Nanoscale Interface Control of High-Quality Electrode Materials for Li-Ion Battery and Fuel Cell

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http://ep.snu.ac.kr

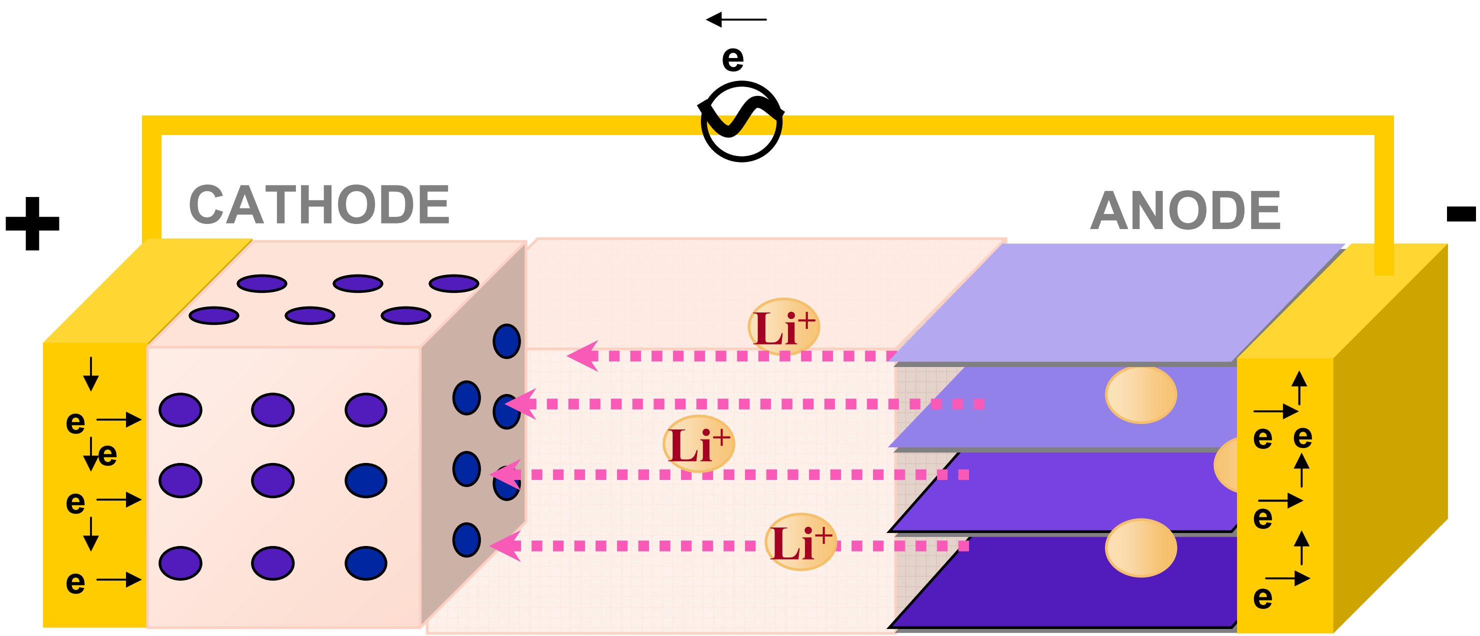
Nanoscale Control for High-Technology Electronics Equipment

Global Warming

TIME (2006)

Electrode Materials for the 2nd Generation Li-Ion Battery

Discharge (Lithiation)



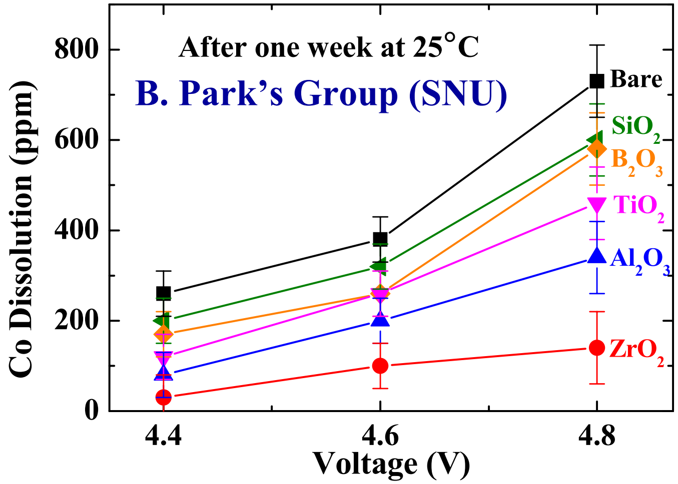
$Li_{1-x}CoO_2$ | Electrolyte | Carbon

- Capacity
- Cycle Life
- Safety

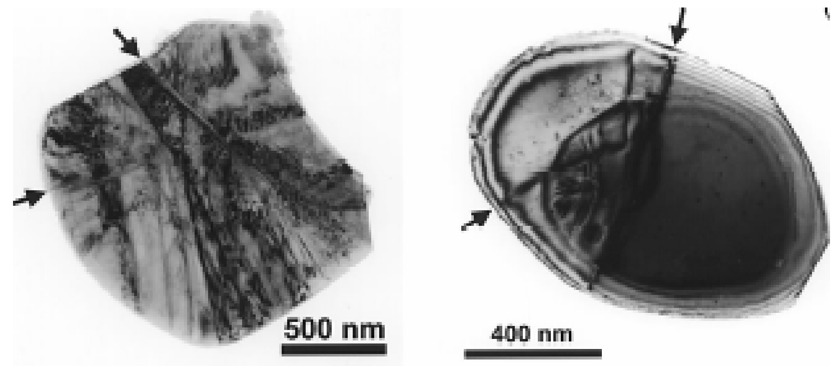
Solution ?

Mechanisms of Capacity Fading and Safety

❖ Cobalt Loss from $Li_{1-x}CoO_2$

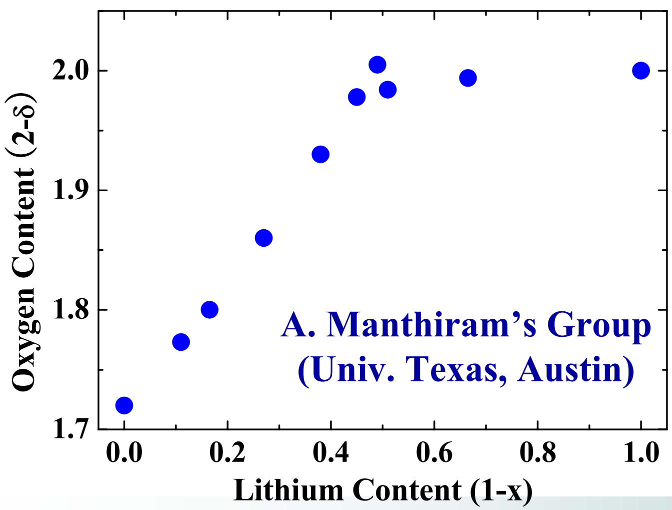


❖ Structural Instability



Y.-M. Chiang's Group (MIT)

❖ Oxygen Loss from $Li_{1-x}CoO_{2-\delta}$



❖ Exothermic Reaction with Electrolyte

The Effect of Al_2O_3 Coating in Thin-Film $LiCoO_2$ Cathodes

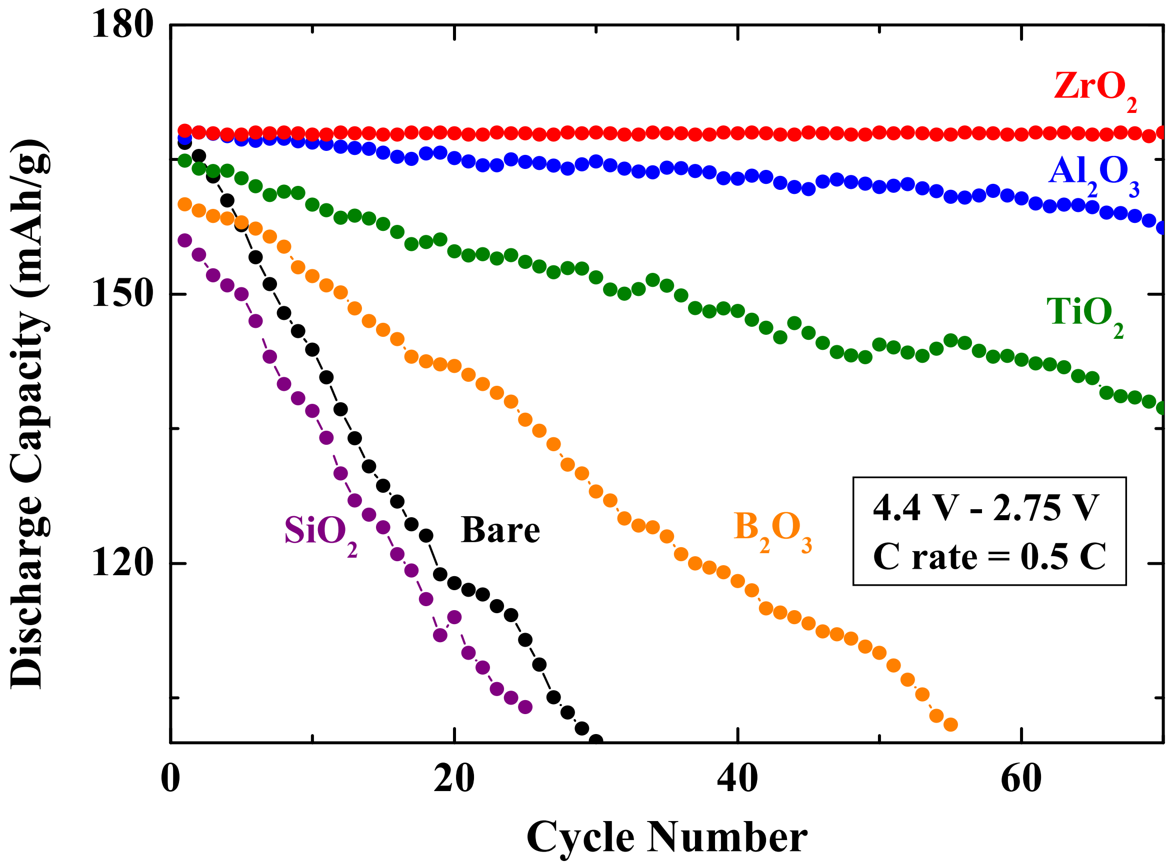
Y. J. Kim, H. Kim, B. Kim, D. Ahn, J.-G. Lee, T.-J. Kim, D. Son, J. Cho, Y.-W. Kim, and B. Park
Chem. Mater. **15**, 1505 (2003).

Y. J. Kim, E.-K. Lee, H. Kim, J. Cho, Y. W. Cho, B. Park, S. M. Oh, and J. K. Yoon
J. Electrochem. Soc. **151**, A1063 (2004).

J. Cho, Y. J. Kim, T.-J. Kim, and B. Park
Angew. Chem. Int. Ed. **40**, 3367 (2001).

Capacity Retention of Metal-Oxide-Coated $LiCoO_2$

❖ Li/Metal-Oxide-Coated $LiCoO_2$



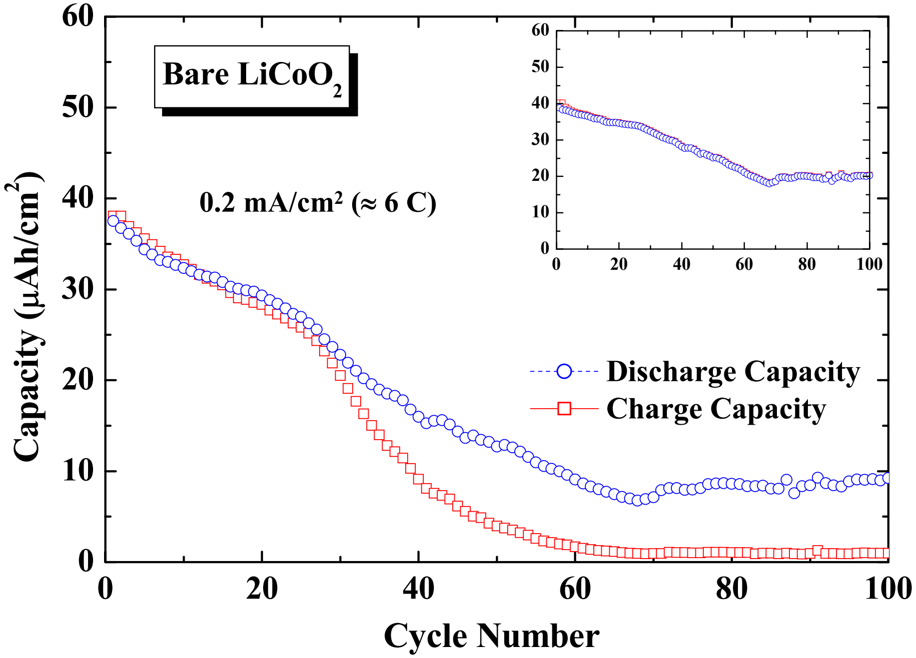
Moderate Metal-Oxide Coating on Cathode

Enhanced Capacity Retention by Protection of Surface

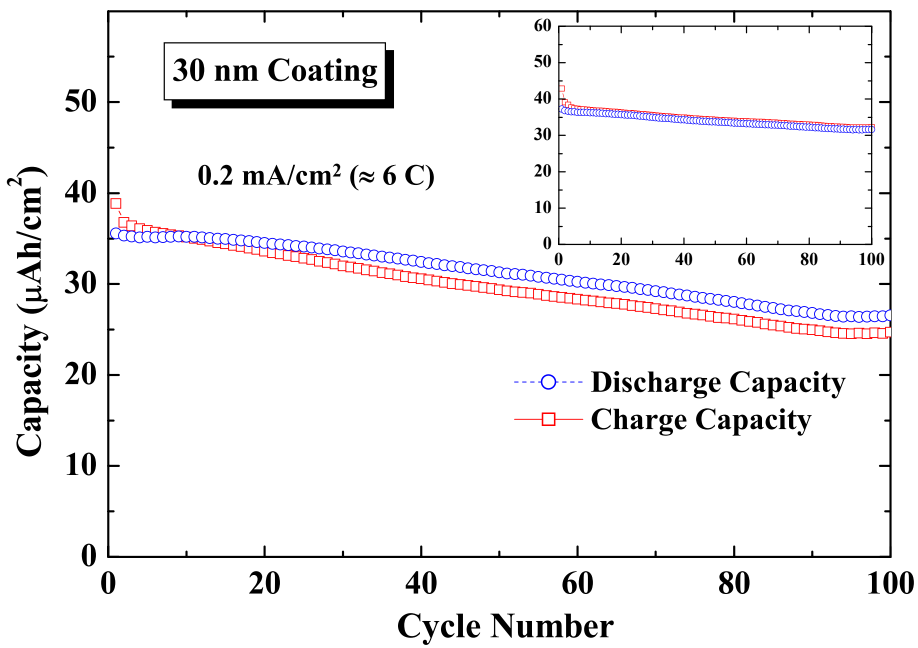
➢ J. Cho, Y. J. Kim, T.-J. Kim, and B. Park *Angew. Chem. Int. Ed.* **40**, 3367 (2001).

