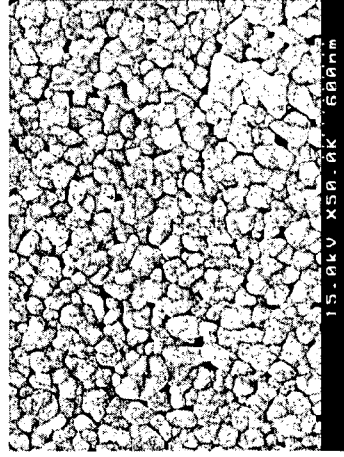


LiCoO<sub>2</sub> thin film (t = 1 μm) annealed at 700°C, 10 min; deposition rate : 1.5 nm/sec

Sputter coated LiCoO<sub>2</sub>



(a) Cross Section View



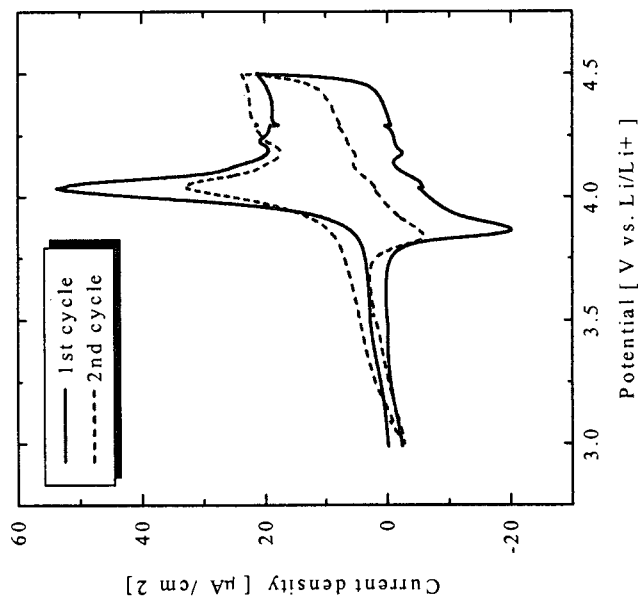
(b) Plane View



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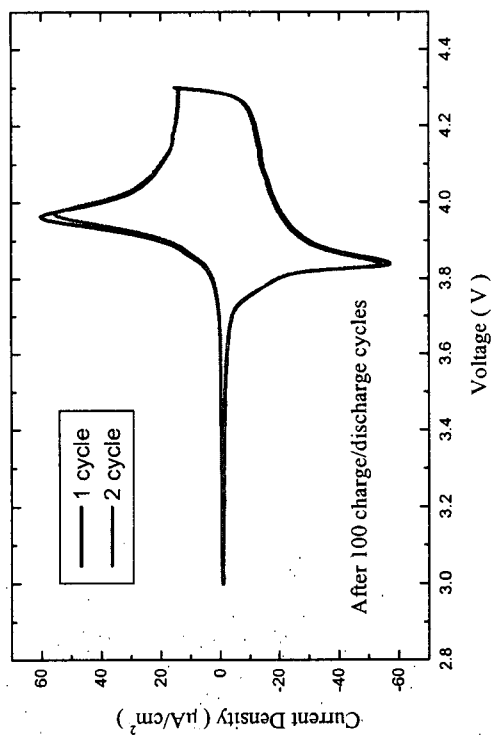
# Cathode-IV(LiCoO<sub>2</sub>, cyclic voltammogram)

E-beam evaporated LiCoO<sub>2</sub>



LiCoO<sub>2</sub> thin film annealed at 700°C, 10 min  
[scan rate : 0.1 mV/s, EC:DMC=1:1 (1M LiPF<sub>6</sub>)]

Sputter coated LiCoO<sub>2</sub>



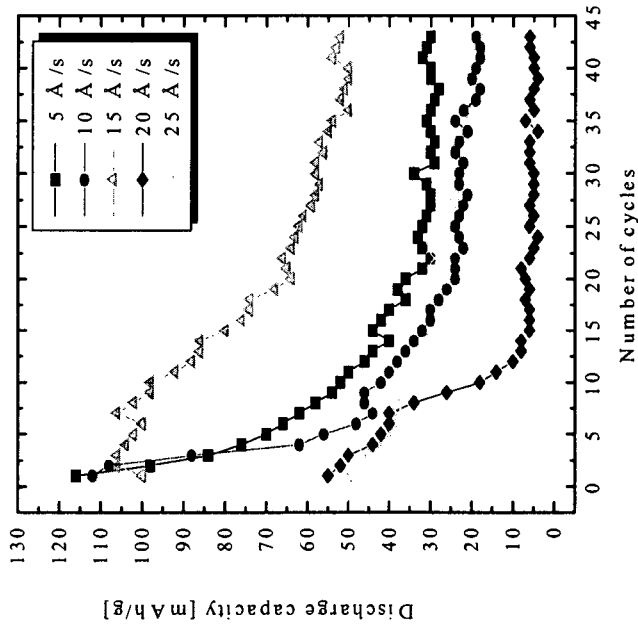
LiCoO<sub>2</sub> thin film annealed at 700°C, 10 min  
[scan rate : 0.1 mV/s, LiPON]



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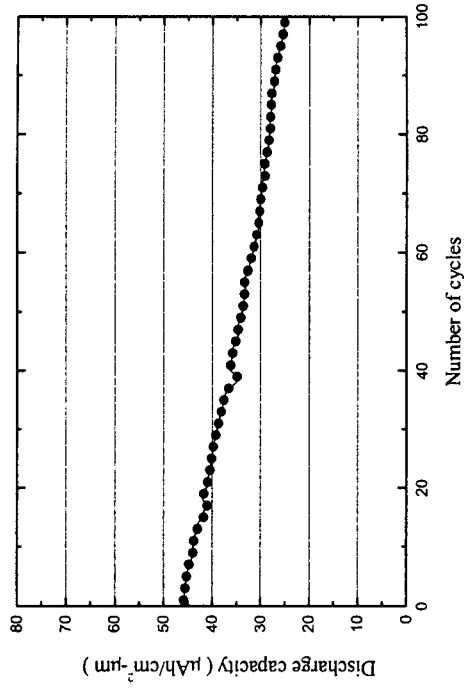
# Cathode-V(LiCoO<sub>2</sub>, cycling performance)

## E-beam evaporated LiCoO<sub>2</sub>



Discharge capacity of 1  $\mu\text{m}$  LiCoO<sub>2</sub> film as a function of deposition rate. [ LiCoO<sub>2</sub>/SPE/Li ]

## Sputter coated LiCoO<sub>2</sub>



LiCoO<sub>2</sub> (9000  $\text{\AA}$ ) / Lipon (1.5  $\mu\text{m}$ ) / Li (2  $\mu\text{m}$ )

