Cathode Materials with Zero Strain for Li-Ion Cell

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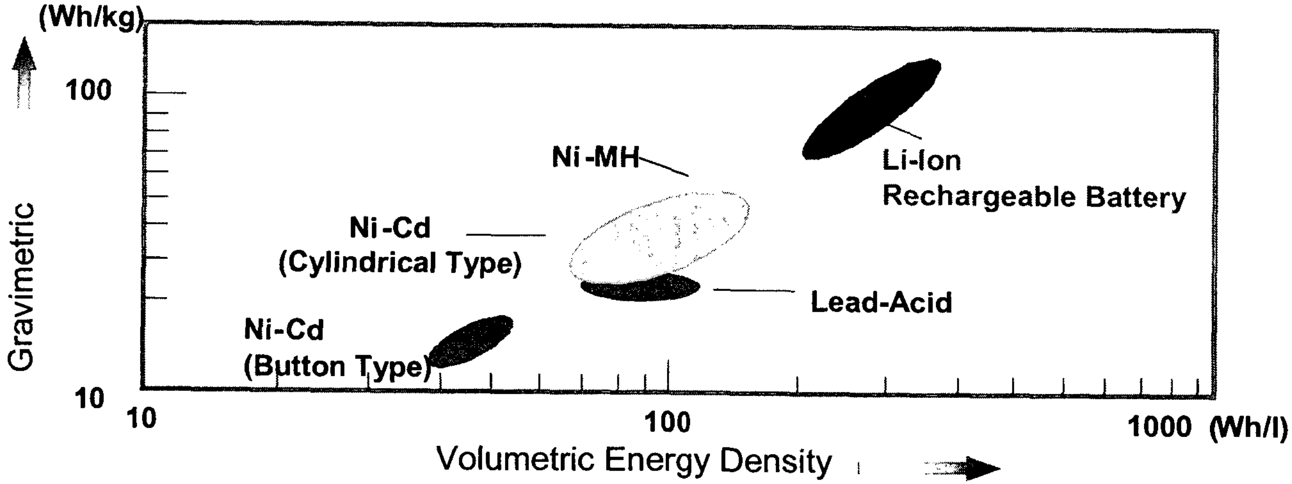
Li-Ion Battery Technology

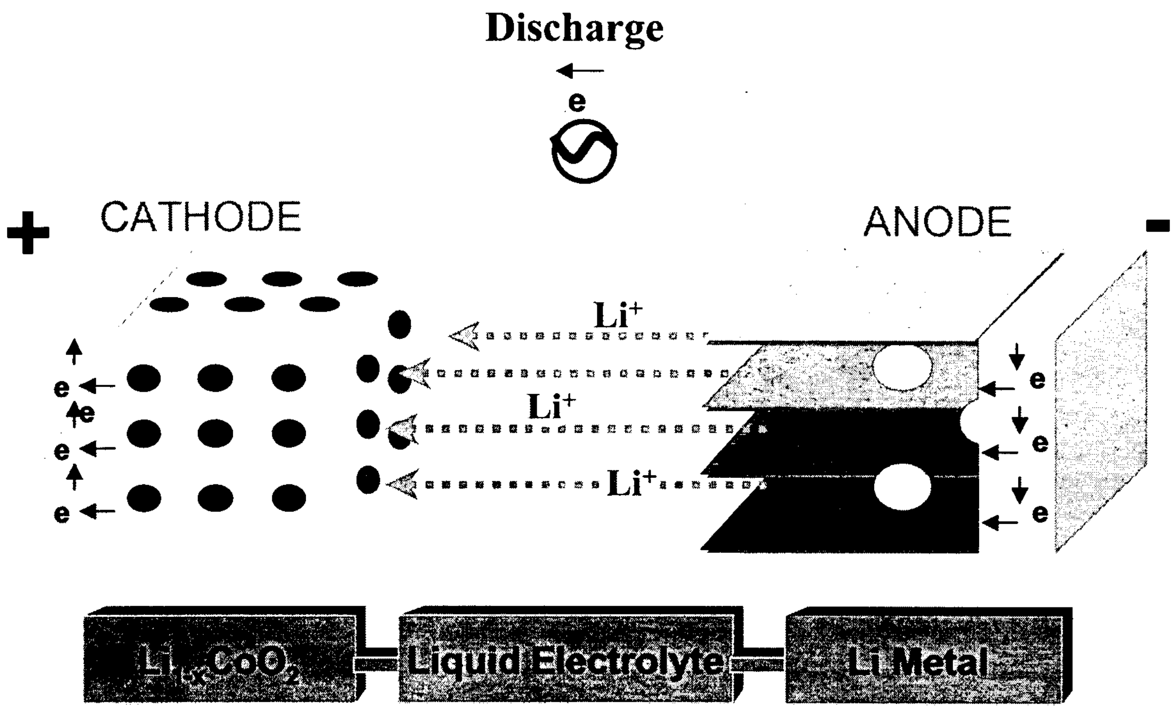
Energy densities of rechargeable batteries



