

Effects of MgO Coating on the Structural and Electrochemical Characteristics of LiCoO₂ as Cathode Materials for Lithium Ion Battery

Jae-Hyun Shim,^{†,‡} Sanghun Lee,^{*,§} and Sung Soo Park^{*,†}

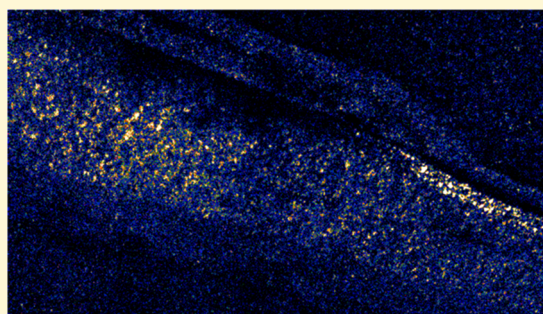
[†]Battery R&D Center, Samsung SDI Co. Ltd., Suwon, Gyeonggi-do, 443-803, Republic of Korea

[‡]Department of Materials Sciences and Engineering, University of Washington, Seattle, Washington 98195, United States

[§]Department of BioNano Technology, Gachon University, Seongnam, Gyeonggi-do, 461-701, Republic of Korea

S Supporting Information

ABSTRACT: To understand the origin of enhanced electrochemical performances of MgO-coated LiCoO₂ as cathode materials for lithium ion battery, we investigate the internal structures of the materials at the nanometer scale. The MgO-coated LiCoO₂ are annealed at various temperatures of 750–810 °C so as to find the optimized heat-treatment condition. The surface morphologies and crystalline structures are characterized by SEM, TEM, EELS, and XRD. The electrochemical results show that the MgO-coated LiCoO₂ delivers a high capacity with excellent retention property. In particular, the sample annealed at 810 °C, which possesses the high doping level of Mg²⁺ ion in the Li sites, exhibits the highest retention capacity without undergoing phase transformation in the interfaces between the MgO-coating layer and the bulk LiCoO₂ during cycling. Lithium and vacancy ordering in the delithiated state is monitored by TEM measurements. By comparison with the bare LiCoO₂, we reveal that the MgO-coating layer plays a role in the prevention of lithium and vacancy ordering in the near-interfaces, which is in agreement with the excellent electrochemical cycling performances of the MgO-coated sample annealed at 810 °C. As a result, depending on the thermal treatment temperature, the Mg²⁺ ions from MgO layer diffuse into Co and Li sites in LiCoO₂, competitively, and affect the structural stability and electrochemical performances.



1. INTRODUCTION

Because of its highly accessible lithium diffusion pathway, LiCoO₂ has been one of the most predominant cathode materials of the lithium ion batteries (LIBs) for portable electronics since the first successful commercialization.¹ The practical capacity is limited to ~140 mAh/g, that is, half of its theoretical capacity (273 mAh/g), because it undergoes phase transformation from monoclinic to hexagonal phase and, therefore, its layered structure is easily collapsed at $x > 0.5$ (Li_{1-x}CoO₂).^{2,3} A cell shows very good capacity retention within the limited composition range of $x < 0.5$, that is, below 4.2 V, whereas above 4.2 V it suffers from rapid capacity fading during charge/discharge cycling.

In order to raise the practical capacity or cycling stability of the LiCoO₂ electrodes at the high voltages, a lot of modifications have been attempted. First, various dopants, for example, Mg,^{4–12} Al,¹⁰ Zr,^{8,12} Sn,¹³ and so forth,¹⁴ have been proposed to improve the electrochemical performances. In particular, the Mg-doped LiCoO₂ has been intensively investigated because of its enhanced electronic conductivity^{4–8} and thermal^{7,9,10} or cycling^{4,8,9,11,12} stability. Alternatively, because it is known that the capacity fade of LiCoO₂ electrode is attributed mostly to changes on their surfaces rather than to

bulk degradation,¹⁵ many studies of LiCoO₂ coated with metal oxides have been reported.^{11,16–31}