Galvanostatic Charge-Discharge Experiments

Uncoated $LiCoO_2$ Thin Film



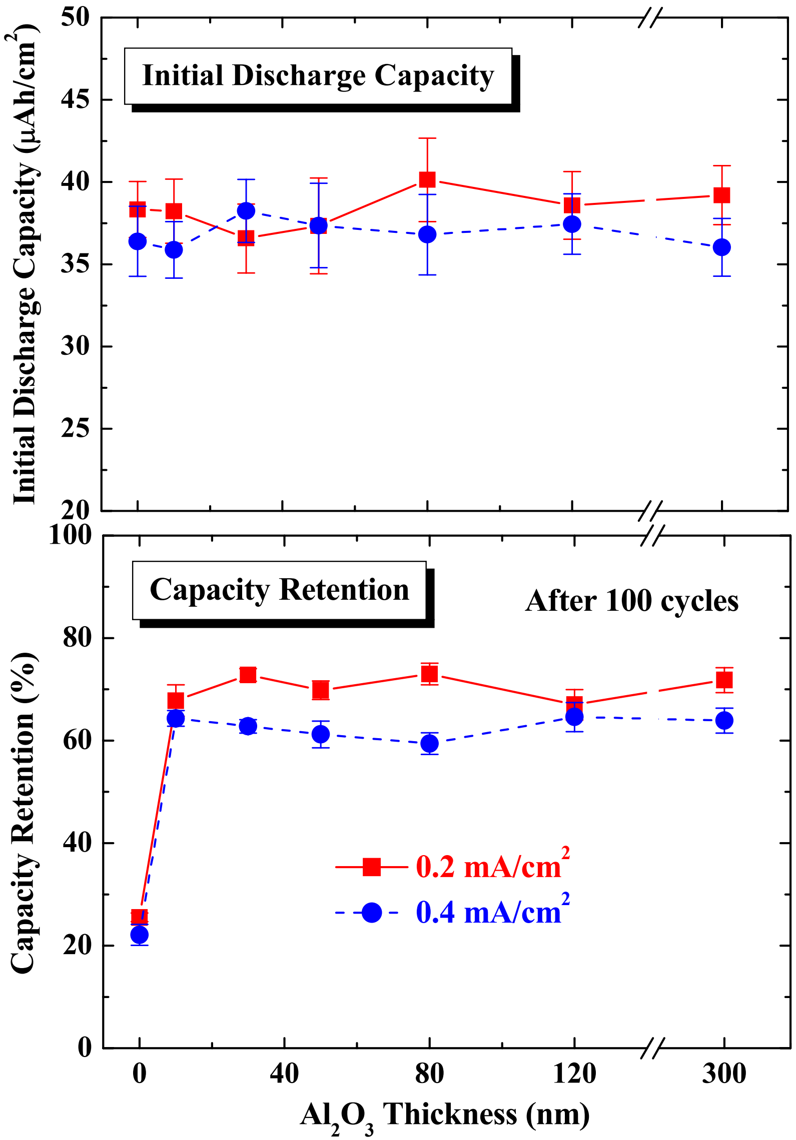
Al_2O_3-Coated $LiCoO_2$ Thin Film

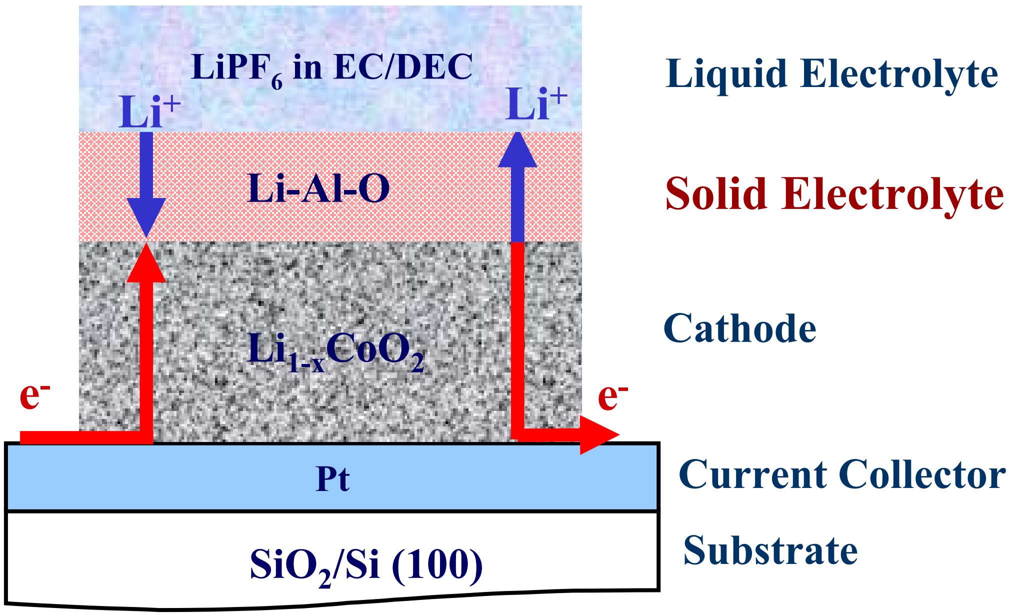


The charge capacity (for Li deintercalation) showed faster deterioration than the discharge capacity (for Li intercalation).

- Cell voltage : <u>4.4 V - 2.75 V</u>
- Current rates : 0.1 - 0.8 mA/cm²
- Half-cells ($Li/LiCoO_2$), 1 M $LiPF_6$ in EC/DEC
- At each cutoff step, the voltage was potentiostated until the current decreased to 10%.

Al_2O_3 Coating Layer as a Solid Electrolyte





Oxidation/reduction reaction occurs at the Li-Al-O / $LiCoO_2$ interface.

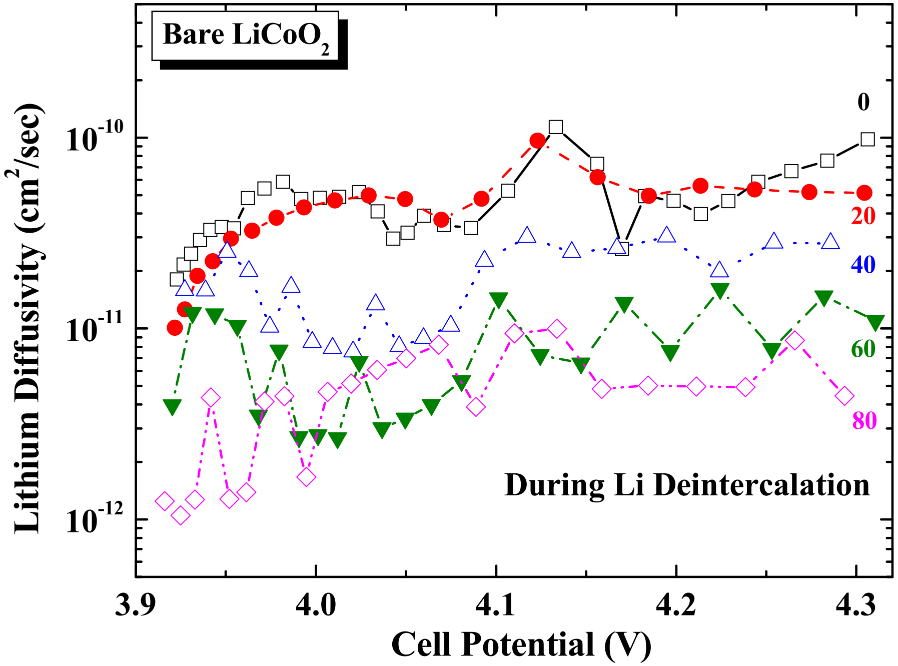
Composition of Li-Al-O needs to be determined.

Ex) $0.7Li_2O$-$0.3Al_2O_3$: ~10^{-7} S/cm at 23°C

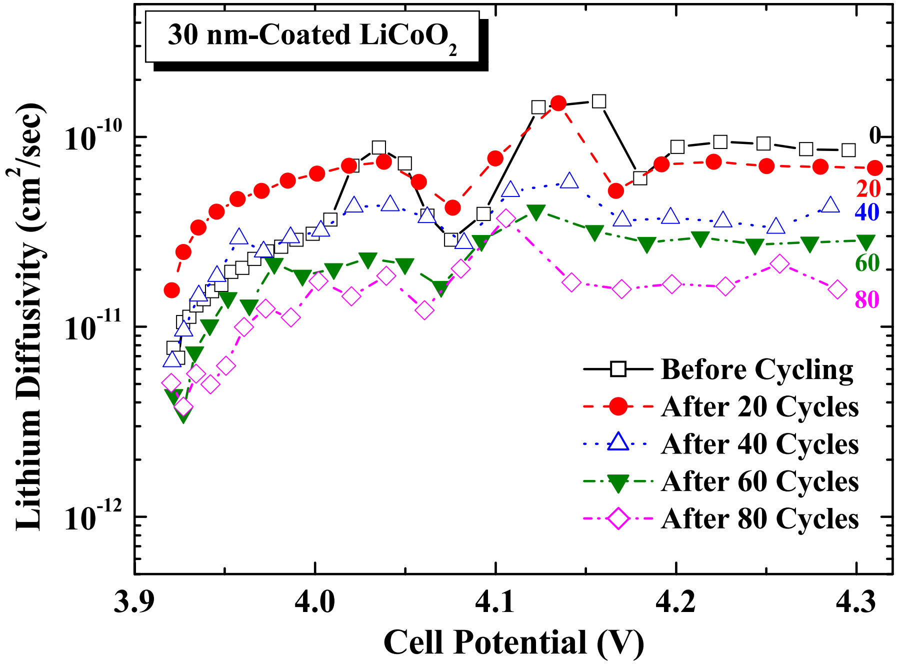
A. M. Glass *et al.*, *J. Appl. Phys.* (1980).

Li Diffusivity during Li Deintercalation (Charging)

Uncoated $LiCoO_2$ Thin Film

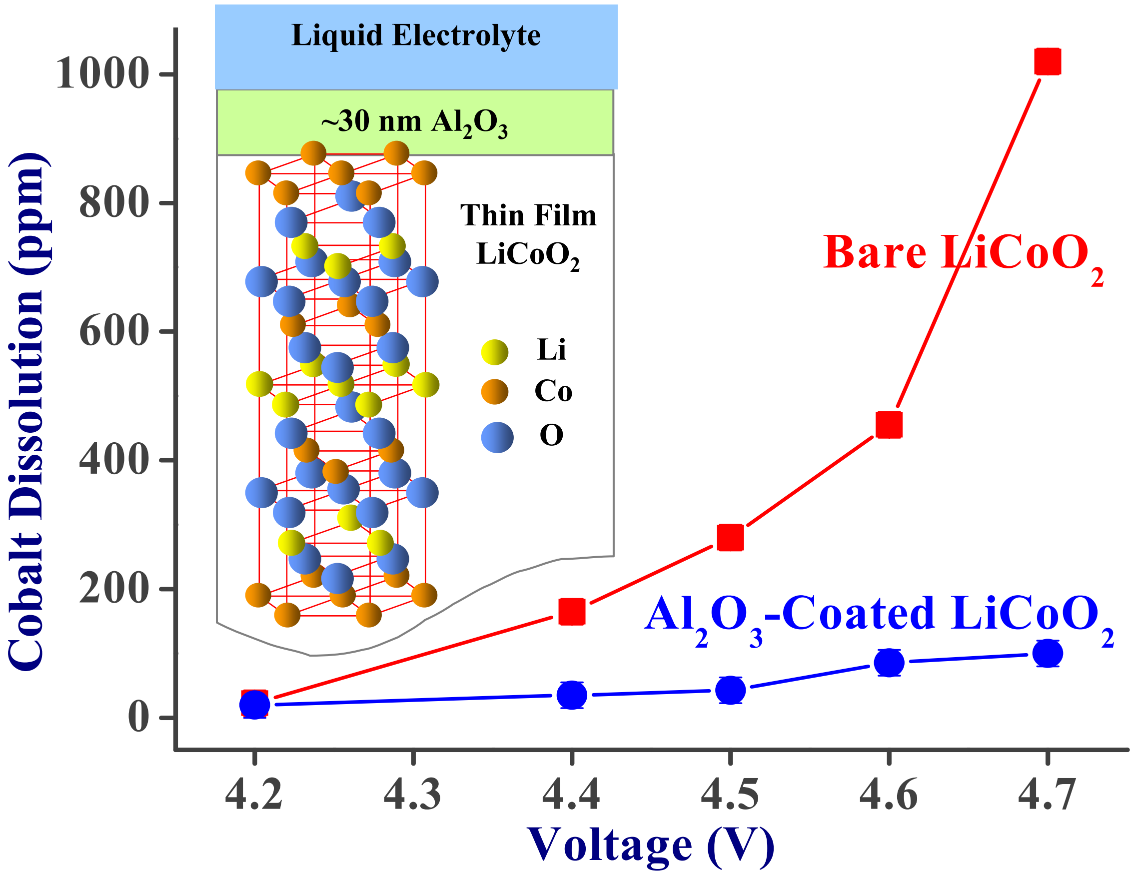


Al_2O_3-Coated $LiCoO_2$ Thin Film



- **Clearly enhanced by 30 nm-thick Al_2O_3 coating.**
- **Maxima at ~4.13 V, corresponding to the monoclinic phase.**
- **Two minima at the cell potential, corresponding to the phase transition between a hexagonal and monoclinic phase.**

Cobalt Dissolution from Thin-Film $LiCoO_2$ Cathodes



ICP-MS after floating for 12 days

Al_2O_3 coating can effectively suppress the Co dissolution

- Y. J. Kim, H. Kim, B. Kim, D. Ahn, J.-G. Lee, T.-J. Kim, D. Son, J. Cho, Y.-W. Kim, and B. Park, *Chem. Mater.* **15**, 1505 (2003).