$LiCoO_2$:
Capacity fade of cathode during cycling

→ **Solution ?**

Li-Ion Battery Mechanisms

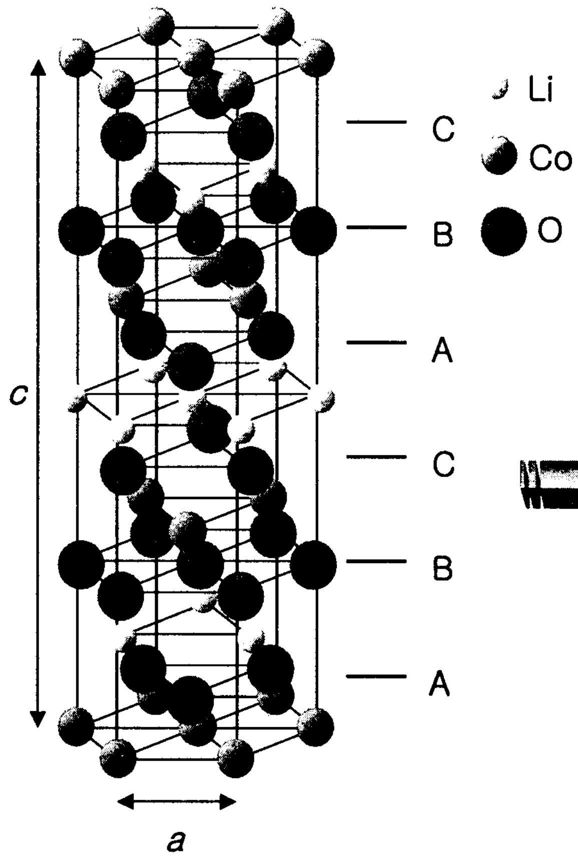


Li Deintercalation (charge)
Li Intercalation (discharge)

Cycling Stability of Various Cathode Materials

Cathode Materials	Capacity	Voltage Range	References
$LiCoO_2$	157 mAh/g (initial) 120 mAh/g (50 cycles)	between 4.35 and 2.5 V 0.4 mA/cm^2	*J. Electrochem. Soc.* **146**, 473 (1999)
$LiAl_{0.25}Co_{0.75}O_2$	127 mAh/g (initial) 64 mAh/g (9 cycles)	between 4.5 and 2.0 V 0.4 mA/cm^2	*J. Electrochem. Soc.* **146**, 862 (1999)
$LiMg_{0.05}Co_{0.95}O_2$	143 mAh/g (initial) 125 mAh/g (30 cycles)	between 4.3 and 3.0 V 0.5 mA/cm^2	*J. Electrochem. Soc.* **144**, 3164 (1997)
$LiMnO_2$	35 mAh/g (initial) 130 mAh/g (40 cycles) 125 mAh/g (130 cycles)	between 4.4 and 2.0 V 45.9 mA/g	*J. Electrochem. Soc.* **146**, 3217 (1999)
$LiMn_2O_4$	95 mAh/g (initial) 75 mAh/g (30 cycles)	between 4.3 and 3.4 V 265 μA/cm^2	*J. Electrochem. Soc.* **147**, 874 (2000)
$LiNiO_2$	220 mAh/g (initial) 70 mAh/g (100 cycles)	between 4.3 and 3.0 V 1 mA/cm^2	*J. Power Sources* **68**, 553 (1997)
$LiNi_{0.70}Co_{0.30}O_2$	160 mAh/g (initial) 108 mAh/g (100 cycles)	between 4.3 and 2.75 V 1 C rate	*J. Electrochem. Soc.* **146**, 3571 (1999)
$Li_{3.1}Mn_{0.91}Cr_{1.09}O_4$	220 mAh/g (initial) 175 mAh/g (100 cycles)	between 4.5 and 2.0 V 0.1 C rate	*Electrochem. Solid-State Lett.* **3**, 355 (2000)