Current density = 50  $\mu\text{A}/\text{cm}^2$

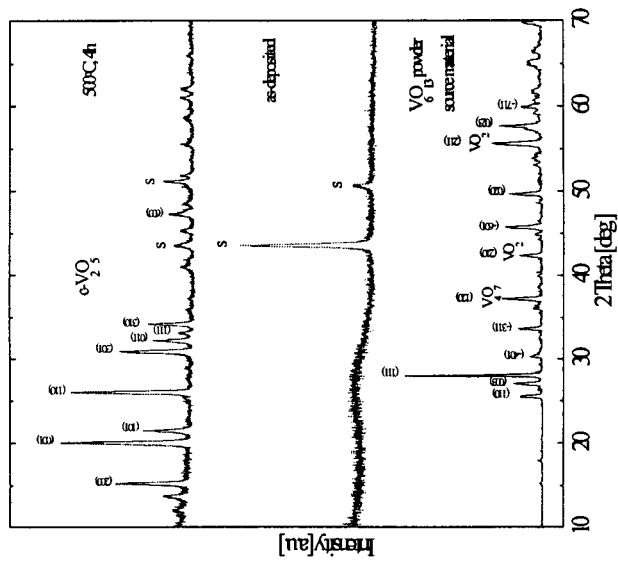
Area = 1  $\text{cm}^2$



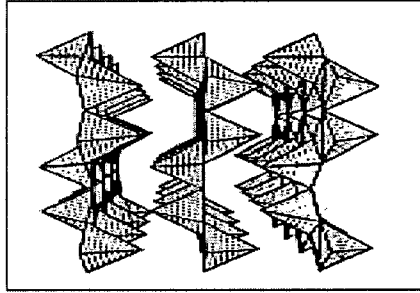
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# Cathode-VI( $V_2O_5$ , crystal structure)

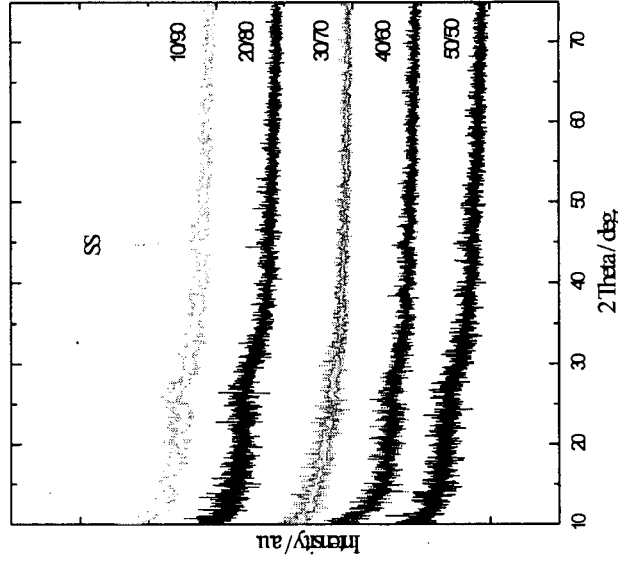
E-beam evaporated  $V_2O_5$



V-O bond (2.81Å)  
V=O bond (1.54Å)



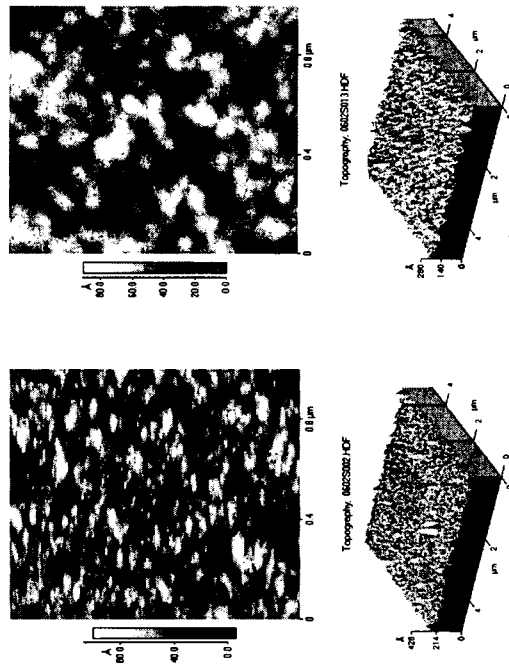
Sputter coated  $V_2O_5$



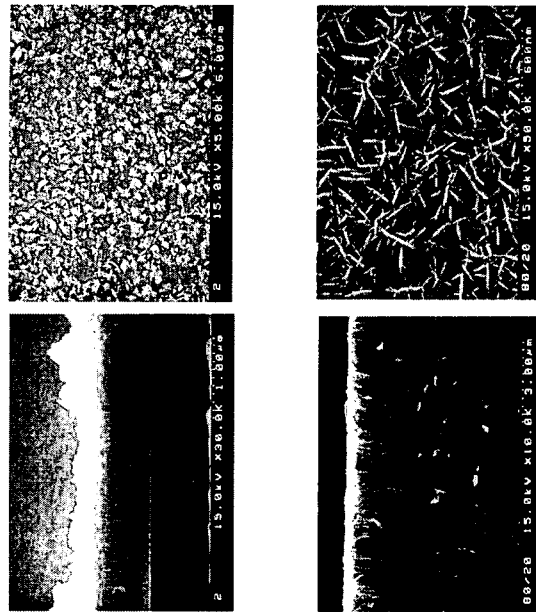
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# Cathode-VII( $V_2O_5$ , morphology)

E-beam evaporated  $V_2O_5$



Sputter coated  $V_2O_5$

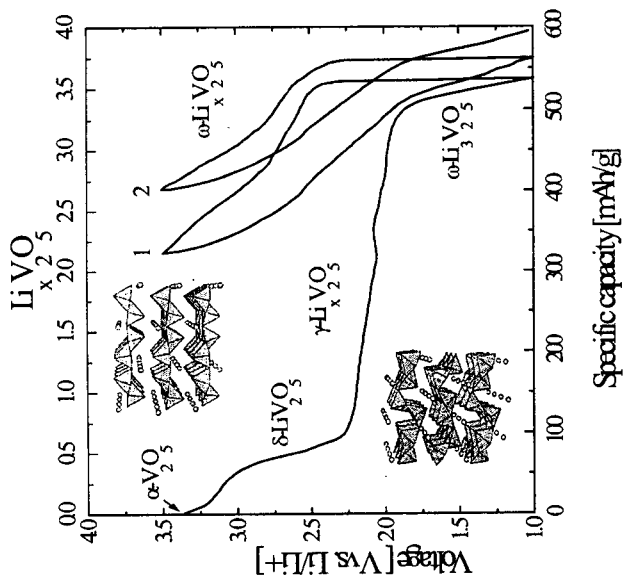


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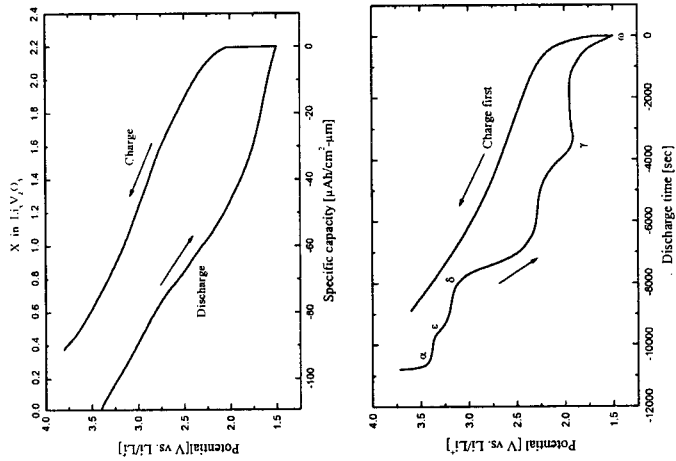