$AlPO_4$-Nanoparticle-Coated $LiCoO_2$ Cathode Materials

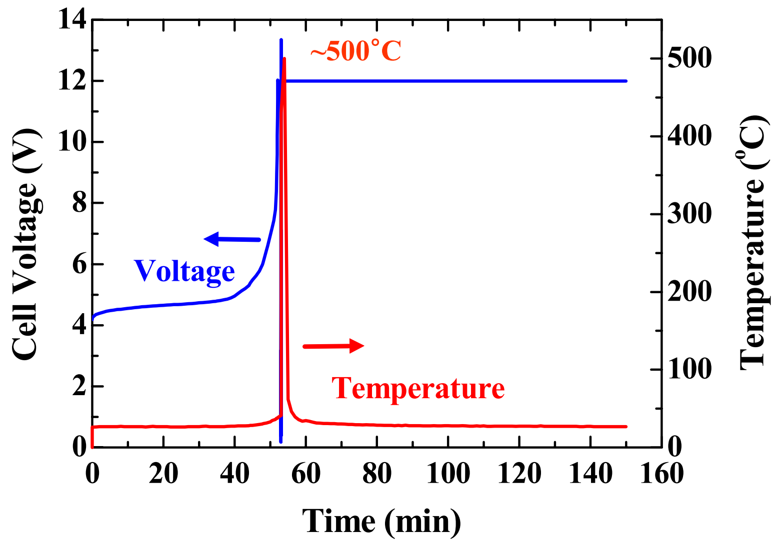
J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, and B. Park
Angew. Chem. Int. Ed. **42**, 1618 (2003).

J.-G. Lee, B. Kim, J. Cho, Y.-W. Kim, and B. Park
J. Electrochem. Soc. **151**, A801 (2004).

B. Kim, C. Kim, D. Ahn, T. Moon, J. Ahn, Y. Park, and B. Park
Electrochem. Solid-State Lett. **10**, A32 (2007).

Breakthrough in the Safety Hazard of Li-Ion Battery

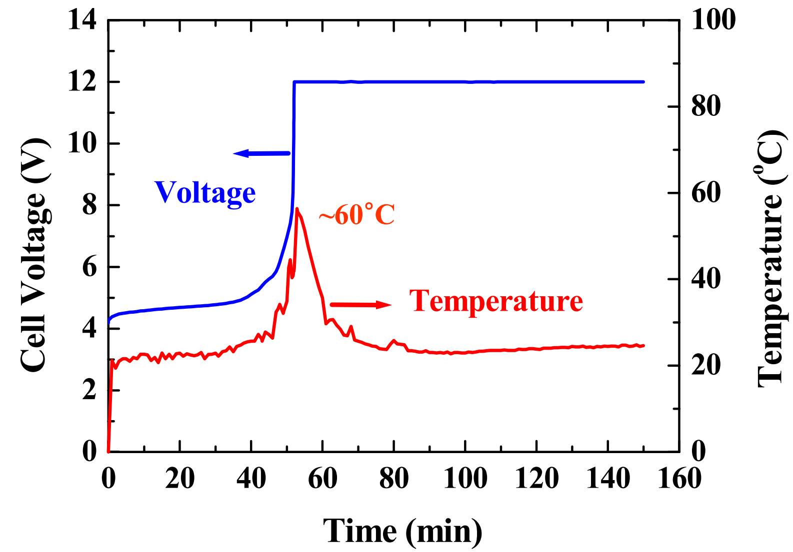
Bare $LiCoO_2$



Short Circuit & Temperature Uprise

Cell Fired and Exploded

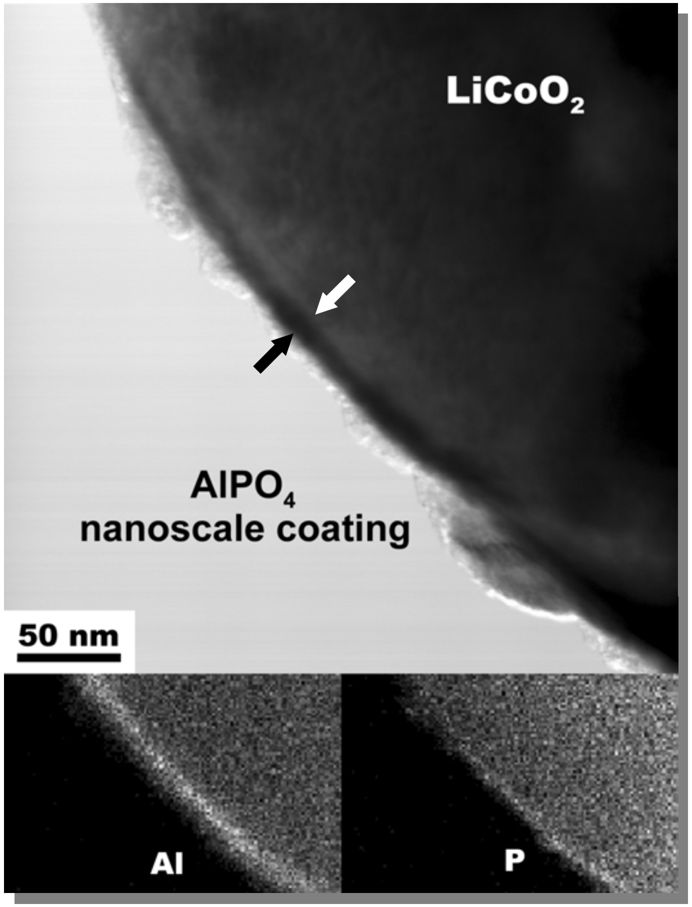
$AlPO_4$-Coated $LiCoO_2$

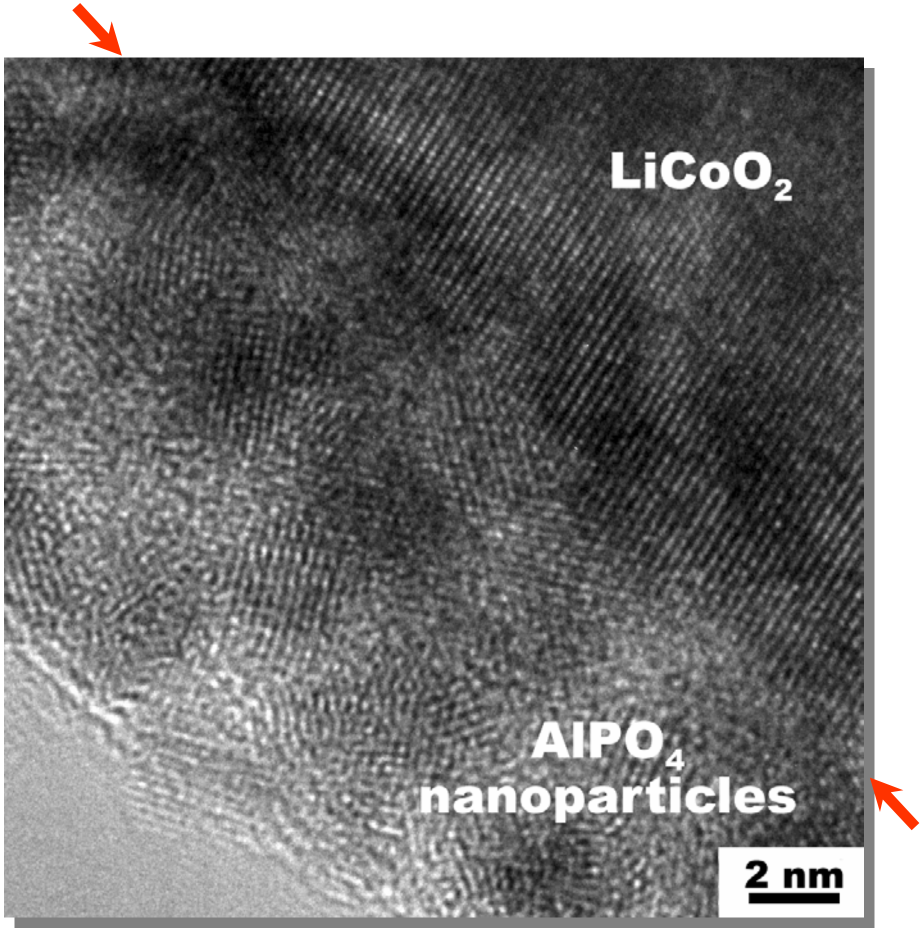


Temperature only ~60°C

Excellent Thermal Stability

TEM Image of $AlPO_4$ Nanoparticle-Coated $LiCoO_2$

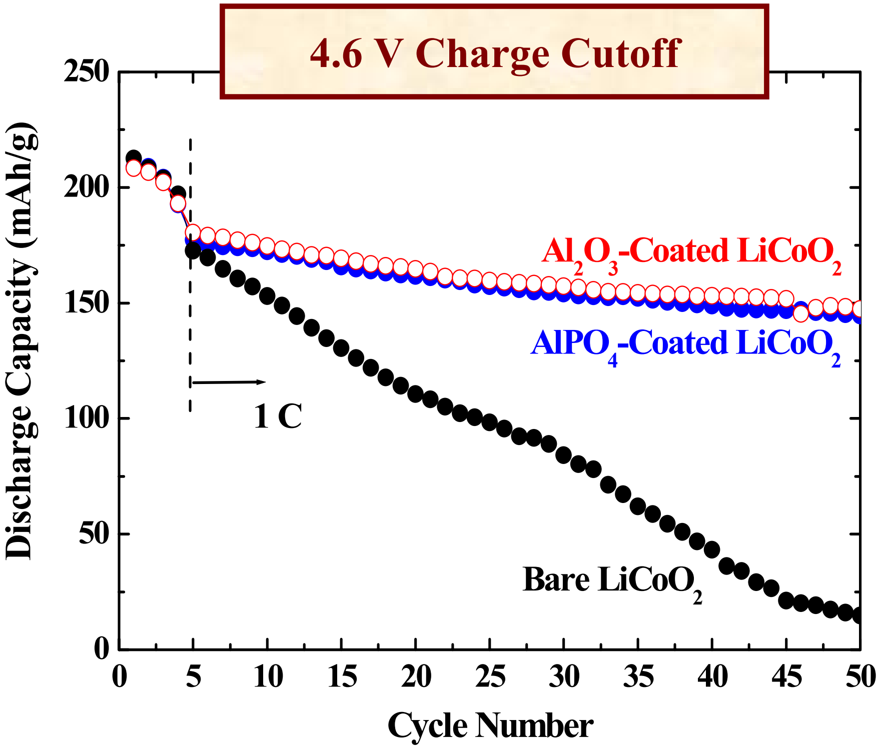


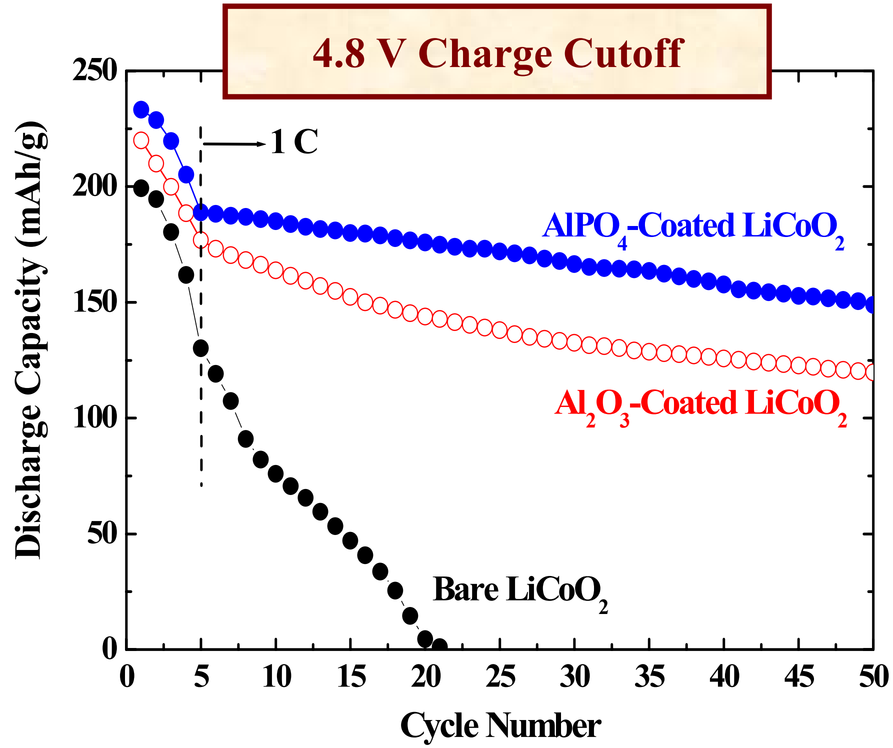


EDS confirms the Al and P components in the nanoscale-coating layer.

$AlPO_4$ nanoparticles (~3 nm) embedded in the coating layer (~15 nm).