Structure of $LiCoO_2$



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

Space group: $R\bar{3}m$
$a = 2.816$ Å and $c = 14.051$ Å

Sol-Gel Coating of Metal Oxides on $LiCoO_2$ (~10 ㎛)

- **Coating Solution:**
  Metal ethylhexanate-diisopropoxide [$M(OOC_8H_{15})(OC_3H_7)_2$]
- **Fired at 400℃ for 10 h**

❖ **Coating materials: ZrO_2, Al_2O_3, TiO_2, B_2O_3, and SiO_2**

Coating materials	ZrO_2	Al_2O_3	TiO_2	B_2O_3	SiO_2
Fracture Toughness ($MPa\sqrt{m}$)	8 ~ 12	2.7 ~ 4.2	2.38	1.44	0.70

- *Angew. Chem. Int. Ed.* **40**, 3367 (2001)
- *J. Electrochem. Soc.* **148**, A1110 (2001)
- *Chem. Mater.* **12**, 3788 (2000)

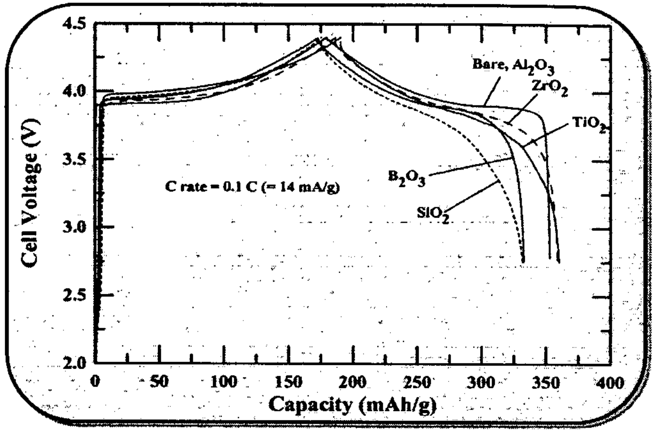
Electrochemical Cycling Test of Coated $LiCoO_2$

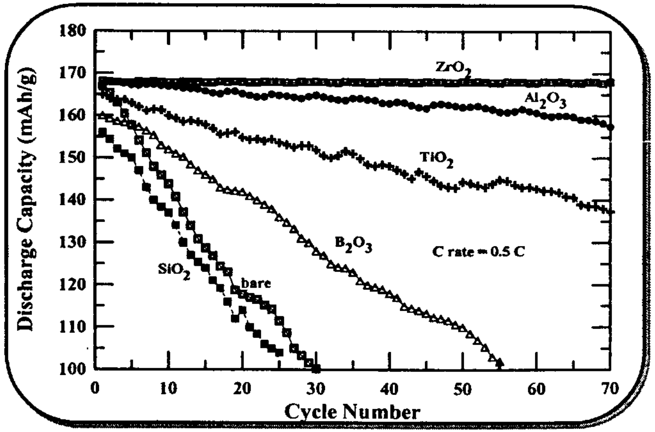
❑ Li / Coated $LiCoO_2$

Metal oxide	Initial capacity	Capacity retention After 70 cycles
ZrO_2	168 mAh/g	100%
Al_2O_3	168 mAh/g	94%
TiO_2	165 mAh/g	83%

- Coin-type half cell ($Li/LiCoO_2$)
- Cell voltage : between 4.4 and 2.75 V
- Current rate
  0.1 C (= 14 mA/g) and 0.2 C rates for 1 and 2 cycles
  0.5 C rate for the rest 67 cycles