Although various coatings have significantly improved the capacity retention, the mechanism of capacity fading and the effects of surface coatings have not been clearly explained and they are still controversial. In Cho et al.'s pioneering study,²⁵ they reported that the capacity retention of metal-oxide-coated LiCoO₂ correlates with the fracture toughness of the coated oxides; particularly, ZrO₂-coated one, which they called a “zero-strain intercalation cathode”, did not exhibit lattice expansion and showed the best cycling performances. Accordingly, they assumed that a layer of LiZr_xCo_{1-x}O₂ would be formed on the surfaces as an origin of improved cycling ability. On the contrary, Chen and Dahn reported that the coated phase on the surfaces was the nanocrystalline ZrO₂.²⁷ They proposed that the enhanced cycling ability is caused by a reduction in the contact area between LiCoO₂ and electrolytes.

Because the above studies examined improvement in the electrochemical performances of LiCoO₂ by coating, a large number of surface modifications using various materials (e.g.,

Received: November 20, 2013

Revised: March 16, 2014

Published: March 24, 2014

MgO,^{11,16–21} Al₂O₃,^{20–26} ZrO₂,^{25–30} SnO₂,³¹) have followed. In particular, we have been interested in the MgO-coating because significant improvement in cycle performances has been achieved. In Amatucci et al.'s study, it was reported that the capacity loss of LiCoO₂ is strongly relevant to the Co⁴⁺ ion resolution.³² Hence, Wang et al. claimed that a uniform surface layer of Li–Mg–Co–O of the MgO-coated one prevents the bulk LiCoO₂ particles from direct contact with the electrolytes and thereby inhibits the escape of Co⁴⁺ ions of the active material.^{16,17} In addition, they speculated that the pillaring effect of diffused Mg²⁺ ions into the interslab space would enhance the improvement of specific capacity. This argument was supported by Zhao et al.'s follow-up study, in which, however, only circumstantial indirect evidence, that is, increased peak intensities from XRD measurements, was suggested.¹⁸ Up to now, there have been no experimental reports providing direct evidence of Mg substitution on the surfaces of LiCoO₂ particles. Moreover, because the XRD technique mainly probes the bulk structures rather than the surfaces, we need to study structural features with techniques distinguishing surfaces and bulk, for example, high-resolution transmission electron microscopy (TEM). Meanwhile, most of the MgO coatings were annealed at 600–800 °C in the previous reports;^{11,16–21} however, the temperature effects on the electrochemical performances or structural features of the MgO-coated materials were not discussed.

In this study, we report investigations on structural and electrochemical characteristics of the MgO-coated LiCoO₂ with various thermal treatments. These materials were calcined by a solid state reaction with MgO nanoparticles. In particular, the interfaces between bulk LiCoO₂ and MgO-coating layers are explored by TEM at the nanometer scale, which explains the structural features induced by Mg substitution. This study also examines the relationship between the structural evolution and the electrochemical performances for the MgO-coated LiCoO₂, which is supported by the density functional theory (DFT) calculations.

2. EXPERIMENTS

Pristine LiCoO₂ powders were synthesized by solid-state reactions (see Supporting Information for SEM image). Li₂CO₃ and Co₃O₄ (>99.9% pure) as starting materials were milled with zirconia ball for 24 h. The ratio of Li:Co was adjusted to 1.04:1, considering lithium loss at high temperature for synthesis. After the ball-milling process, powder mixture was heated at 1000 °C for 6 h in air. MgO-coated LiCoO₂ powders were made from these pristine one and ~50 nm-sized MgO nanopowders which were obtained by ball-milling with a high impact milling machine. The MgO particles were physically mixed with 20 μm-sized LiCoO₂ particles in a mechanical mixer with a rotating speed of 150 rpm for 10 h. The relative concentration of Mg (0.15 ± 0.05 wt %) was determined by the inductive coupled plasma measurements. Then, the mixed powders were heat-treated at various temperatures of 750, 770, 790, and 810 °C in air for 6 h, respectively, and slowly cooled to room temperature.