# Cathode-VIII( $V_2O_5$ , cyclic voltammogram)

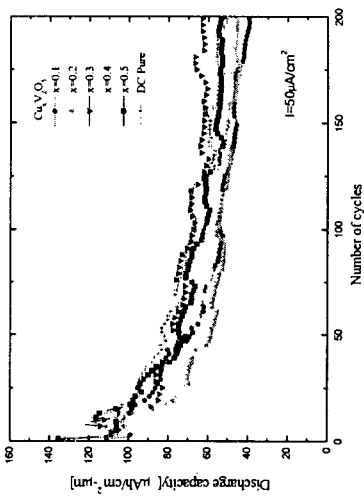
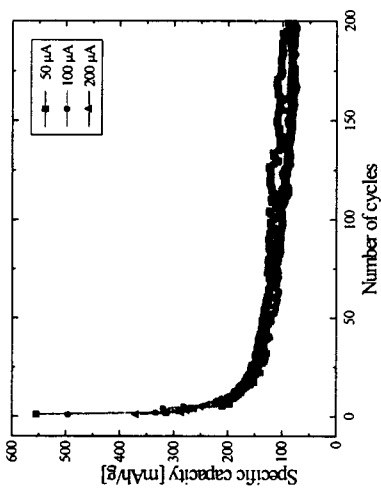
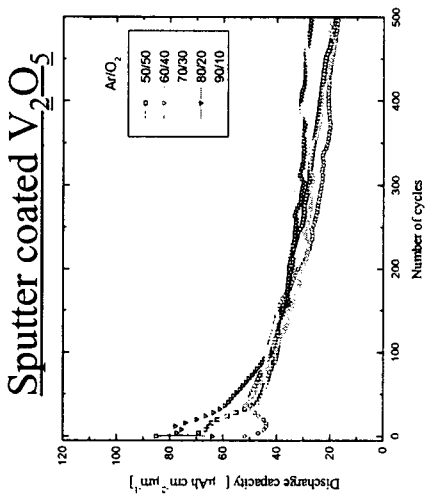
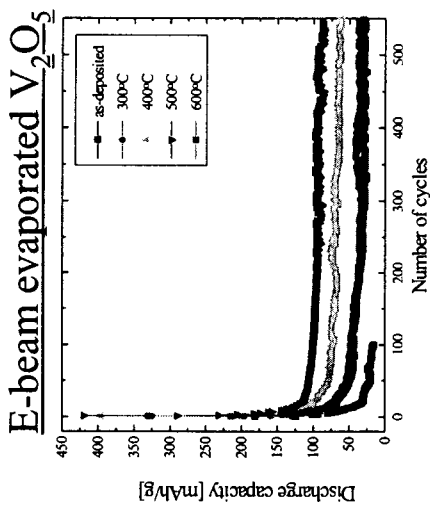
E-beam evaporated  $V_2O_5$



Sputter coated  $V_2O_5$



# Cathode-IX( $V_2O_5$ , cycling performance)



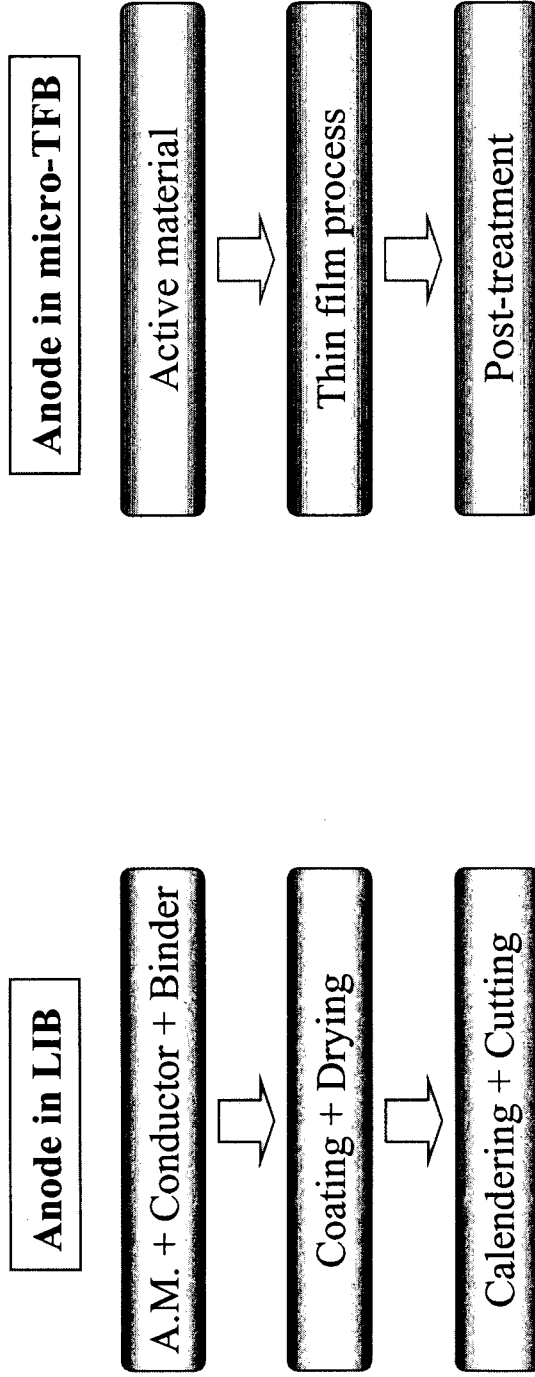
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# Anode-I

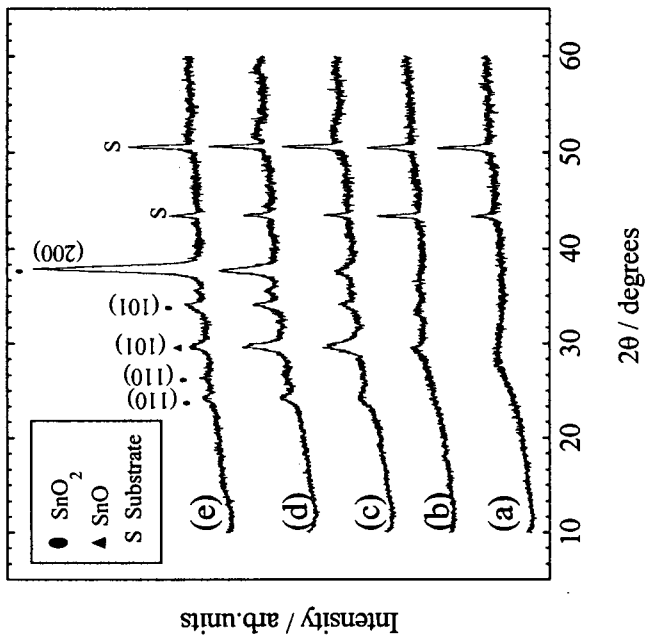
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- ◆ Anode materials ;
- ☒ Carbon(amorphous, graphite), Li, Li alloys, SnO<sub>2</sub>, TiO<sub>2</sub>, etc.

