fullerene in solution increases. When the fullerene was removed from the solution, we could release DNA out of the condensate. Thus, when the fullerene in the $R = 2.6$ mixture was extracted with $CHCl_3$, AFM analysis of the aqueous phase (the same sample used for the gel analysis in Figure 1) largely showed individual DNA molecules together with a small number of large aggregates surrounded by numerous partially folded DNA molecules (Figure 3g). The image in Figure 3g resembles the classical picture of an *E. coli* nucleus from which histone protein was washed away after surfactant treatment.[7]

In summary, we have demonstrated that the fullerene **1** can fold a supercoiled DNA molecule into a single-molecule condensate through adhesion of DNA double strands. The rough estimate indicated that the fullerene folds the DNA with only a small increase of the volume of DNA. Such high efficiency of histone-like activity is remarkable since natural histone protein forms a chromatin structure with a volume increasing of ten to hundred times that of DNA.[8] The formation of disklike condensates composed of a single to a few DNA molecules is unique among the cases of other DNA-condensating agents based on lipid or dendrimers, which create much larger and less structurally defined DNA aggregates.[9] In the light of remarkably high tendency of water-soluble fullerene to form robust vesicles,[4] the process of fullerene–DNA condesation must involve collisions between a fullerene vesicle and a DNA molecule rather than a molecule–molecule interaction. The condensation process is largely kinetically controlled rather than thermodynamically controlled, as is known generally for polyelectrolyte–surfactant complexes.[10] We have found that the DNA condensation is dependent on the concentration of the DNA-binding fullerene. Translation of this observation into biology, we can speculate that in the cytoplasm the ester linkage in the fullerene **1** gradually yields to hydrolase activity,[11] which will detach the tetramino DNA binding sites from the fullerene core and hence results in the release of DNA from the aggregate. We are currently studying the structure activity relationship in the fullerene-mediated transfection.

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Zero-Strain Intercalation Cathode for Rechargeable Li-Ion Cell

Jaephil Cho, Yong Jeong Kim, Tae-Joon Kim, and Byungwoo Park*

The market for Li-ion batteries is undergoing rapid expansion, as portable electronic devices demand a higher energy density and a better cycle life. Even though the $Li_{1-x}CoO_2$ cathode has been widely used in commercial Li-ion batteries, electrochemical charge (Li de-intercalation) and discharge (Li intercalation) produces a phase transition accompanying nonuniform strain, which is closely related to capacity fading.[1–3] This nonuniform dimensional change induces a shearing stress within each particle, and consequently fractures occur in most oxides.[2–4] Hence, a zero-strain cathode material, the lattice constants of which do not change during cycling, is ideal for a long operational lifetimes.[5–7] Here we report a zero-strain $LiCoO_2$ cathode material produced by thin-film coating of high-fracture-toughness

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[*] Prof. Dr. B. Park, Y. J. Kim, T.-J. Kim
School of Materials Science and Engineering
Seoul National University
Seoul 151-744 (Korea)
Fax: (+82) 2-883-8197
E-mail: byungwoo@snu.ac.kr

Dr. J. Cho
Energy Laboratory
Samsung SDI Co., Ltd, Chonan, Chungchongnam-Do (Korea)

oxides, which suppresses the phase transition during cycling. This novel method for making zero-strain compounds has potential applications in various fields of materials design.

During electrochemical charging, $Li_{1-x}CoO_2$ exhibits c-axis expansion of up to ~2.6% at $x \sim 0.5$ (corresponding to the formation of a monoclinic phase from the original hexagonal phase of $LiCoO_2$), with negligible variation in the a axis. Hence, the typical reversible limit for $Li_{1-x}CoO_2$ delithiation is $x \sim 0.5$, which corresponds to a discharge capacity of ~140 mA h g^{-1}. This property has been mainly attributed to the mechanical failure associated with the large lattice expansion along the c-axis direction.[8–10] Although many attempts have been made to stabilize the $Li_{1-x}CoO_2$ structure for $x > 0.5$ through either Al or Mg substitution into the $3a$ sites to give $LiCo_{1-y}M_yO_2$, these results failed to stabilize the hexagonal symmetry, and the materials even showed a decrease in specific capacity when compared with $LiCoO_2$.[1, 10, 11] On the other hand, $LiTi_2O_4$ materials are known for exhibiting little dimensional change. Still, this material can only be used as an anode material because of its low average voltage of 1.5 V in spite of a specific capacity of 150 mA h g^{-1}.[5] However, no cathode material with zero strain has been reported to date.

We used $LiCoO_2$ particles with a coating consisting of various metal oxides having a wide range of fracture toughness, the included ZrO_2, Al_2O_3, TiO_2, and B_2O_3 (see Table 1).