The X-ray diffraction (XRD) patterns were obtained by a Bruker diffractometer using Cu Kα radiation. Step-scan recording for structure refinement was carried out with 0.02° 2θ step increment of 6 s duration. The Rietveld refinement method was done for all data by TOPS-R V4.2 software. The diffractometer point zero, Lorentzian/Gaussian fraction of the pseudo-Voigt peak function, scale factor, lattice constants (*a*

and *c*), oxygen parameter (*z*), thermal factors for 3a, 3b, and 6c positions, half-width parameters, preferred orientation and asymmetry parameters were refined. The morphology of the particles was studied using a scanning electron microscope (SEM) (Magellan XHR, FEI Co., Oregon, U.S.A.) in the secondary electron mode. The scanning transmission electron microscopy (STEM) observations were performed using a Cs-corrected STEM (JEM-2100F, JEOL, Co., Tokyo, Japan) at 200 kV, which is equipped with a spherical aberration corrector (CEOS GmbH, Heidelberg, Germany) and provides a minimum probe of about 1 Å in diameter. The EELS spectra were obtained in STEM mode with a total beam current of 0.2 nA for a probe size of about 0.5 nm, which were collected with a Gatan GIF-200 spectrometer. For characterization of electrochemical performances, the LiCoO₂/Li coin-cells were produced with the 1 M LiPF₆ electrolytes (solvent: mixture of ethylene carbonate and diethyl carbonate, 1:1 by weight ratio) in the drybox with atmospheric condition. The cells were cycled between 3.0 and 4.35 V at a rate of 0.2 C to determine the capacities.

3. RESULTS AND DISCUSSION

3.1. Structural Features of MgO-Coated LiCoO₂. Figure 1a is a SEM image exhibiting the morphology of MgO-coated LiCoO₂, which was heat-treated at 810 °C. This sample is covered with a layer of uniformly distributed beads of MgO, which is confirmed by the energy-dispersive X-ray (EDX) spectroscopy. The average size of the MgO beads is about 50 nm as shown in Figure 1b. The surface morphologies from the SEM reveal no distinguishable characteristic at the micrometer

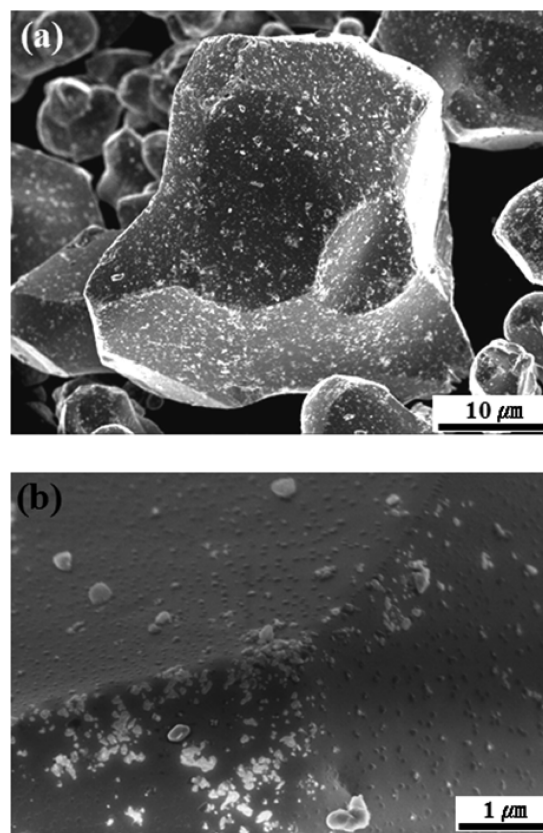


Figure 1. (a) Morphology of MgO-coated LiCoO₂ heat-treated at 810 °C and (b) its enlarged image from SEM.

scale depending on the heat-treatment temperature from 750 to 810 °C (Supporting Information).