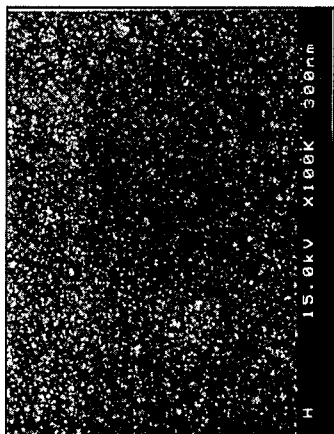
- ◆ Fabrication process ;



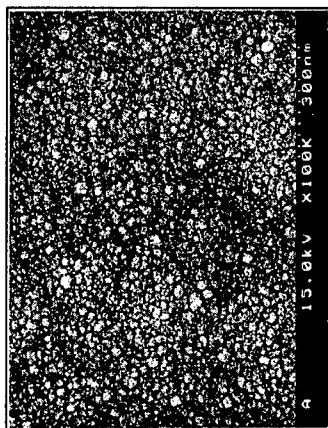
# Anode-II(SnO<sub>2</sub>, crystal structure & morphology)



XRD patterns of as deposited (a) and heat treated at 300°C (b), 400°C (c), 500°C (d), 600°C for 4 hr. (e).



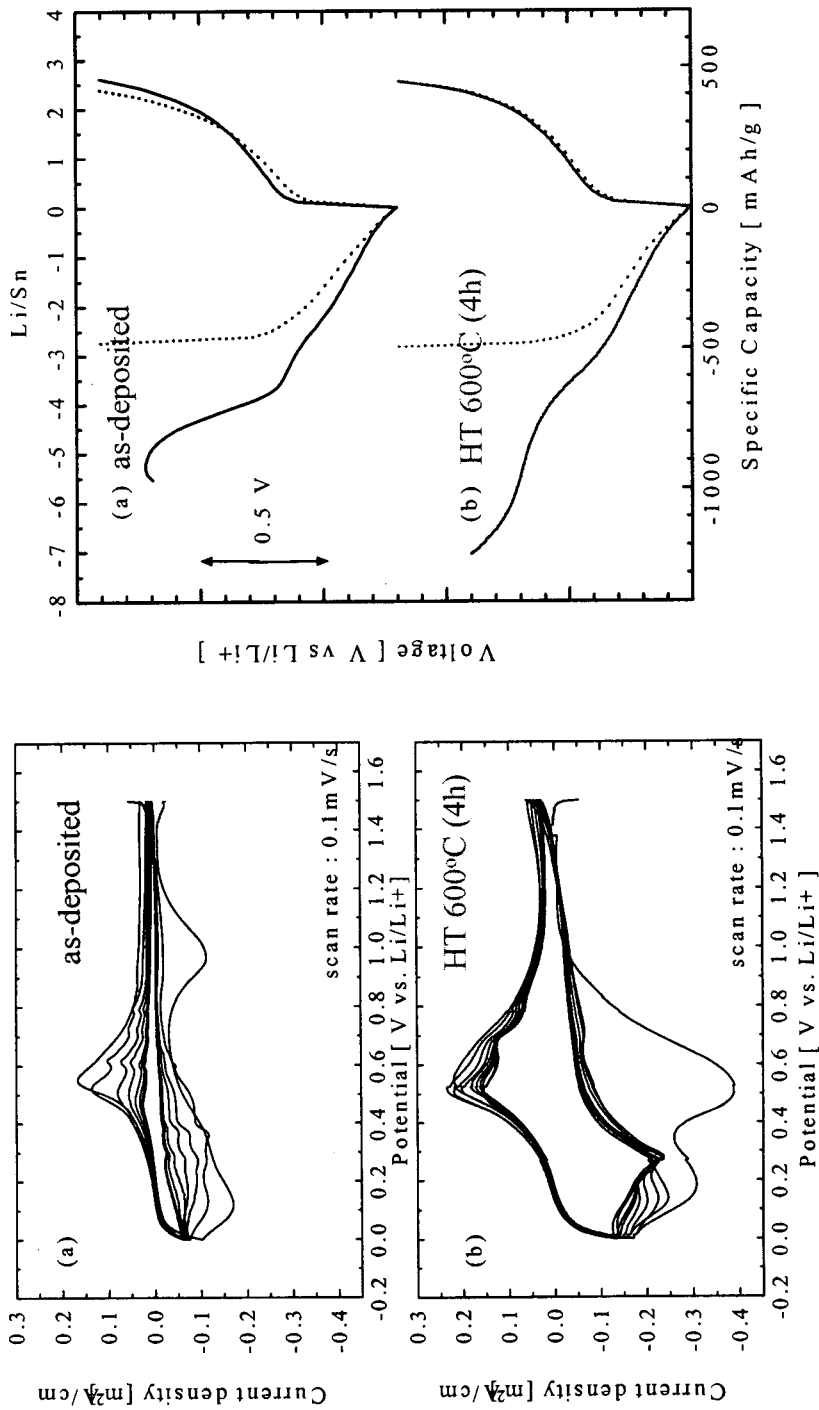
(a) as-deposited



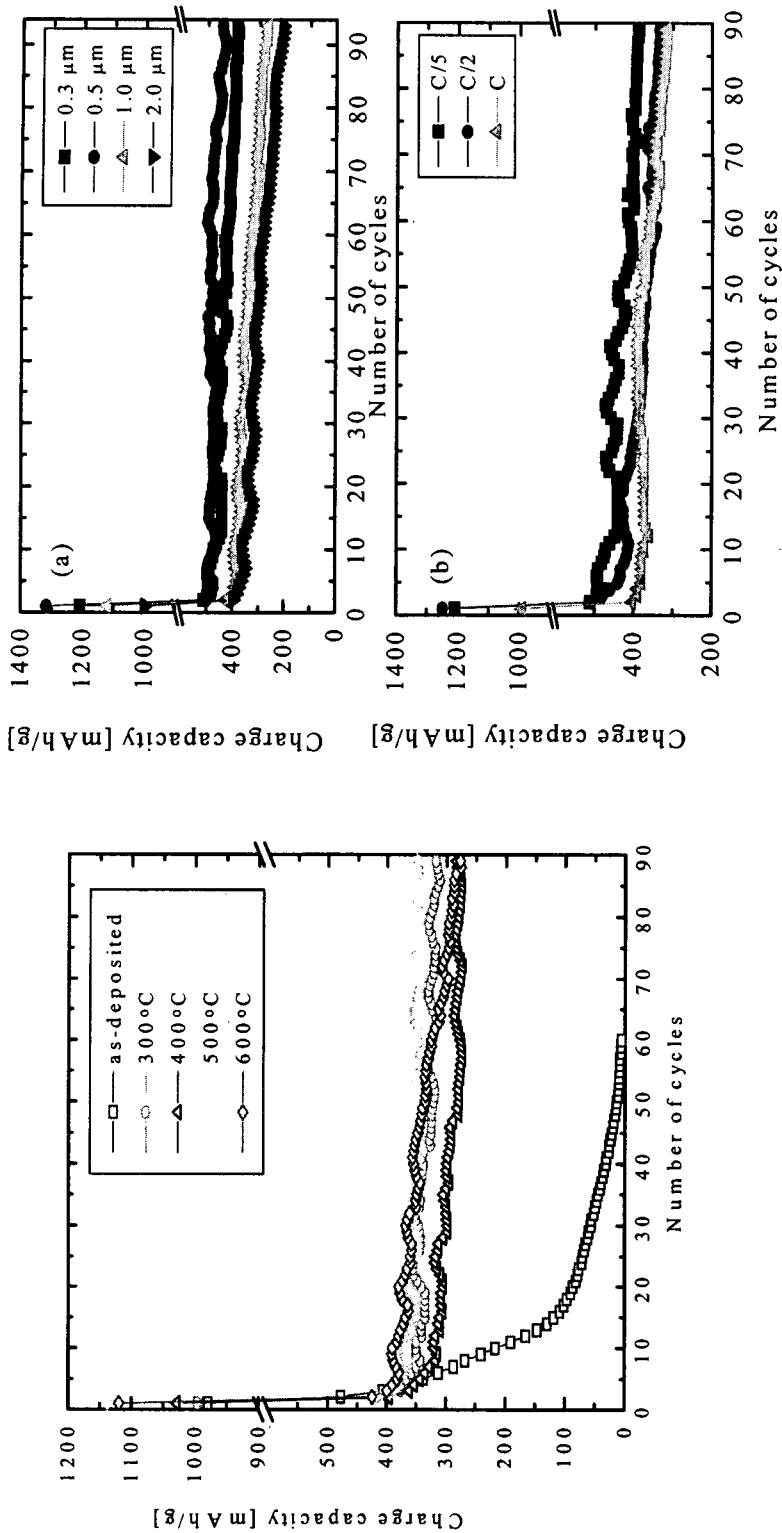
(b) HT 600°C (4h)