Charge-Discharge Tests

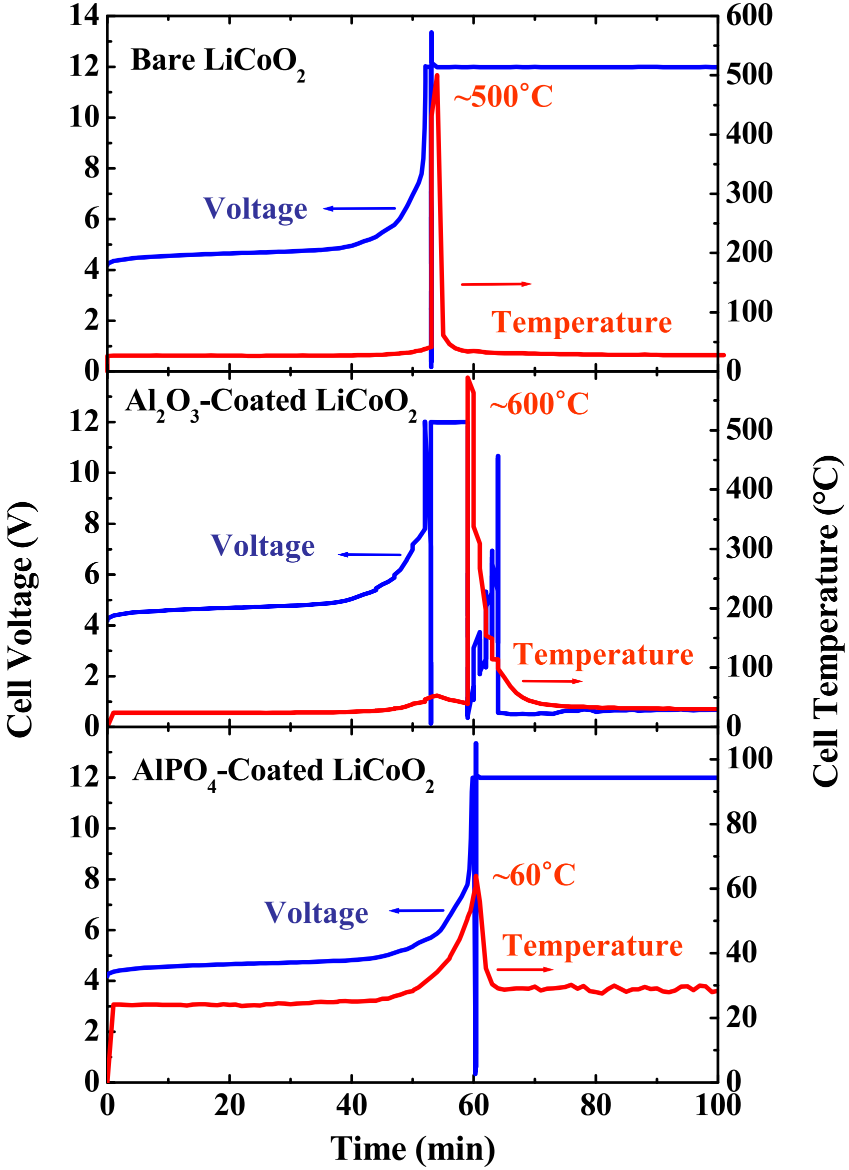




$AlPO_4$-coated $LiCoO_2$ is very stable at the high-charged state.

- J. Cho, T.-G. Kim, C. Kim, J.-G. Lee, Y.-W. Kim, and B. Park *J. Power Sources* **146**, 58 (2005).

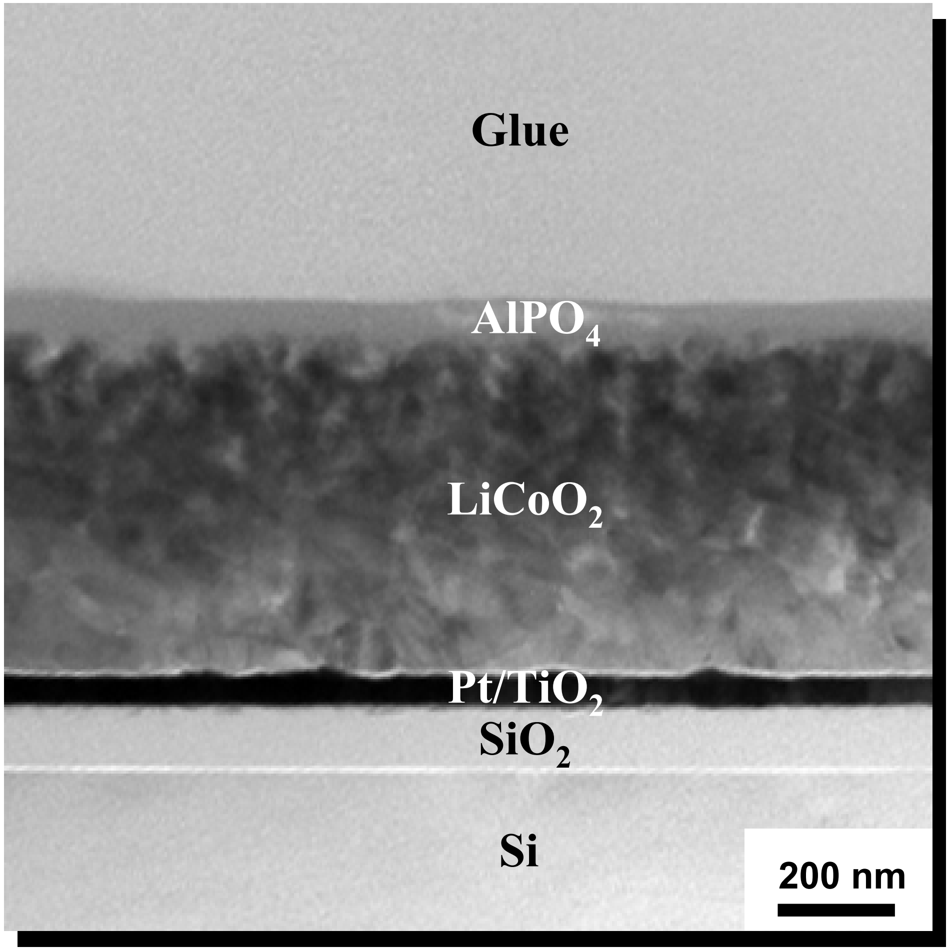
12 V Overcharge Test at 1 C Rate



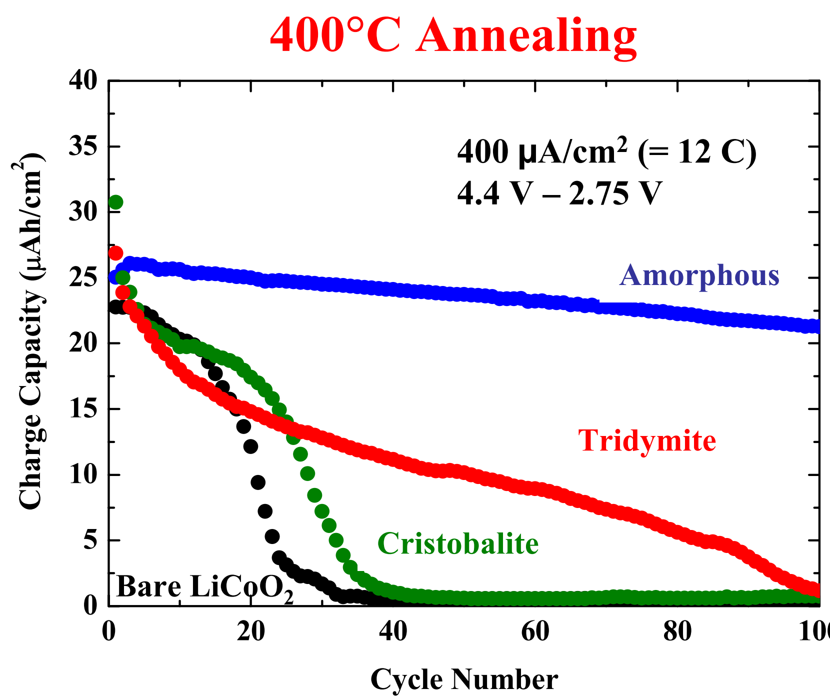
- **Short Circuit at 12 V**
  - **Direct contact between the anode and cathode as a result of separator shrinkage.**
  - **Thermal runaway with exothermic heat release.**

- **Bare and Al_2O_3-Coated $LiCoO_2$**
  - **Rapid temperature upsurge above 500°C.**
  - **Firing and explosion.**
- **$AlPO_4$-Coated $LiCoO_2$**
  - **Temperature increases to only ~60°C.**

Spin Coating of $AlPO_4$ Nanoparticles with Various Nanostructures



TEM confirms the uniform coating layer on $LiCoO_2$ thin film.



- Cycle-life performances with various nanostructures
- Optimum performance with amorphous coating layer

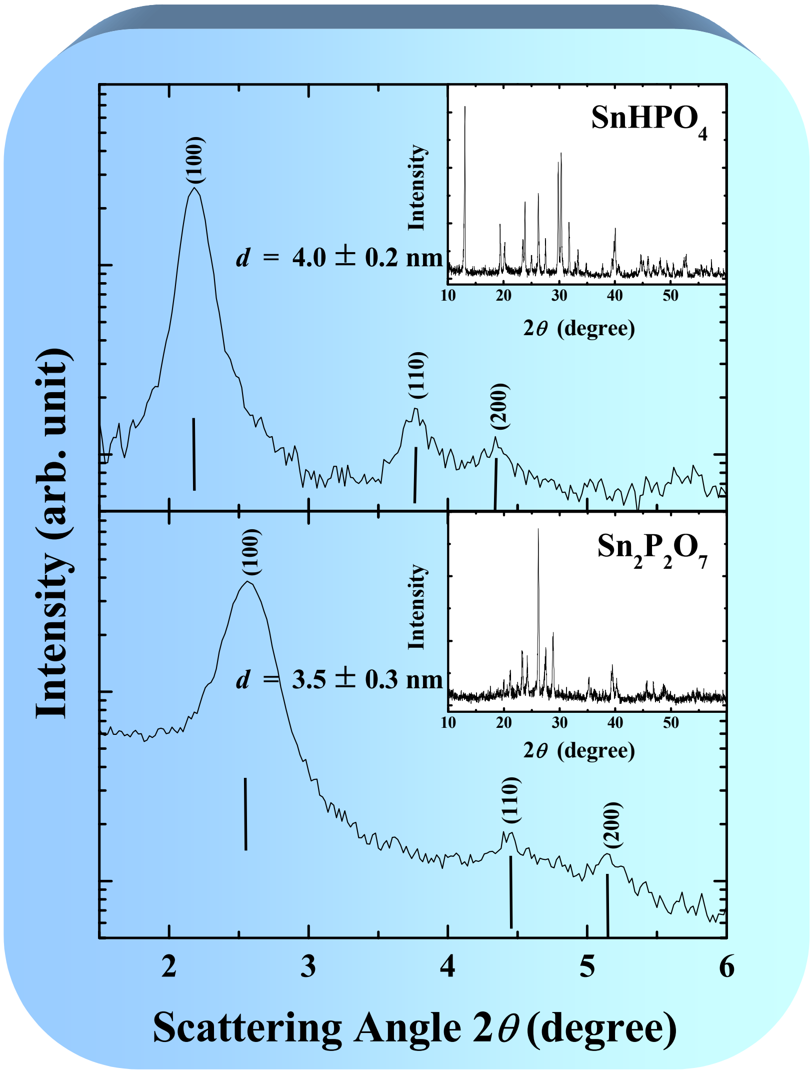
Development of High-Efficient Anode Nanomaterials

E. Kim, D. Son, T.-G. Kim, J. Cho, B. Park, K.-S. Ryu, and S.-H. Chang
Angew. Chem. Int. Ed. **43**, 5987 (2004).

C. Kim, M. Noh, M. Choi, J. Cho, and B. Park
Chem. Mater. **17**, 3297 (2005).

T. Moon, C. Kim, S.-T. Hwang, and B. Park
Electrochem. Solid-State Lett. **9**, A408 (2006).

Mesoporous Tin Phosphates



SnF_2 and H_3PO_4 dissolved in distilled water
+
CTAB ($CH_3(CH_2)_{15}N(CH_3)_3Br$)
90°C Aging

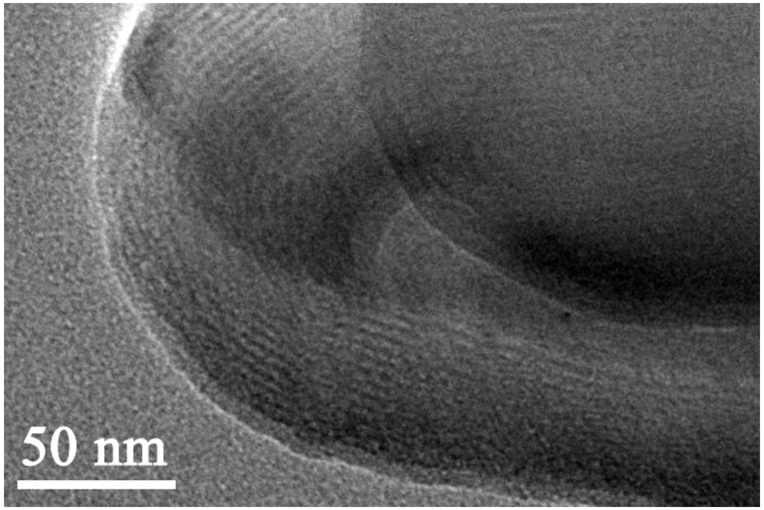
As Synthesized
Mesoporous Tin Phosphate / $SnHPO_4$

400°C Calcination
Mesoporous Tin Phosphate / $Sn_2P_2O_7$

- E. Kim, D. Son, T.-G. Kim, J. Cho, B. Park, K.-S. Ryu, and S.-H. Chang *Angew. Chem. Int. Ed.* **43**, 5987 (2004).