➢**Correlate with fracture toughness of metal oxides**

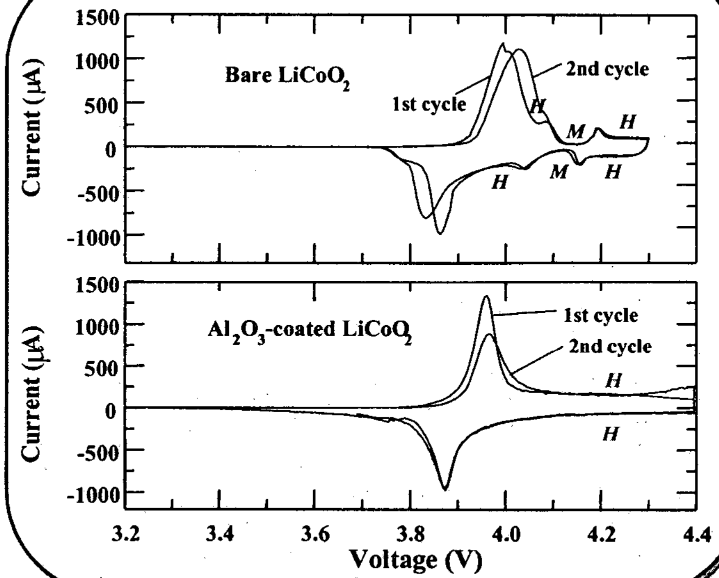




❑ Li / Bare $LiCoO_2$

- Initial Capacity : 168 mAh/g
- Capacity after 30 cycles : 100 mAh/g

Cyclic Voltammograms

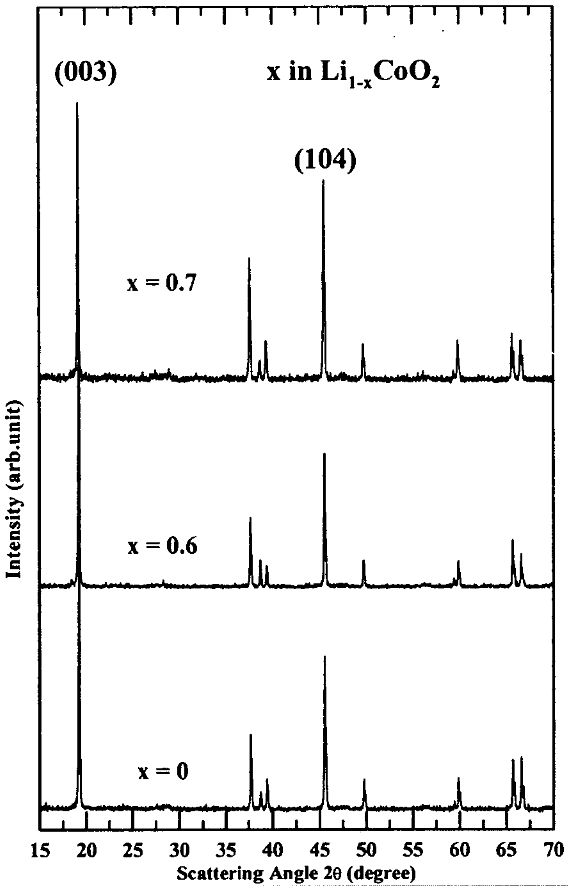


The scan rate: 0.02 mV/sec

- Symbols *H* and *M*
  - hexagonal and monoclinic phases
- Peaks in the 4.1–4.2 V range
  - coated $LiCoO_2$: no monoclinic phase
  - bare $LiCoO_2$: phase transition from *H* to *M*
- Sharper peak between 3.9 and 4.1 V (coated $LiCoO_2$)
  - enhanced Li-diffusion rates

Disappearance of phase transition improves capacity retention of the cathode

XRD Measurements



ZrO_2 coating

XRD data with the corresponding charge state (x in $Li_{1-x}CoO_2$)

(*ex-situ* measurements)

Coated samples do not show any evidence of metal oxide.

- **The crystallinity of thin-film metal oxide is poor.**
- **A thin-film $LiCo_{1-y}M_yO_2$ solid solution is formed near the particle surface (tens of nm range).**

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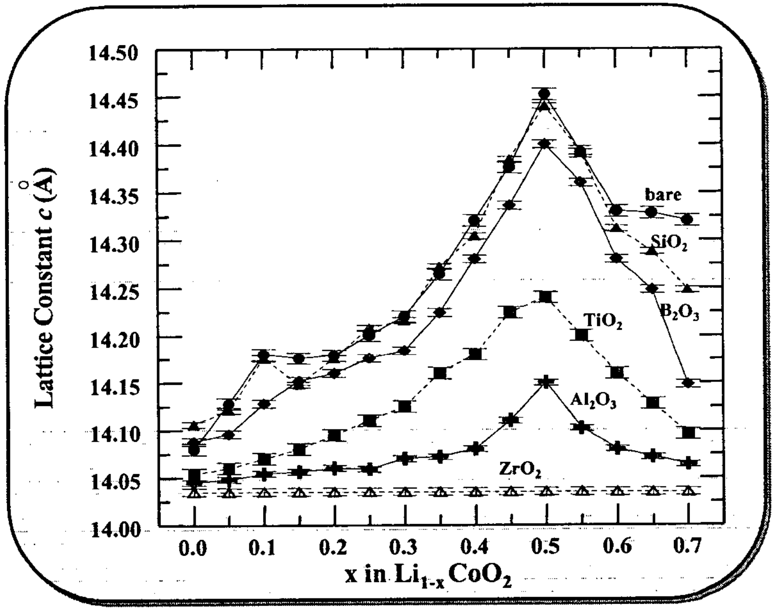
Structural Stability of Coated $LiCoO_2$