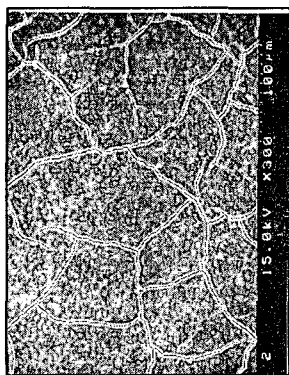
# Anode-III(SnO<sub>2</sub>, electrochemical properties)



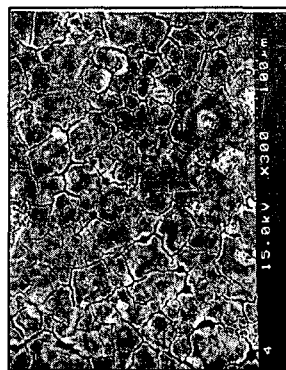
# Anode-IV(SnO<sub>2</sub>, cycling performance)



# Anode-V(SnO<sub>2</sub>, morphology change on cycling)



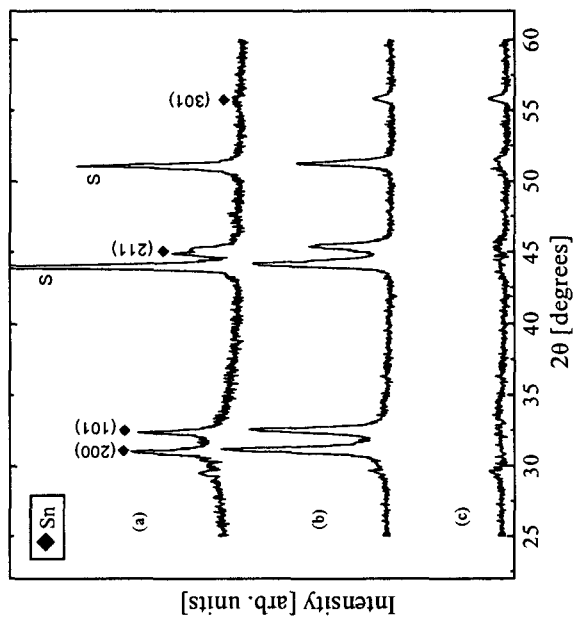
(a) after 1st discharge



(b) after 2nd discharge



(c) after 200 cycles



# Electrolyte-I(LiPON, solid electrolyte)

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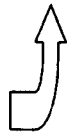
Why LiPON?

Polymer electrolyte



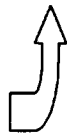
Difficulty to make a thin film

Inorganic crystalline materials



Need heat treatment to make a crystalline structure

Sulfide electrolyte



Environmental problems

LiPON

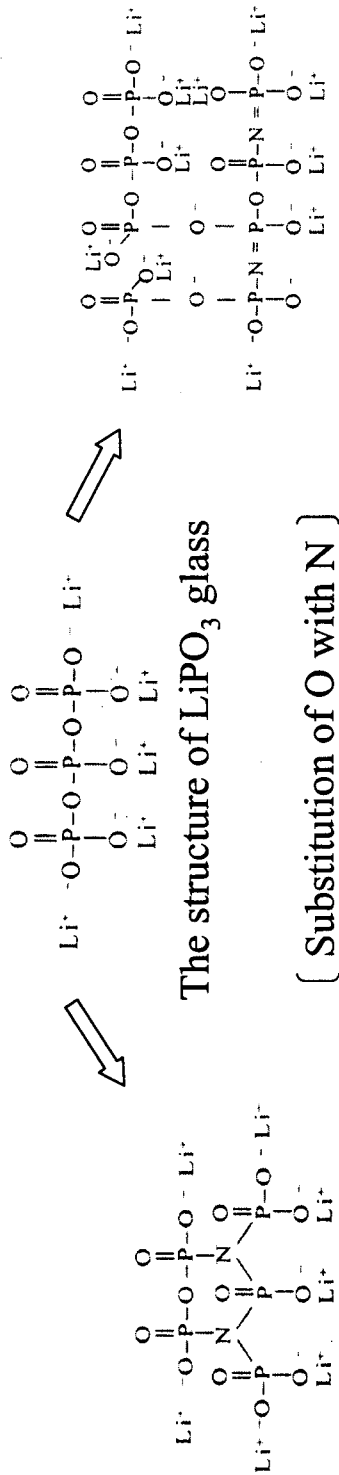
Highly stable at atmospheric condition

Pretty high ionic conductivity ( $\sim 10 \times 10^{-6}$  S/cm)