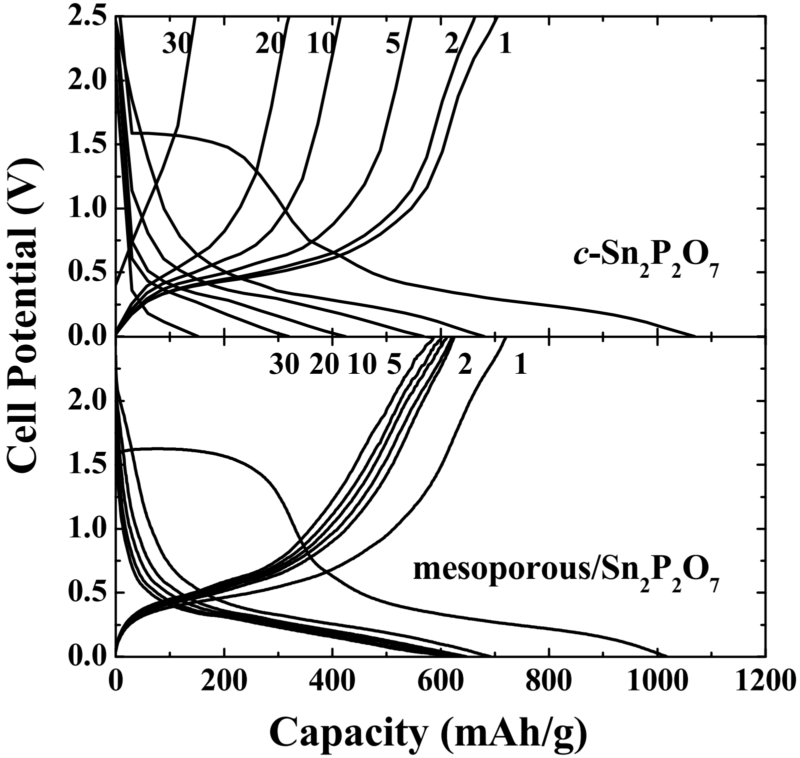
Mesoporous Tin Phosphates

TEM Image



Mesopores

Electrochemical Properties

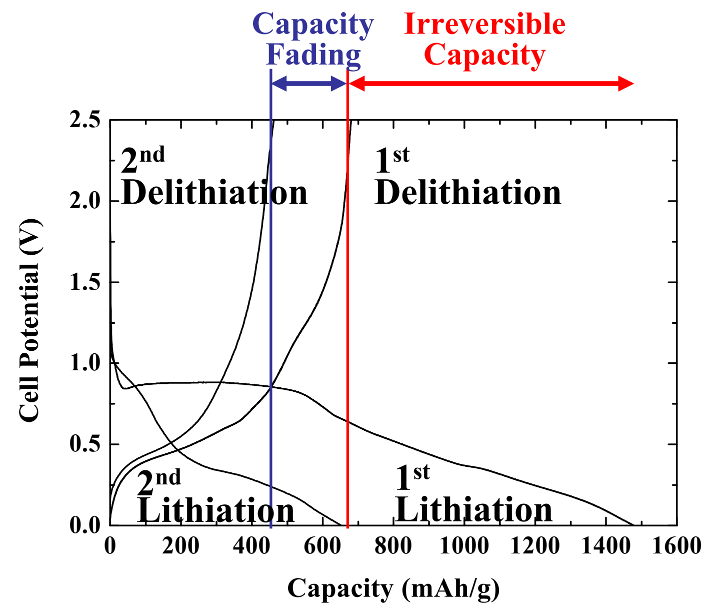


Novel Mesoporous/Crystalline Composite:
- Highest initial charge capacity (721 mAh/g)
- Excellent cycling stability (among the tin-based anodes)

SnO_2 Nanoparticles: Mechanisms and Synthesis

Problems of SnO_2 Electrode

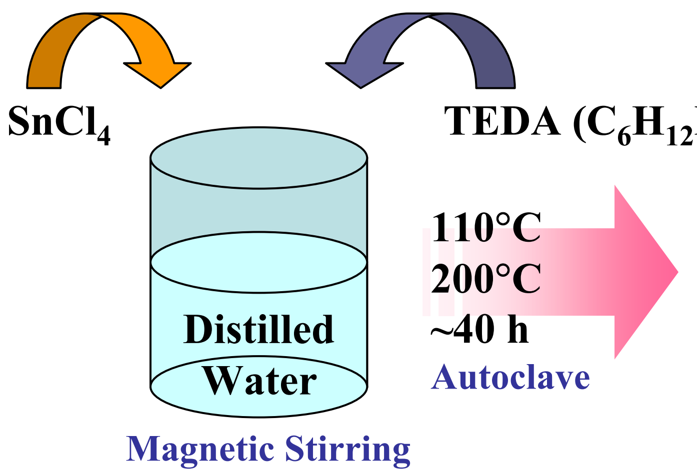
- Severe capacity loss by volume change between Li_xSn and Sn phases (~300%).
- Particles become detached and electrically inactive.



Voltage Profile of ~10 ㎛ SnO_2

- T.-J. Kim, D. Son, J. Cho, B. Park, and H. Yang *Electrochim. Acta* **49**, 4405 (2004).

SnO_2 Nanoparticles: Effective Solution



~3 nm or ~8 nm SnO_2 Nanoparticles

1st Lithiation:

$$8.4Li + SnO_2 \rightarrow 2Li_2O + Li_{4.4}Sn$$

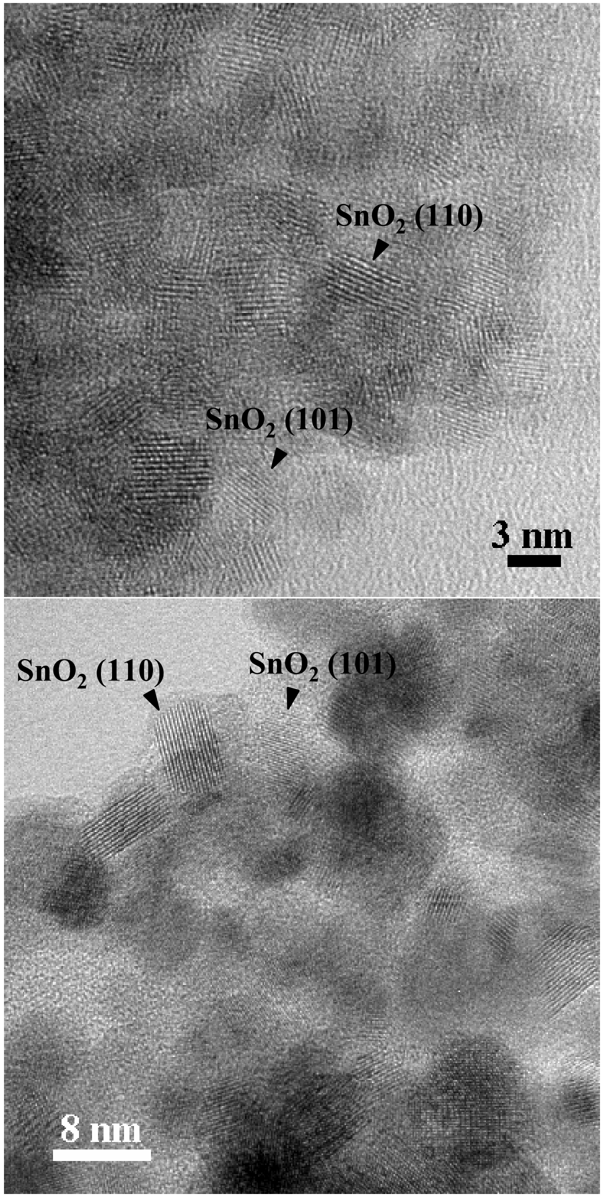
~1490 mAh/g

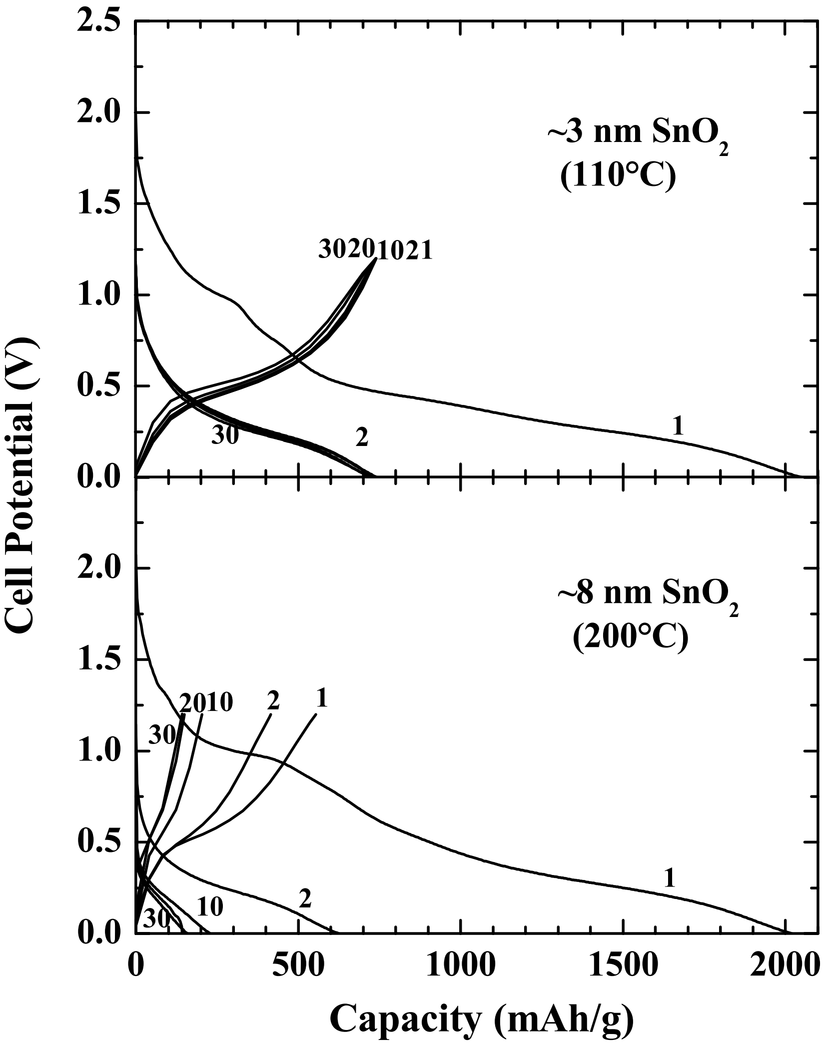
1st Delithiation:

$$4.4Li + Sn \leftarrow Li_{4.4}Sn$$

~780 mAh/g

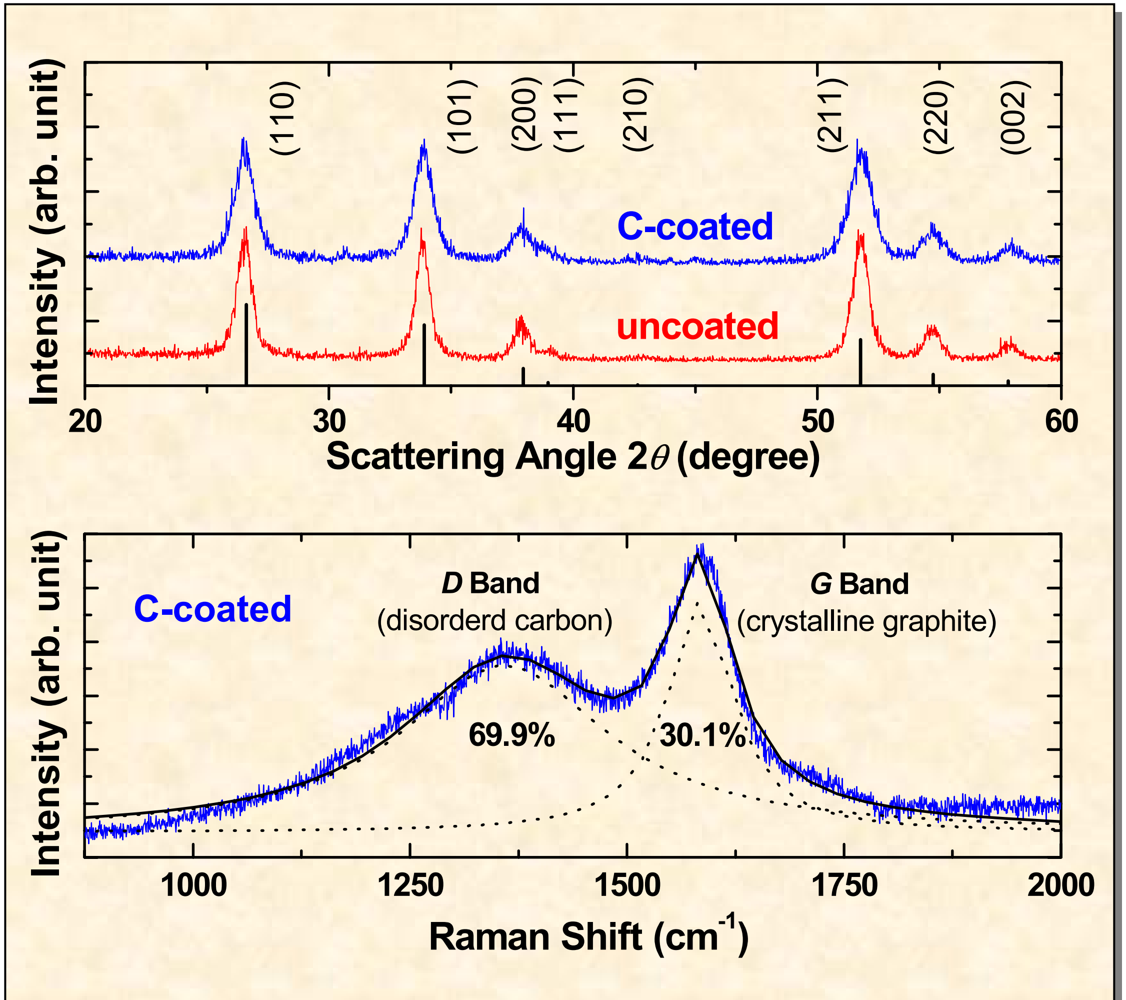
SnO_2-Nanoparticle Anode with Different Particle Sizes

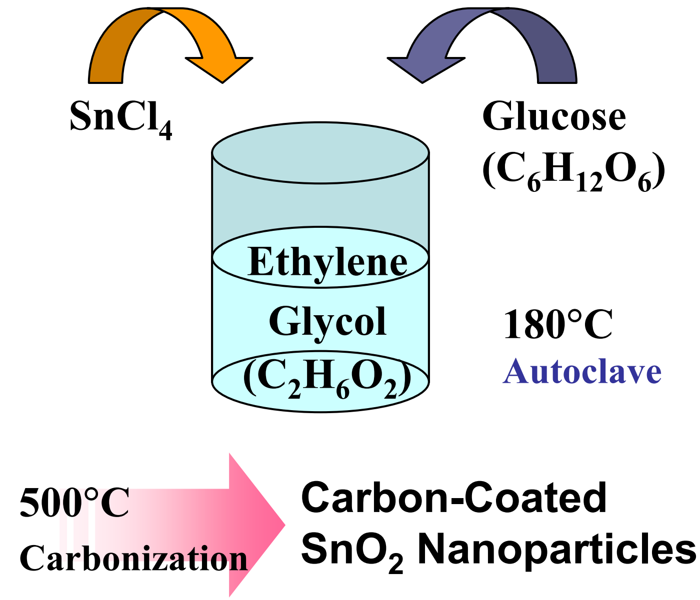




- C. Kim, M. Noh, M. Choi, J. Cho, and B. Park *Chem. Mater.* **17**, 3297 (2005).