Change of lattice constant *c*

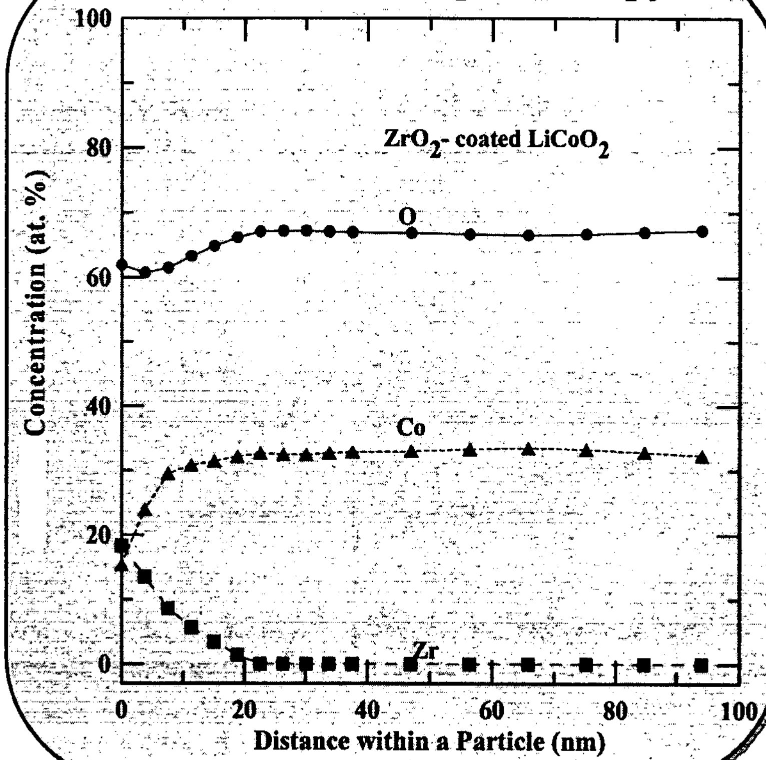
- ZrO_2- coated $LiCoO_2$: negligible
  Al_2O_3-coated $LiCoO_2$: 0.75%
- Bare $LiCoO_2$: 2.6%

The fracture toughness of coated oxides
(ZrO_2 > Al_2O_3 > TiO_2 > B_2O_3 > SiO_2)

The encapsulation of $LiCoO_2$ powders by thin-film coating of high-fracture-toughness oxides (ZrO_2-coated $LiCoO_2$: Zero-Strain Compound)