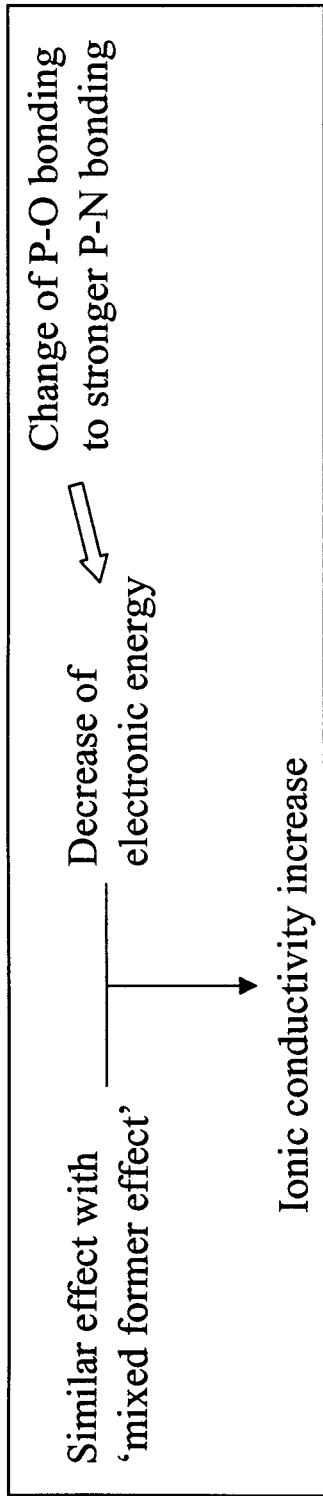


# Electrolyte-II(LiPON, mechanism)

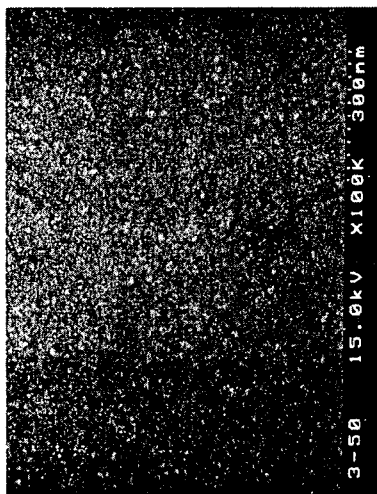


Cross linking of  $>N-$

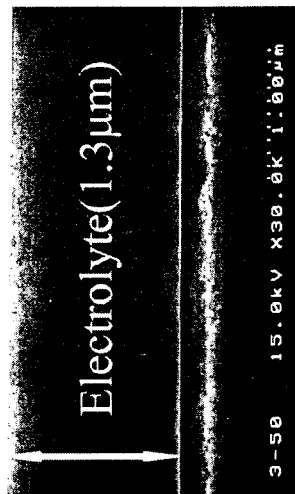
Cross linking of  $-N=$



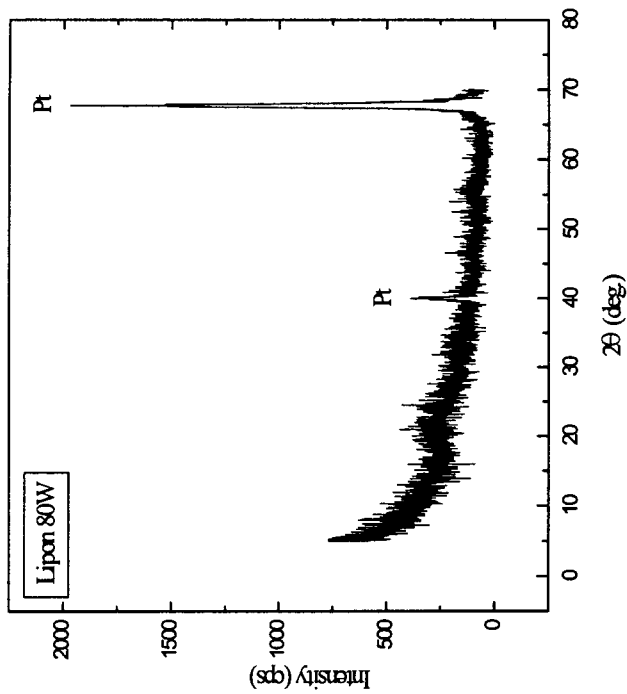
# Electrolyte-III(LiPON, morphology & structure)



Top view

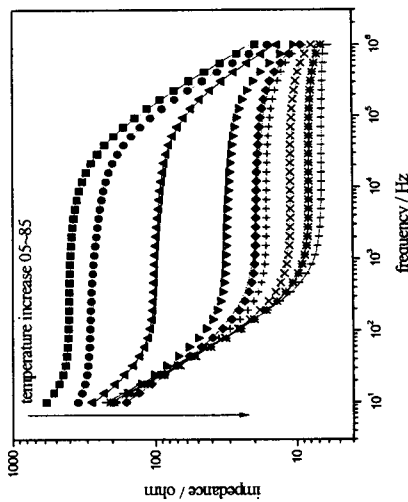


Cross sectional view



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# Electrolyte-IV(LiPON, ionic conductivity)

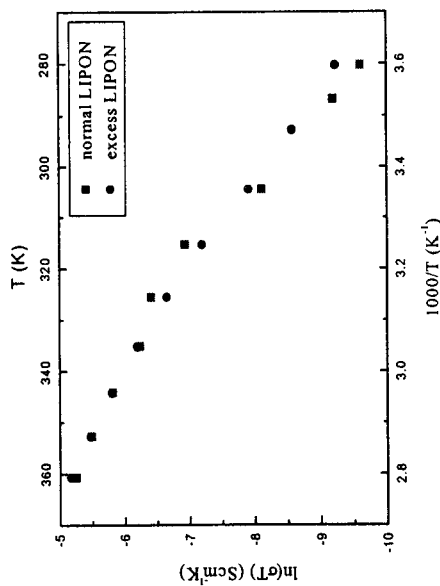


Normal LiPON

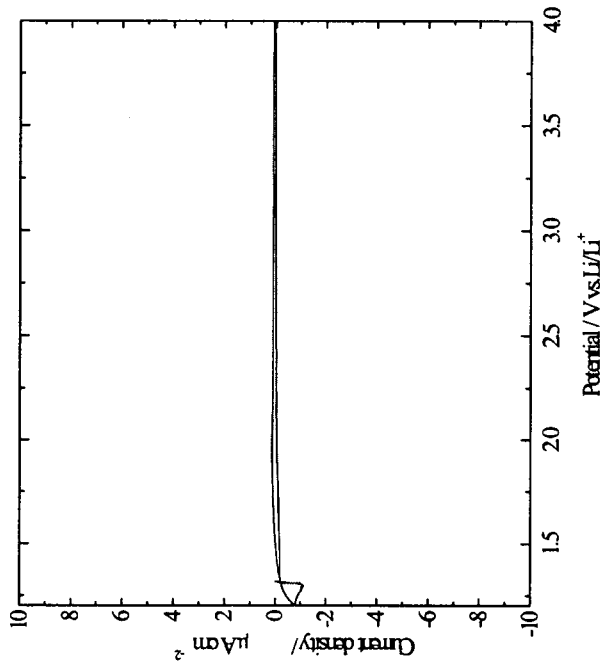
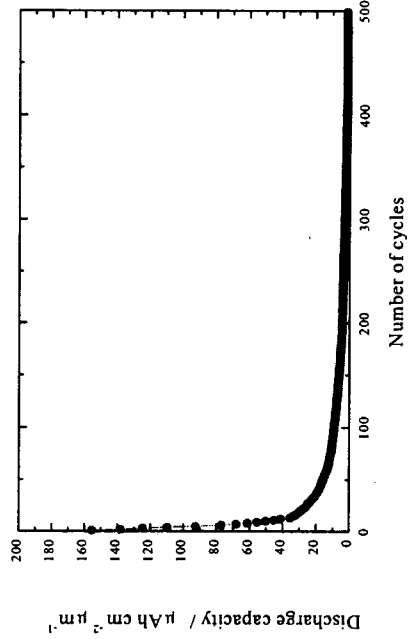
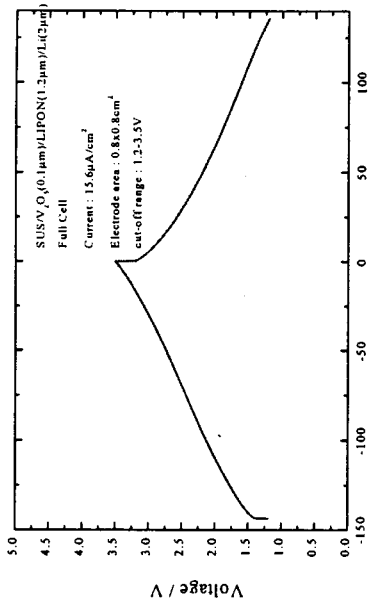
Process gas composition	Li/P	Film composition	Ionic Conductivity	Ea(eV)
N <sub>2</sub>	2.94	Li <sub>2.94</sub> PO <sub>2.37</sub> N <sub>0.75</sub>	9.5×10 <sup>-7</sup>	0.51
N <sub>2</sub> +10%O <sub>2</sub>	2.81	Li <sub>2.81</sub> PO <sub>3.1</sub> N <sub>0.7</sub>	9.0×10 <sup>-7</sup>	-
N <sub>2</sub> +50%O <sub>2</sub>	2.41	Li <sub>2.41</sub> PO <sub>3</sub> N <sub>0.4</sub>	6.7×10 <sup>-7</sup>	-