Carbon-Coated SnO_2 Nanoparticles: Synthesis





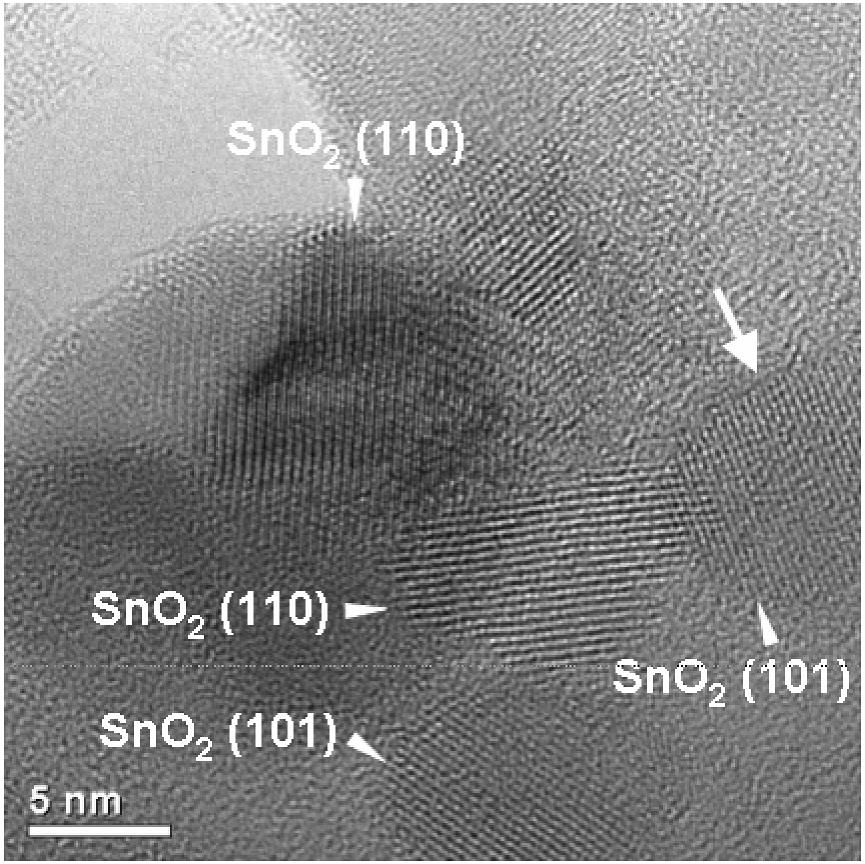
	Size	Local Strain
C-coated	8.8 ± 0.9 nm	0.59 ± 0.13%
uncoated	13.2 ± 1.1 nm	0.13 ± 0.08%

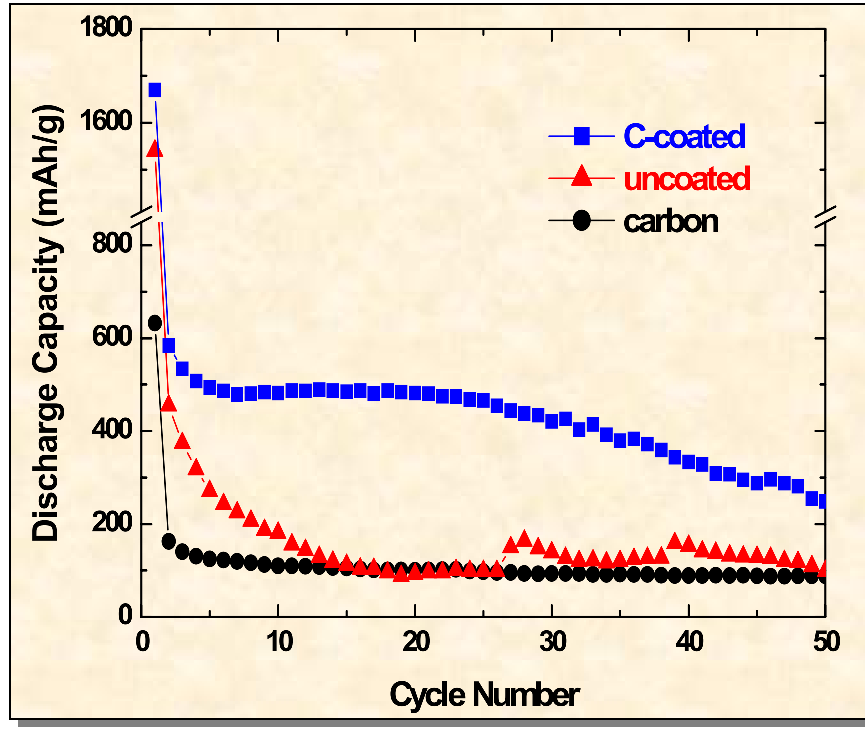
	SnO_2 (wt. %)	C (wt. %)	H (wt. %)
C-coated	90	4.9	0.35
uncoated	97	0.061	0.074

by ICP

Disordered-carbon-coated SnO_2 nanoparticles

Carbon-Coated SnO_2 Nanoparticles





➤ T. Moon, C. Kim, S.-T. Hwang, and B. Park
Electrochem. Solid-State Lett. **9**, A408 (2006).

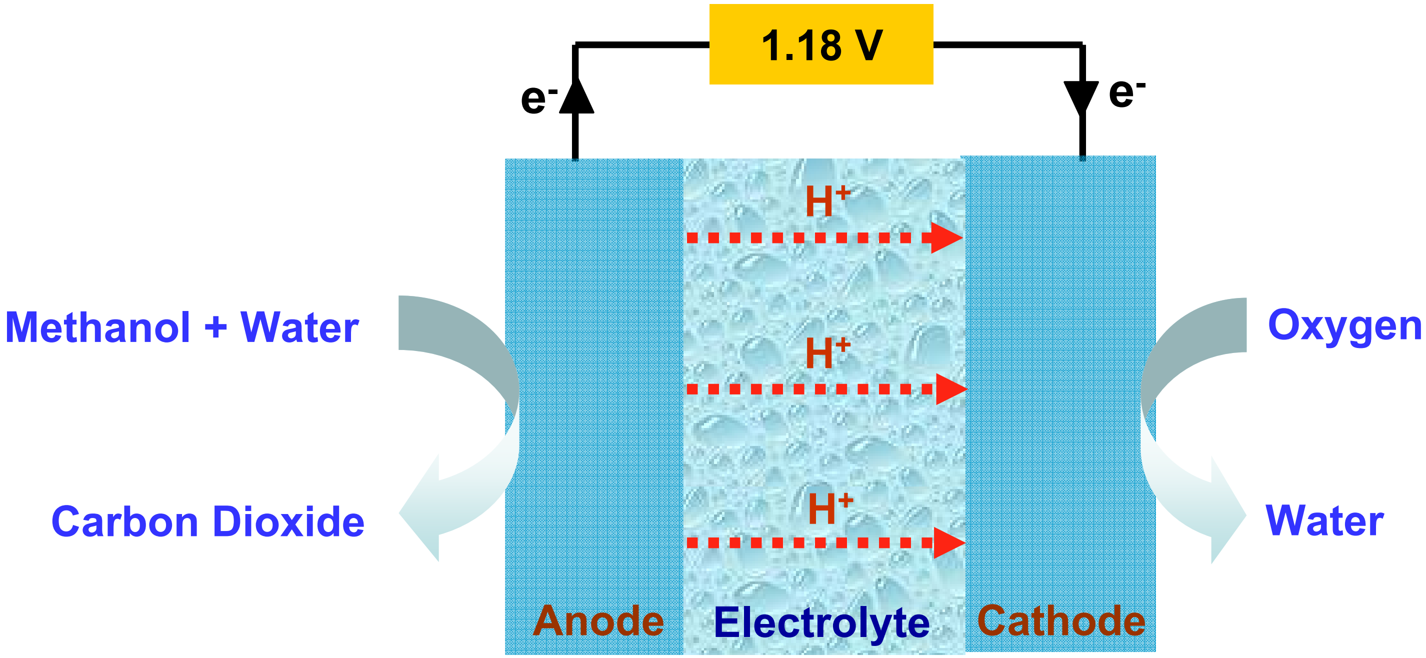
- **Most of the nanoparticles are well dispersed.**
- **SnO_2 nanoparticles are surrounded by disordered carbon. (graphite-interlayer spacing ≅ 0.35 nm)**
- **Capacity contribution of disordered carbon is ~10 mAh/g.**

Nanostructured Pt-$FePO_4$ Thin-Film Electrodes for Methanol Oxidation

B. Lee, C. Kim, Y. Park, T.-G. Kim, and B. Park
Electrochem. Solid-State Lett. **9**, E27 (2006).

C. Kim, B. Lee, Y. Park, J. Lee, H. Kim, and B. Park
Appl. Phys. Lett. (submitted).

Direct Methanol Fuel Cell



$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
$E_a = 0.05$ V (Methanol Oxidation)

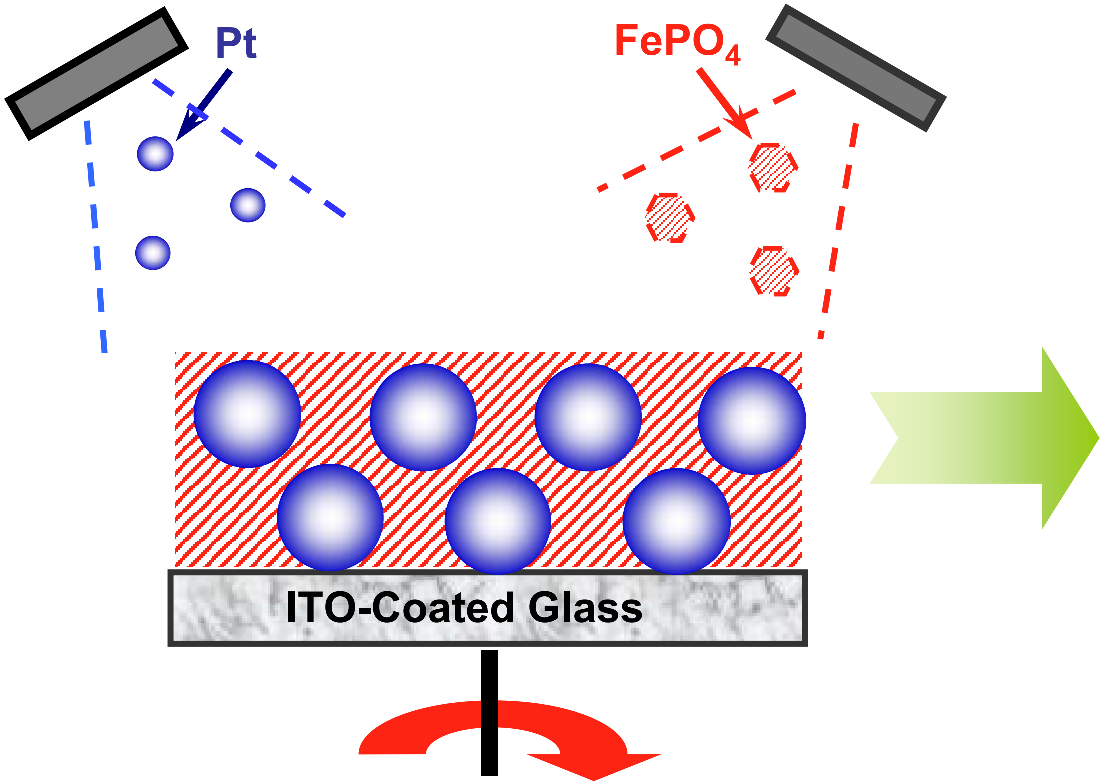
$3/2\, O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
$E_c = 1.23$ V (Oxygen Reduction)

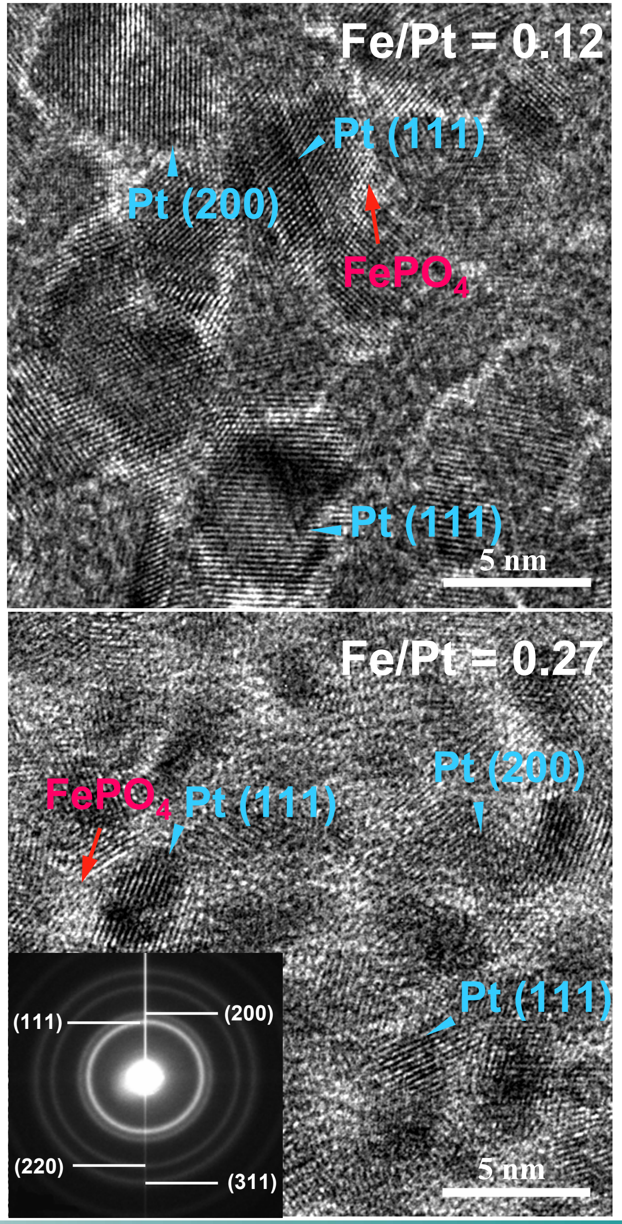
➢ **Goals:**
- Catalytic Activity
- Stability