Concentration Profile in Coated $LiCoO_2$

Auger electron spectroscopy

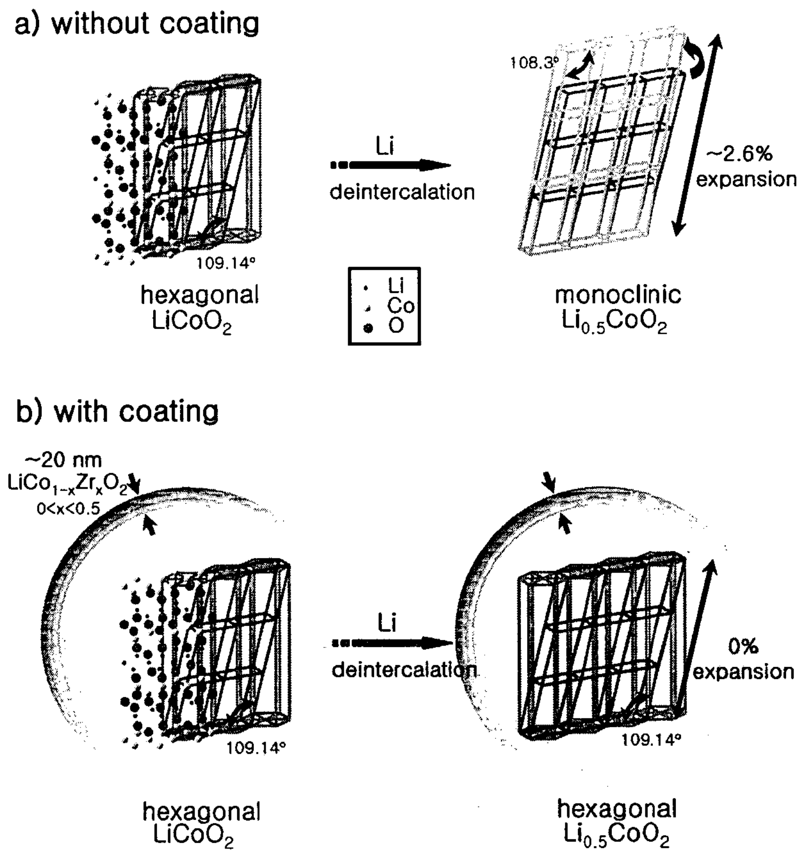


Zr atoms were distributed within ~20 nm of the particle surface

Solid-solution formation near the particle surface by ZrO_2 sol-gel coating

Currently performing cross-sectional TEM to identify the morphology of thin-layer coating and concentration (interdiffusion) profile

Schematic Illustration of Enclosing Effect



Enclosure of $LiCoO_2$ powders by a fracture-toughened metal-oxide coating

Suppress the non-uniform lattice-constant changes during Li deintercalation

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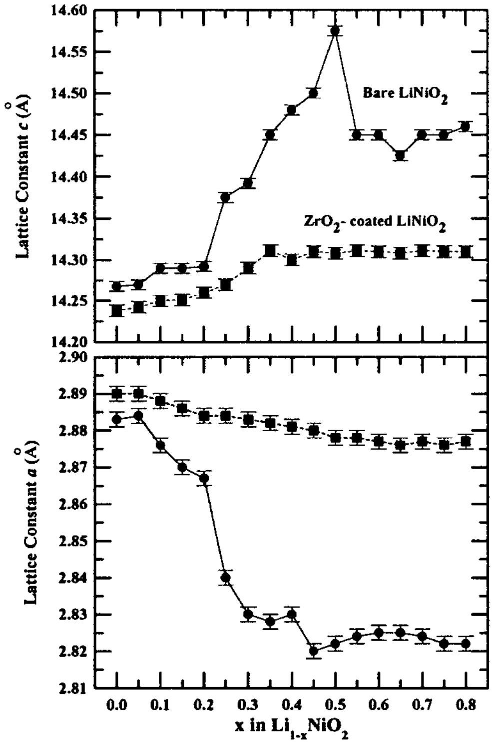
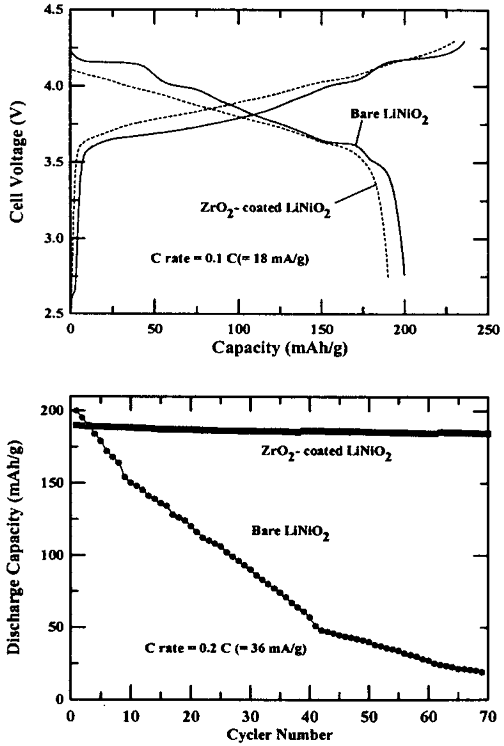
ZrO_2-Coated $LiNiO_2$

Structural Modification



Cycle Performance



➢ *Electrochem. Solid-State Lett.* **4**, A159 (2001)

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Conclusions

1. Thin-film coating of high-fracture-toughness oxides significantly enhanced the structural stability of $LiCoO_2$ materials.

2. The order of capacity retention correlates well with the fracture toughness of the coated thin-film oxides.

3. A zero-strain $LiCoO_2$ cathode material was produced by thin-film coating of high-fracture-toughness oxides (ZrO_2) on the particle surface.

4. The mechanism needs to be further identified.