Excess LiPON

Process gas composition	Li/P	Film composition	Ionic Conductivity	Ea(eV)
N <sub>2</sub>	3.02	Li <sub>3.02</sub> PO <sub>2.35</sub> N <sub>0.79</sub>	1.2×10 <sup>-6</sup>	0.50
N <sub>2</sub> +10%O <sub>2</sub>	2.80	Li <sub>2.80</sub> PO <sub>2.67</sub> N <sub>0.65</sub>	4.73×10 <sup>-7</sup>	-
N <sub>2</sub> +50%O <sub>2</sub>	-	-	-	-

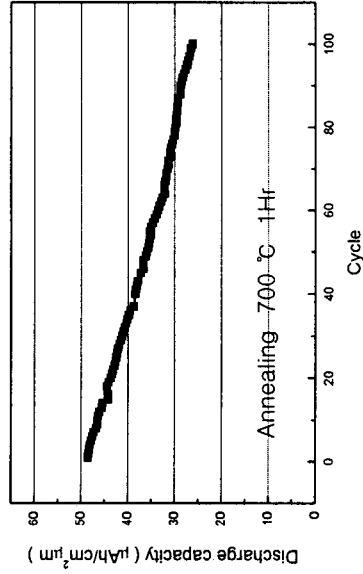
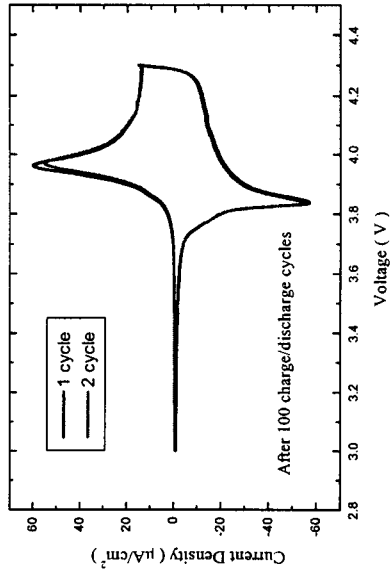
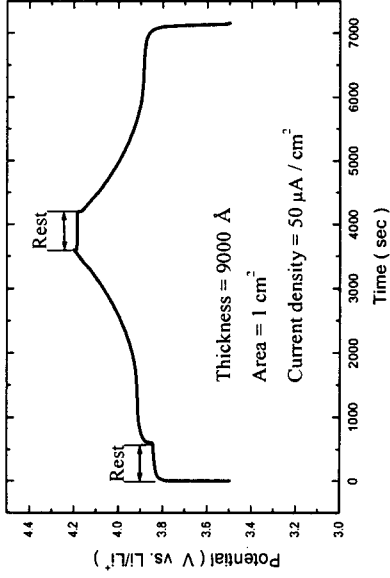
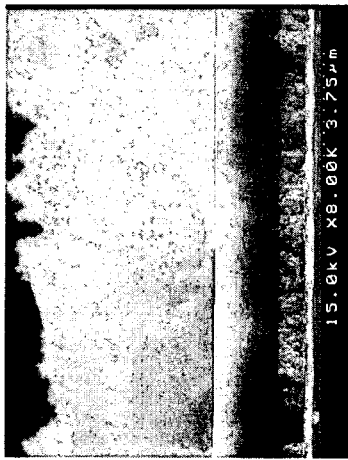


# Electrolyte-V(LiPON, electrochemical properties)

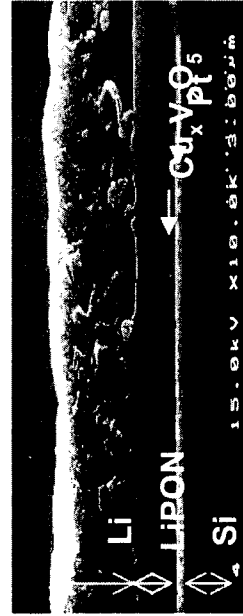
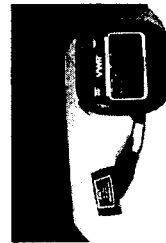
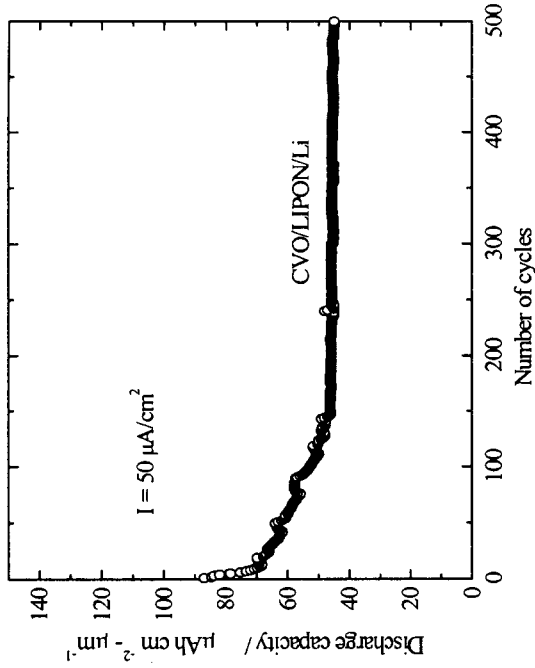
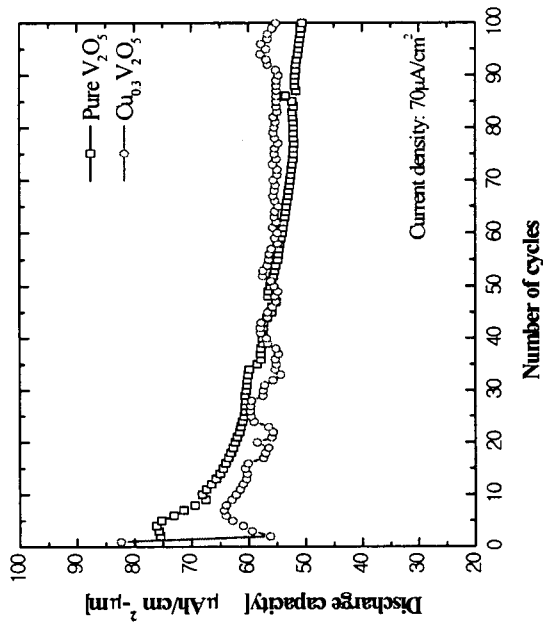