Table 1. Fracture toughness of various oxides: ZrO_2, Al_2O_3, TiO_2, and B_2O_3.[12–14]

Oxide	Fracture toughness [MPa$\sqrt{m}$]	Reference
ZrO_2	8–12	[12]
Al_2O_3	2.7–4.2	[12]
TiO_2	2.38	[13]
B_2O_3	1.44	[14]

X-ray diffraction (XRD) patterns of the as-prepared samples were found to be consistent with a single phase (α-$NaFeO_2$ structure) of the $R\bar{3}m$ space group, where the cobalt and lithium ions are located at the $3a$ and $3b$ octahedral sites, respectively, in a close-packed oxygen array. In addition, the XRD patterns of the coated samples do not show any evidence of metal oxide, and this is because of the formation of a thin-film $LiCo_{1-y}M_yO_2$ (M = Zr, Al, Ti, B) solid solution (tens of nm thick) on the particle surface, as confirmed by Auger electron spectroscopy. The enclosing of $LiCoO_2$ powders by a fracture-toughened solid-solution metal-oxide coating can effectively suppress the nonuniform lattice-constant changes during Li de-intercalation (Figure 1).

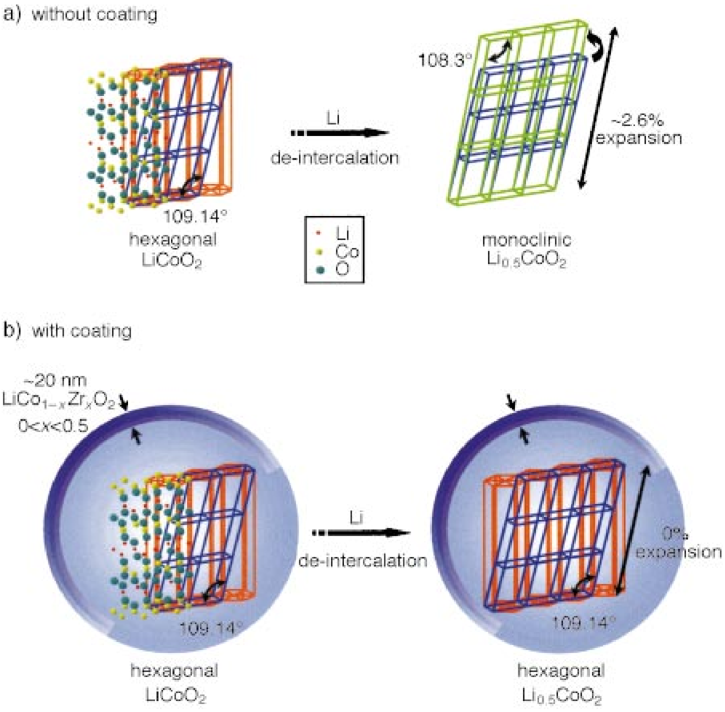

Figure 1. a) The formation of a monoclinic phase with nonuniform lattice-constant expansion (~2.6%) in bare $LiCoO_2$ during charging (Li de-intercalation), and b) the suppression of phase transition from hexagonal to monoclinic phase by a fracture-toughened thin-film metal-oxide coating.

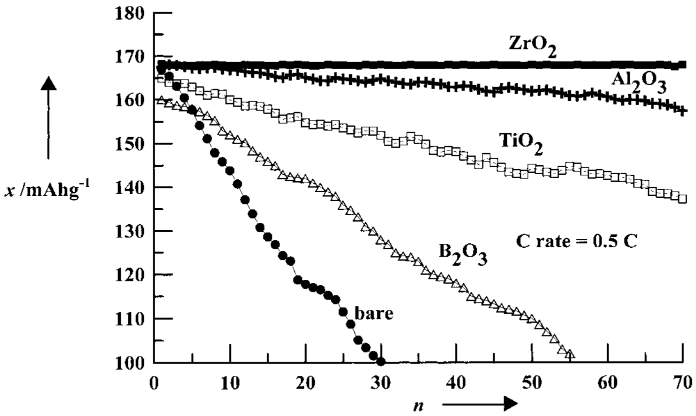

Figure 2. The cycle-life performances for ZrO_2-, Al_2O_3-, TiO_2-, B_2O_3-coated, and uncoated (bare) $LiCoO_2$. The cells were initially cycled at the rate of 0.1 C, followed by 0.5 C rate between 4.4 and 2.75 V at 21 °C (n: cycle number, x: discharge capacity).

To test the cycle–life performance of each cathode material, coin-type half cells (Li/$LiCoO_2$) were cycled at a 0.1 C rate (= 14 mA g^{-1}) for the first two cycles between 4.4 and 2.75 V, then cycling was continued at a 0.5 C rate for up to 70 cycles. The initial discharge capacities of the ZrO_2- and Al_2O_3-coated samples are similar to that of the uncoated sample (Figure 2), and the cycle–life performance trend is consistent with the fracture toughness of coated metal oxide (Table 1). In addition, the ZrO_2-coated sample does not show any noticeable capacity fading over 70 cycles, thereby retaining its original capacity. In contrast, bare $LiCoO_2$ has ~60% of its original capacity after only 30 cycles.