➡ ***Nanocomposite Materials***

Nanostructured Pt-$FePO_4$ Thin-Film Electrode

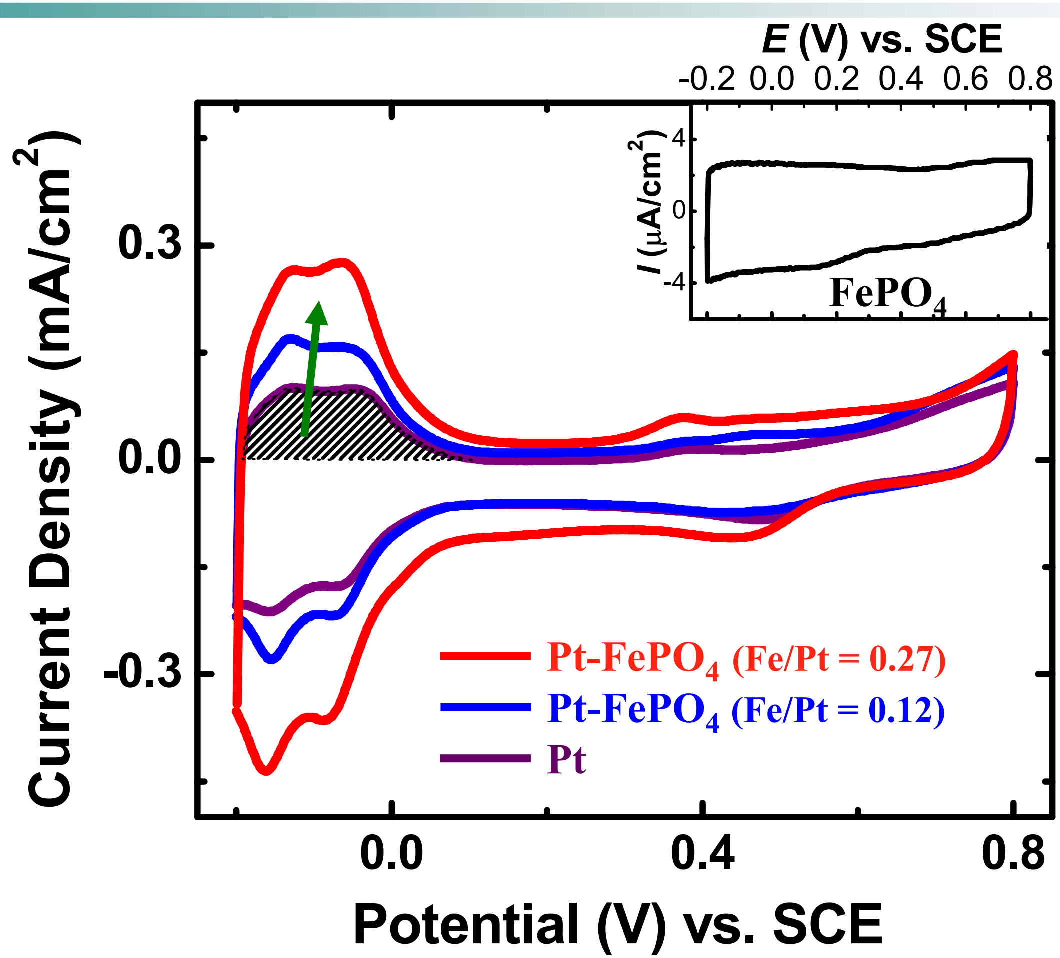
Co-Sputtering System





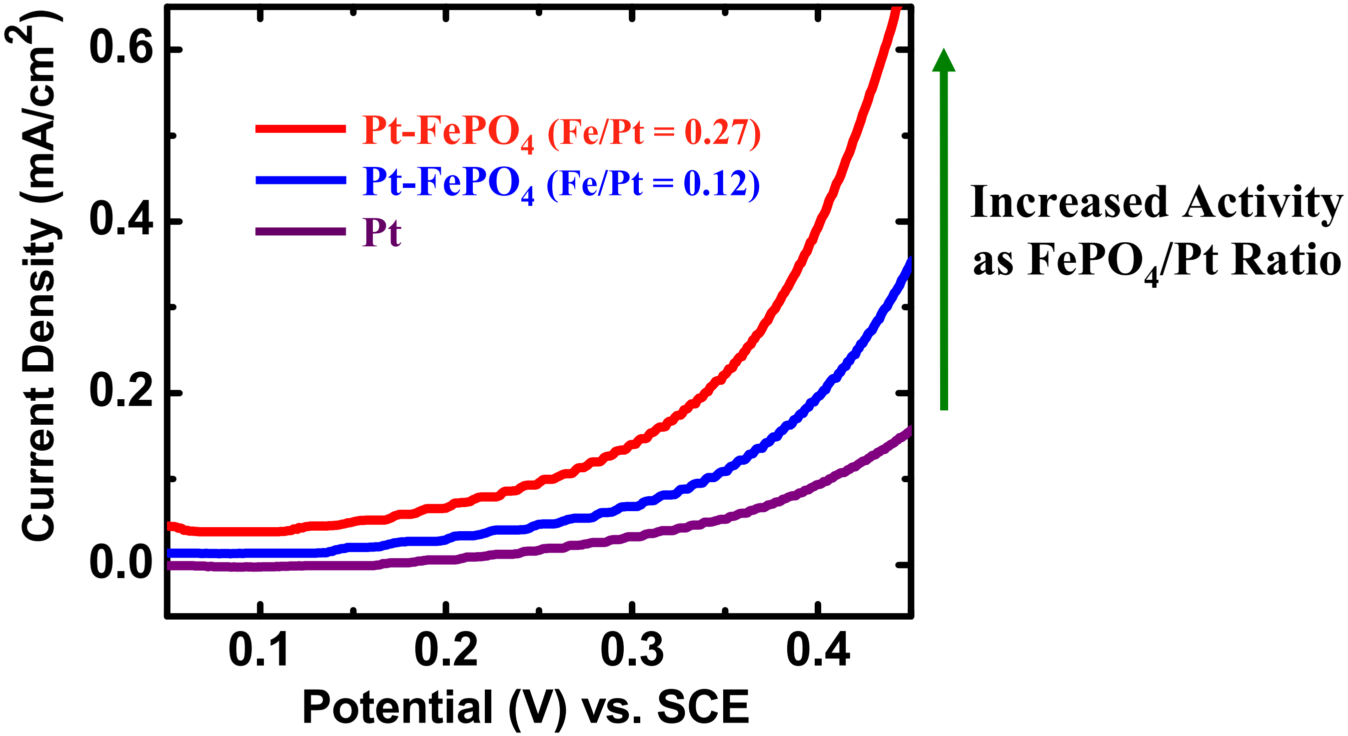
❖ Metal/Metal-Phosphate Nanocomposites
❖ Control of Nanostructures

Increased Active Surface Area



- ❖ Cyclic voltammograms in 0.5 M H_2SO_4 (-0.2 and 0.8 V at 50 mV/s)
- ❖ Shaded Area: Oxidation of hydrogen adsorbed on Pt

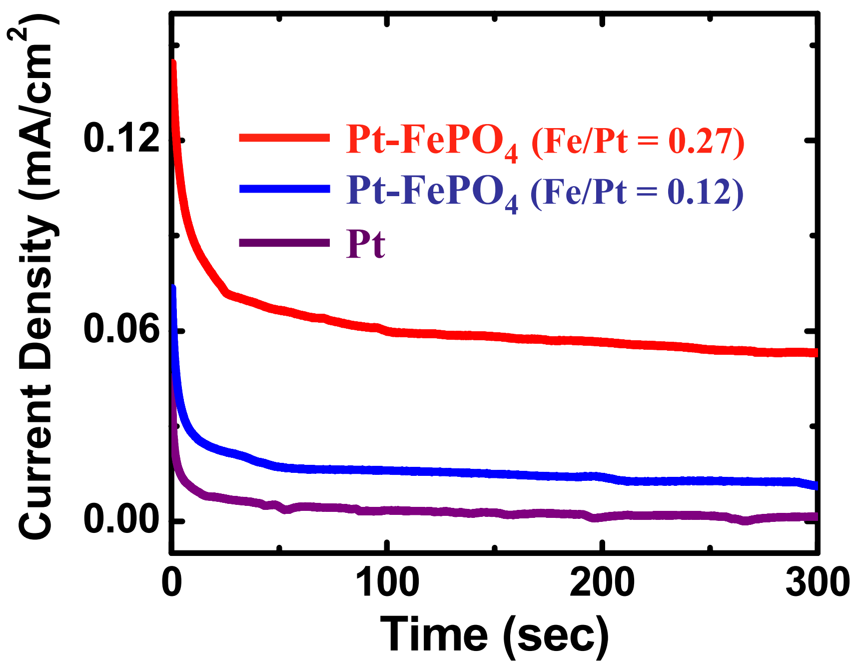
Enhanced Methanol Oxidation



❖ Pt-$FePO_4$ nanocomposite electrodes:

- Higher current density for methanol oxidation
  - Increased active surface area of Pt nanophases
  - Enhanced activity of Pt by the possible ability of $FePO_4$ matrix

Steady-State Activities



- $Pt\text{-}FePO_4$ Nanocomposites:
  - High steady-state activity
  - Low decay rate
- As the atomic ratio (Fe/Pt) increases, the steady-state activity is enhanced.

➡ • Effective transfer of protons
• Improved CO oxidation

❖ *Summary*

Electrode	Active surface area	Current density at 0.3 V	Current density at 0.3 V at 300 sec
$Pt\text{-}FePO_4$ (Fe/Pt = 0.27)	5.7 cm^2	140 $\mu A/cm^2$	53 $\mu A/cm^2$
$Pt\text{-}FePO_4$ (Fe/Pt = 0.12)	3.6 cm^2	70 $\mu A/cm^2$	13 $\mu A/cm^2$
Pt	2.5 cm^2	35 $\mu A/cm^2$	2 $\mu A/cm^2$

Conclusions

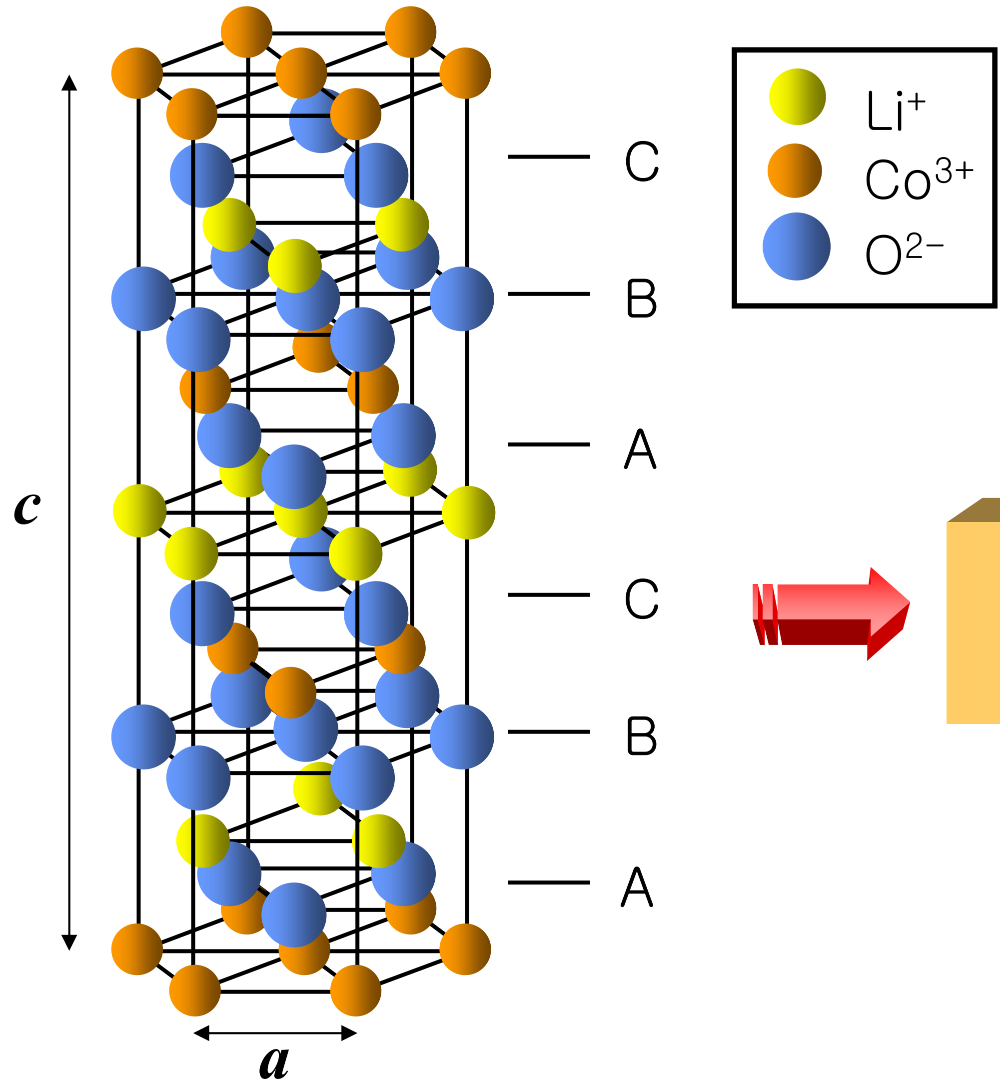
Nanoscale Interface Control

- Nanostructures?
- Compositions?
- Mechanisms?

http://ep.snu.ac.kr

Current and Former Members

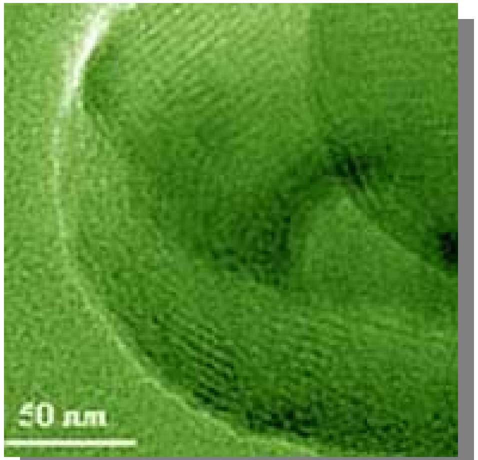
Structure of $LiCoO_2$



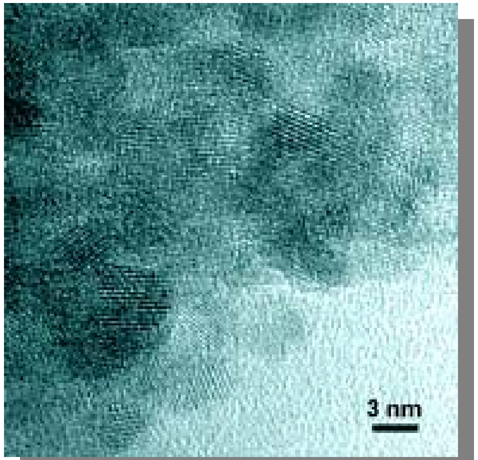
$Li_{1-x}CoO_2$ for $0<x<0.5$

Space group: $R\bar{3}m$
a = 2.81 Å and c = 14.08 Å

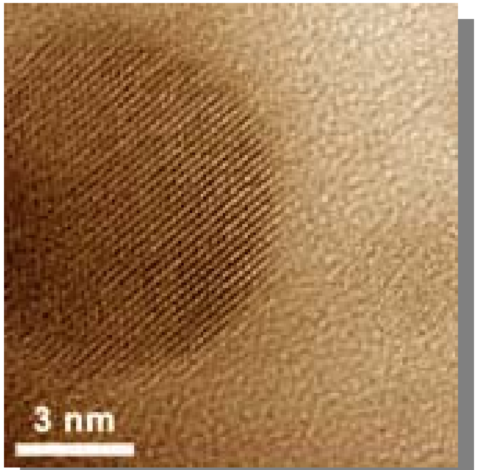
Synthesis/Control of Nanostructures for Desirable Applications