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# Full cell-I(LiCoO<sub>2</sub>/LiPON/Li)

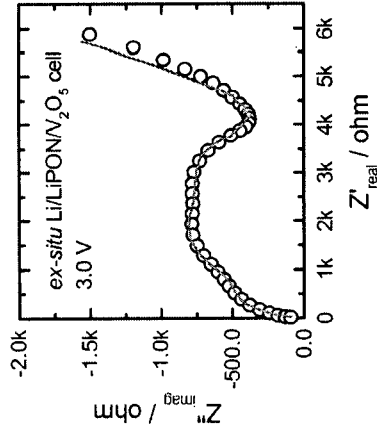
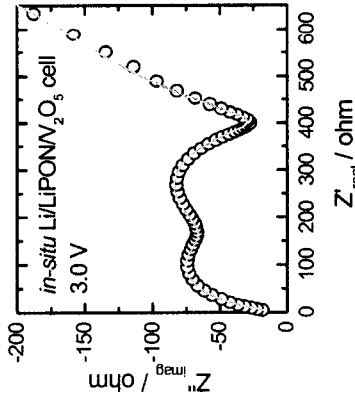
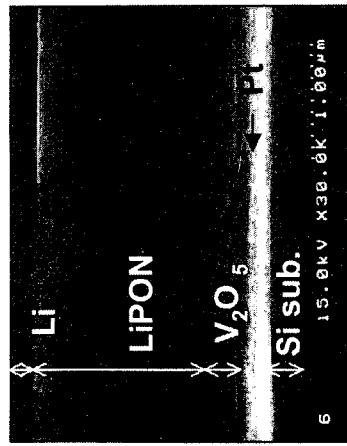
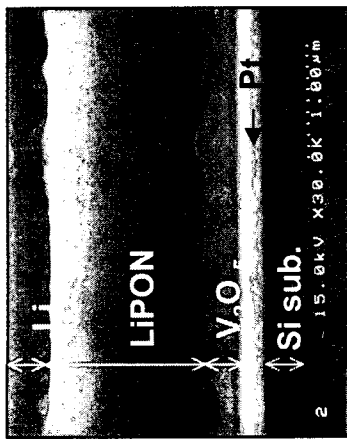


# Full cell-II( $V_2O_5$ /LiPON/Li)

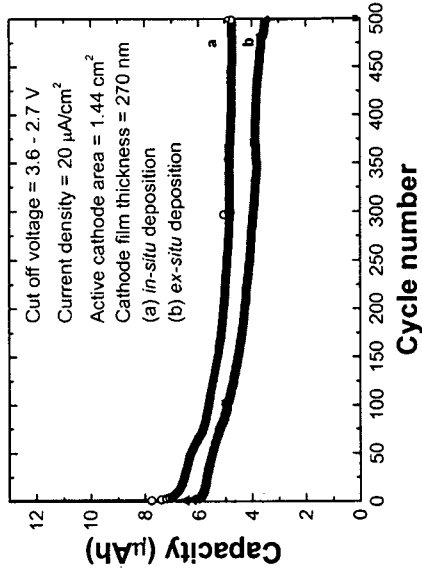


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# Fabrication process (*ex-situ* & *in-situ*)



***in-situ TFB***

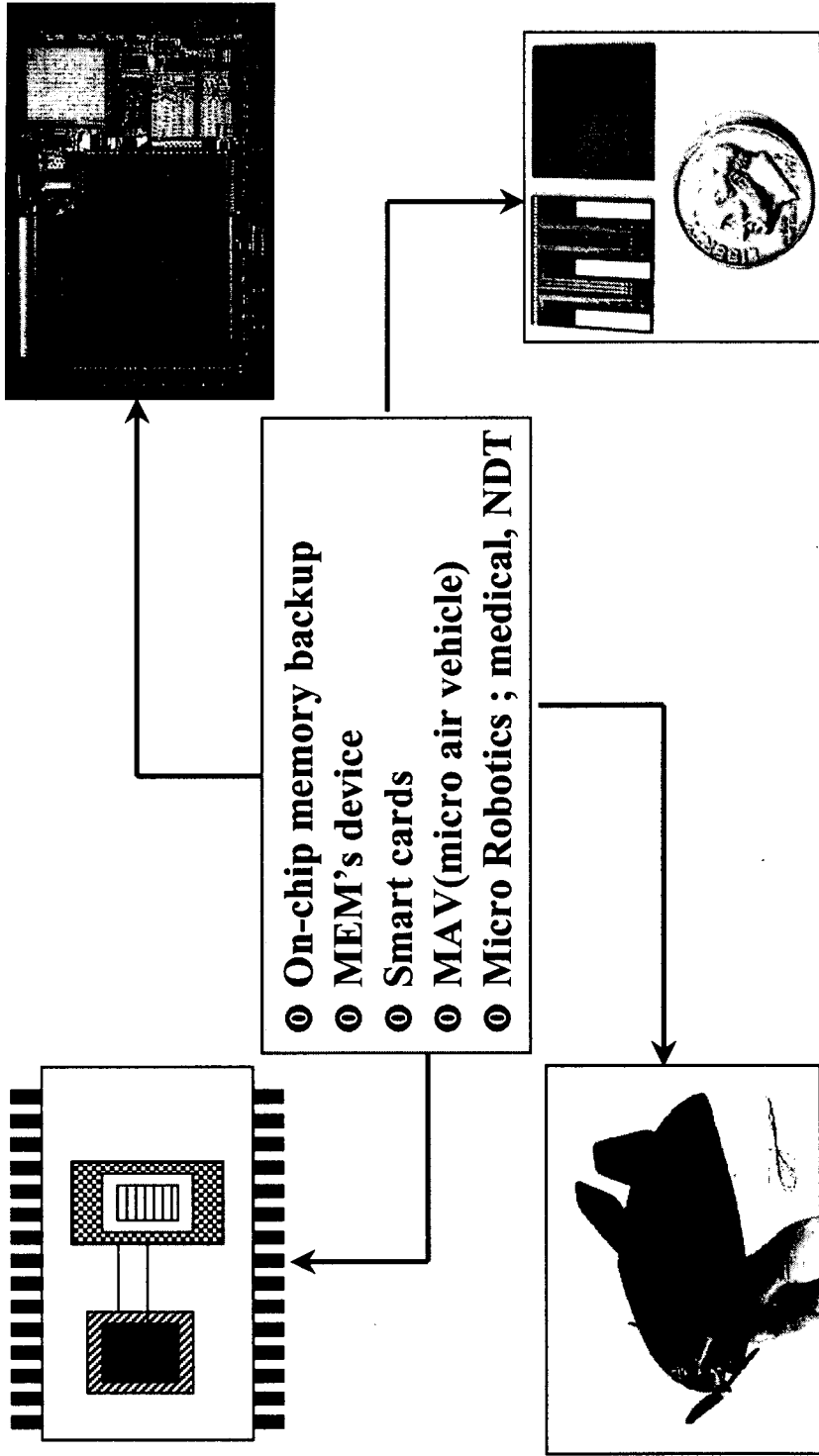


***ex-situ TFB***



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# Application





# CONCLUSIONS