The lattice constant c as a function of x in hexagonal $Li_{1-x}CoO_2$ from $x = 0$ to 0.7 during the first charge is shown in Figure 3. Even though the lattice constant a shows a little variation during charging in both the bare and coated $Li_{1-x}CoO_2$, the lattice constant c shifts from $x = 0$ to 0.7, depending on the choice of metal-oxide coating. The invariability of c-axis dimension correlates extremely well with the fracture toughness of the coated oxides, in the order $ZrO_2 > Al_2O_3 > TiO_2 > B_2O_3$. This result confirms that suppression of

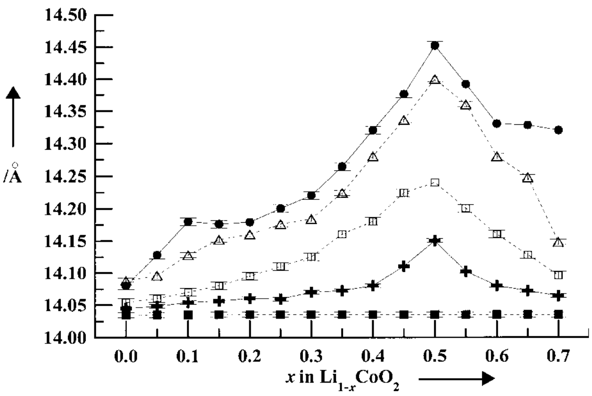

Figure 3. Lattice constants c in ZrO_2 (■), Al_2O_3 (+), TiO_2 (□), B_2O_3 (△) coated, and bare $LiCoO_2$ (●) as a function of x in $Li_{1-x}CoO_2$ during the first charge (c = lattice constant).

nonuniform strain during delithiation produces a new-class of cathode materials, which are extremely tolerant to electrochemical cycling. Note that the lattice constant c of the ZrO_2-coated $LiCoO_2$ exhibits negligible shift in the range $0 < x < 0.7$, which indicates that the original hexagonal symmetry is unaffected by delithiation. A sol–gel coating of ZrO_2, which has the highest fracture toughness, leads to the formation of a fracture-toughened thin-film solid solution (tens of nm thick) near the particle surface. This film significantly improves the structural stability of the cathode material by suppressing c-axis expansion (or phase transition), thereby preventing capacity fading during electrochemical cycling.

In conclusion, the encapsulation of $LiCoO_2$ powders by thin-film coating of high-fracture-toughness oxides effectively suppresses the lattice-constant changes during electrochemical cycling and thereby suppresses phase transitions. The order of capacity retention correlates well with the fracture toughness of the coated thin-film oxides. This innovative technology can be applied to any cathode material that has an accompanying lattice strain (or phase transition) during cycling. The commercial potential of a rechargeable Li-ion battery is enormous.

Experimental Section

Metal (or boron) ethylhexanate-diisopropoxide ($M(OOC_8H_{15})(OC_3H_7)_2$) was dissolved in 2-propanol, and stirred continuously for 20 h at 21 °C. The $LiCoO_2$ powder was then mixed with the coating solution, and the resulting solution was further aged at 50 °C for 24 h to give strong bonds between the metal-oxide (or boron-oxide) gel and the $LiCoO_2$ particle surface. After drying, each coated $LiCoO_2$ powder was fired at 400 °C for 10 h.

To test the cycle-life performance of each cathode material, a slurry of the desired viscosity was prepared by mixing the cathode materials, super P carbon black, and a poly(vinylidene fluoride) (PVDF) binder in a weight ratio of 92:4:4 in N-methyl-2-pyrrolidene (NMP; water content was below 0.01 wt%). The coin-type half cell (2016-size) contained a test cathode, a lithium metal counter-and-reference electrode, a 15 μm thick microporous polyethylene separator, and an electrolyte solution of 1 M $LiPF_6$ in EC/DMC (1:1 vol% EC = ethylene carbonate, DMC = dimethyl carbonate). Each cell was aged for 24 h at room temperature prior to commencing the electrochemical tests at 21 °C. The coin-type half cells in Li/$LiCoO_2$ were charged with 0.1 C rate to the pre-determined voltages, then potentiostated for 10 h until the current density was equivalent to 0.01 C.

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Aromatic Mercury Clusters in Ancient Amalgams[**]

Aleksey E. Kuznetsov, John D. Corbett,[*]
Lai-Sheng Wang,[*] and Alexander I. Boldyrev[*]

Mercury and its alloys, named amalgams, were known to the Ancients. Amalgams were used for metal extraction from about 500 BC and one of the most interesting influences of

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[*] Prof. Dr. J. D. Corbett
Department of Chemistry and Ames Laboratory
Iowa State University
Ames, IA 50011 (USA)
Fax: (+1) 515-294-5718
E-mail: jdc@ameslab.gov

Prof. Dr. L.-S. Wang
Department of Physics
Washington State University
Richland, WA 99352 (USA)
and
W. R. Wiley Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory, MS K8-88
P. O. Box 999, Richland, WA 99352 (USA)
Fax: (+1) 509-376-6066
E-mail: ls.wang@pnl.gov

Prof. Dr. A. I. Boldyrev, A. E. Kuznetsov
Department of Chemistry and Biochemistry
Utah State University
Logan, UT 84322 (USA)
Fax: (+1) 435-797-3390
E-mail: Boldyrev@cc.usu.edu

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