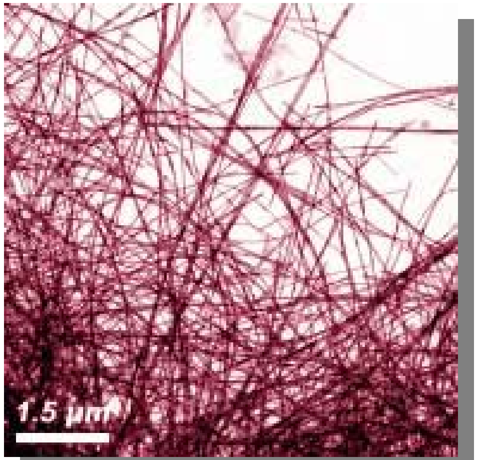
Mesoporous Structure



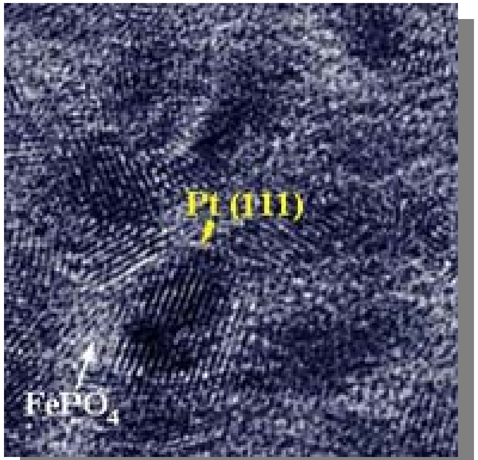
Oxide Nanoparticles



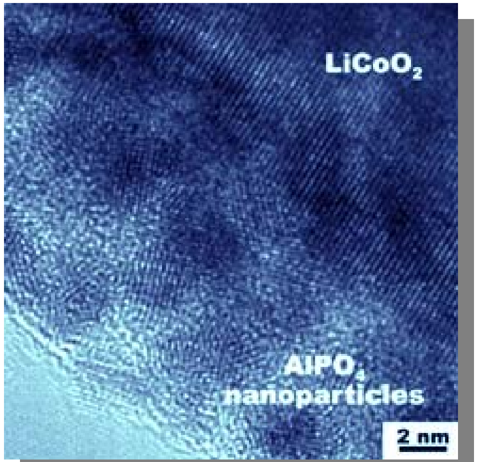
Metal Nanoparticles



Nanowires

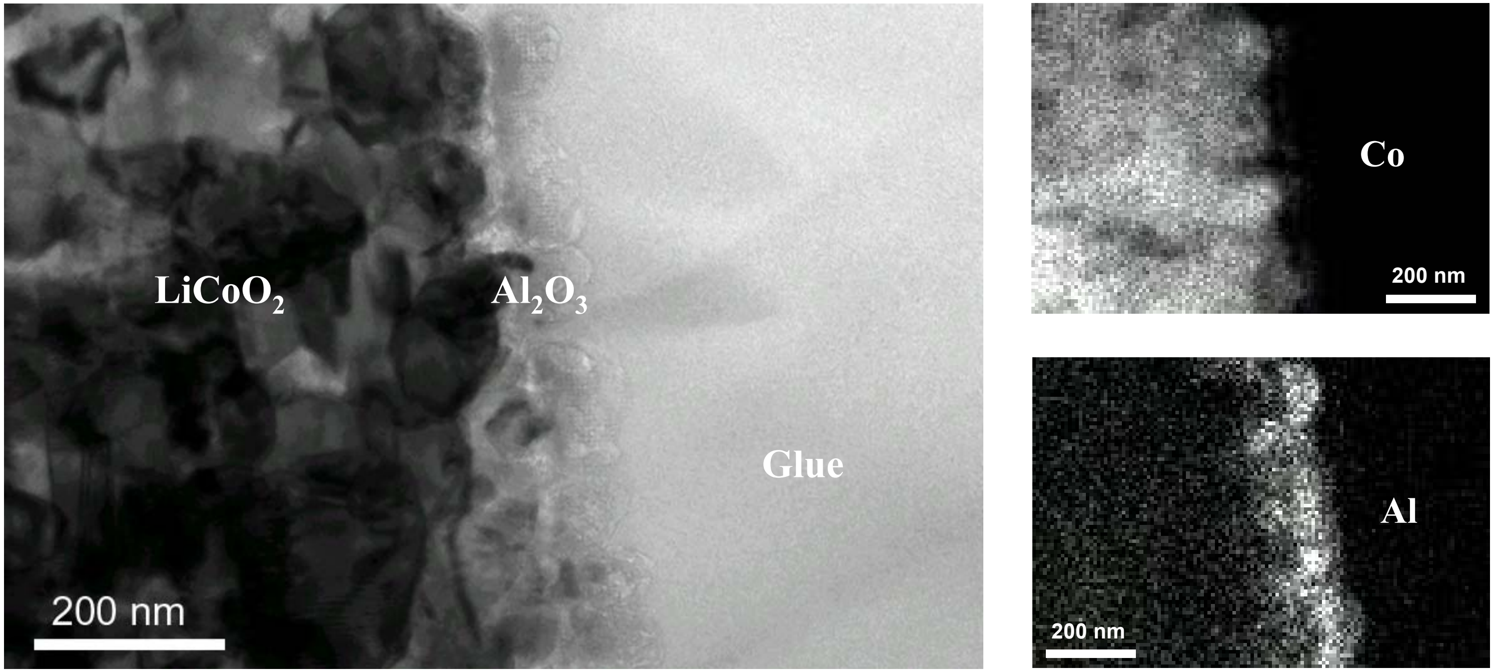


Nanocomposites



Nanoscale Coating

Cross-Sectional TEM



- TEM image shows continuous Al_2O_3-coating layer on $LiCoO_2$ thin film.
- EDS shows Al components in the coating layer.

Sample Preparation

Metal-Oxide Coating

$M(OOC_8H_{15})_2(OC_3H_7)_2$

AlPO$_4$-Nanoparticle Coating

$Al(NO_3)_3 \cdot 9H_2O$ + $(NH_4)_2HPO_4$

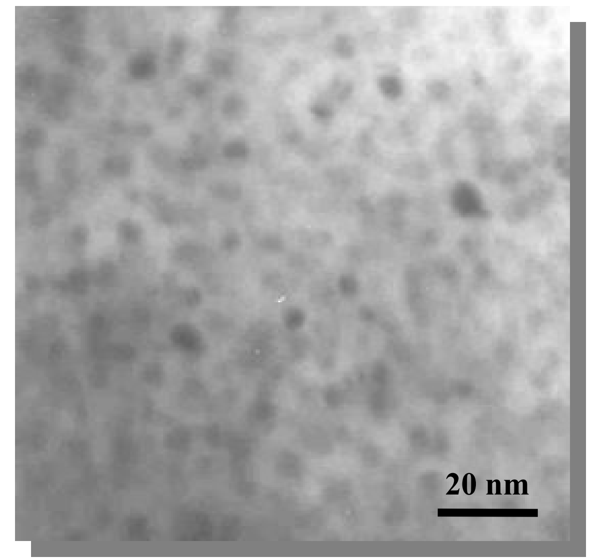
Isopropanol (Flammable)

Distilled Water

Mixing with $LiCoO_2$ Powders (~10 μm in diameter)

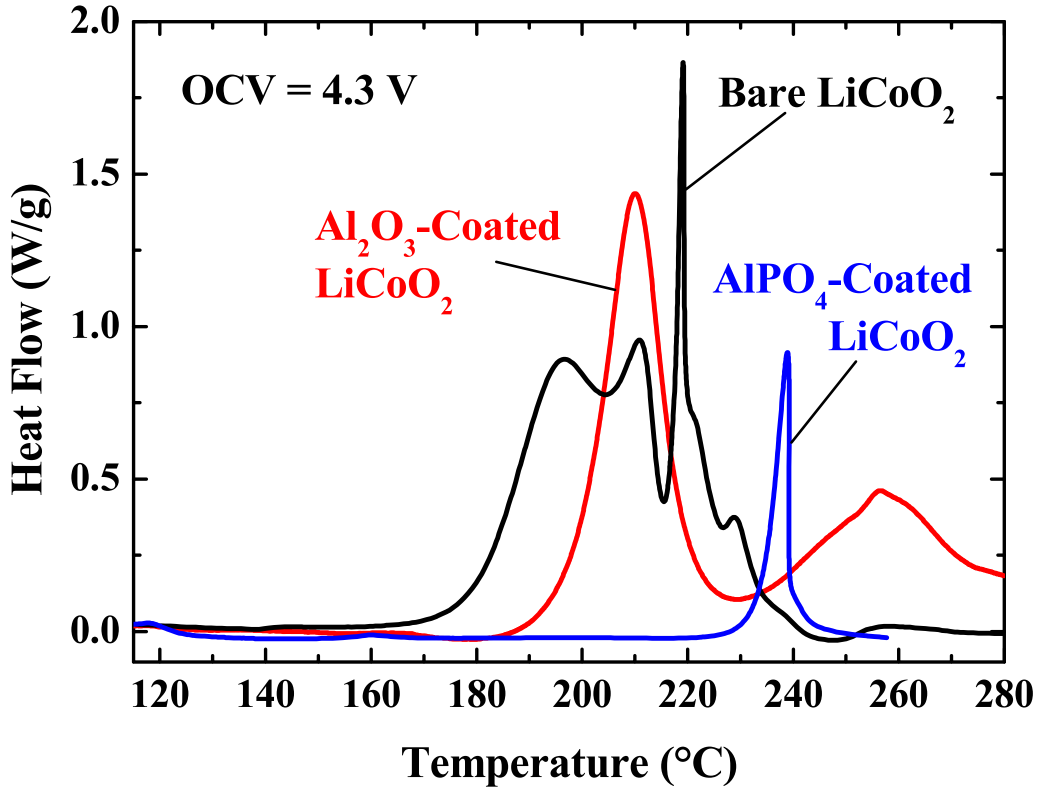
Drying at 130°C and firing at 700°C for 5 h

AlPO$_4$-Nanoparticle Solution



- **AlPO$_4$-Nanoparticle Coating**
  - Continuous Coating Layer
  - Easy Control (shape, size, coating thickness)

DSC Scans of 4.3 V-Charged Cathodes

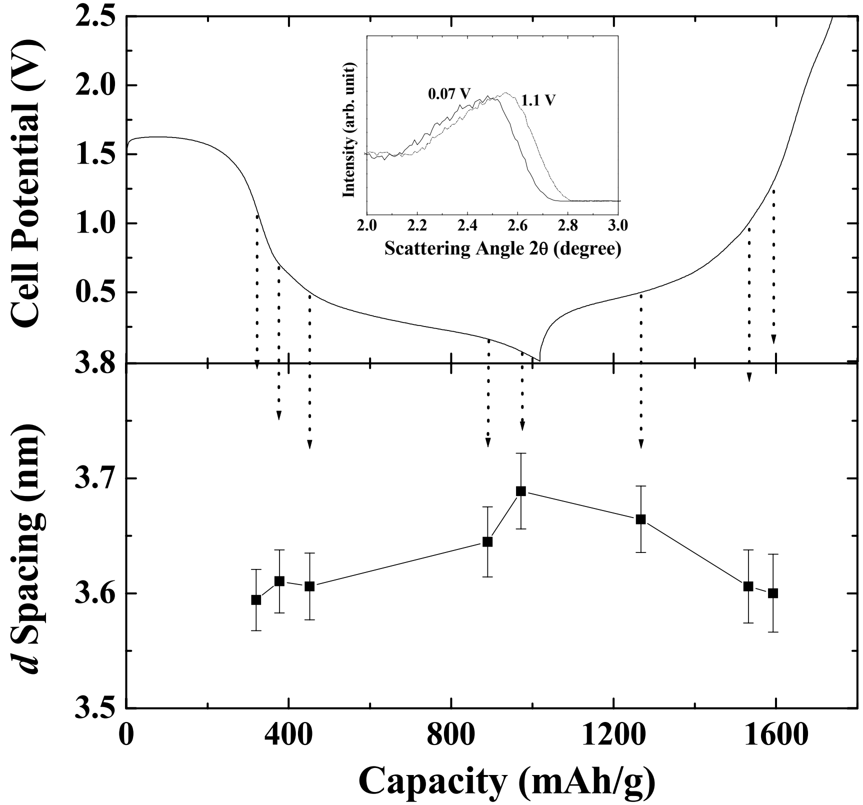


	Onset Temp.	Exothermic Heat
Bare $LiCoO_2$	~170°C	~650 J/g
Al_2O_3-Coated	~190°C	~550 J/g
$AlPO_4$-Coated	~230°C	~100 J/g

$AlPO_4$-coating layer effectively retards the initiation of oxygen generation.

Mesoporous Tin Phosphates

The Corresponding *d* Spacing



Reaction Mechanisms

$$12.8\ Li + Sn_2P_2O_7 \rightarrow 2\ Li_{4.4}Sn + Li_3PO_4 + LiPO_3$$
$$\leftrightarrow 8.8\ Li + 2\ Sn + Li_3PO_4 + LiPO_3$$

- The *d* spacing expands and shrinks with Li alloying/dealloying.
- The mesopores do not collapse during discharge and charge.