Figure 2 shows the XRD patterns (upper figure) and c parameter of the unit-cells (lower figure). In addition, the

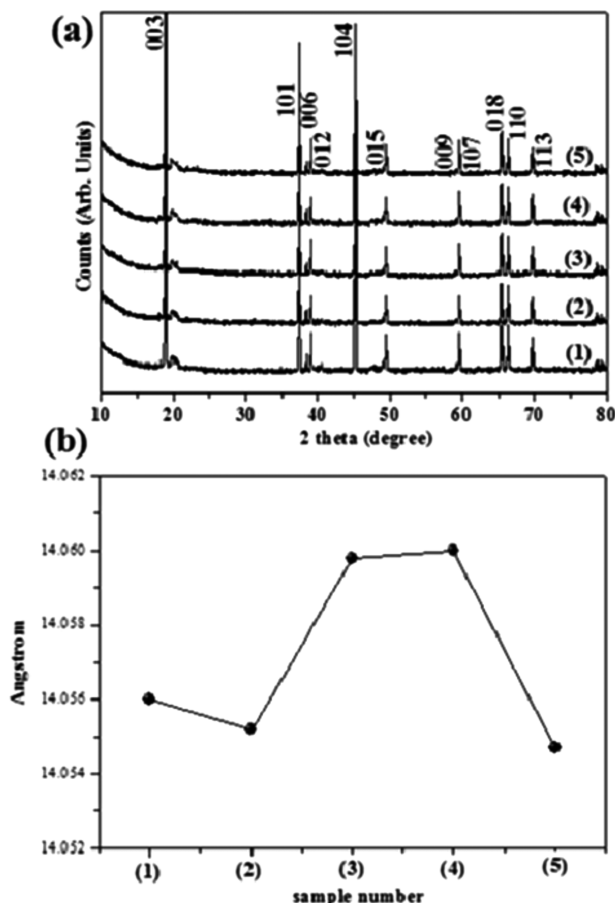


Figure 2. (a) XRD patterns and (b) obtained lattice parameters of (1) pristine and MgO-coated LiCoO₂ heat-treated at (2) 750 °C, (3) 770 °C, (4) 790 °C, and (5) 810 °C, respectively.

Table 1. Structural Parameters of Pristine and MgO-Coated LiCoO₂ Obtained from the Rietveld Refinement of X-ray Diffraction Data

	a (Å)	c (Å)	V (Å ³)
pristine	2.81676(6)	14.0560(6)	96.58
MgO-coated samples			
750 °C	2.81658(6)	14.0552(6)	96.56
770 °C	2.81743(6)	14.0598(6)	96.65
790 °C	2.81743(6)	14.0600(6)	96.65
810 °C	2.81639(6)	14.0547(6)	96.55

refined structural parameters are summarized in Table 1. The XRD patterns of the pristine LiCoO₂ powders exhibit single-phase α -NaFeO₂ layered structure and are indexed assuming a hexagonal axes option of rhombohedral $R\bar{3}m$ space group. The well-defined doublets of 006/012 and 018/110 indicate the stabilization of the 2D structure and an ordered distribution of Li⁺ and Co³⁺ in the lattice.³³ The lattice constants of the pristine LiCoO₂ are in good agreement with the previous study by Akimoto et al. ($a = 2.8161(5)$ Å, $c = 14.0536(5)$ Å).³⁴ With

increasing heat-treatment temperature up to 790 °C, the c parameter increases. This is due to that the Co ions are replaced by the diffused Mg ions from MgO, which observation is consistent with Levasseur et al.'s study of the Mg-doped LiCoO₂.⁹ However, the c parameter of the sample heat-treated at 810 °C is not different from that of the pristine LiCoO₂. This is an evidence of the Mg replacement for Li sites at the high temperature of 810 °C. Due to the disparity in ionic radii (Li⁺: 0.90 Å, Mg²⁺: 0.86 Å, Co³⁺: 0.685 Å), the Mg substitution on Co sites expands c parameter due to larger size of Mg ion whereas the Mg substitution on Li sites does not induce significant change of the unit cell. This is also supported by the DFT calculations (Supporting Information).

Typical cross-sectional TEM image of the MgO-coated LiCoO₂ annealed at 790 °C is shown in Figure 3a, which reveals the microstructure of the outer edge of a particle. The coating layer appears to cover part of the particle surface with ~50 nm-sized MgO lumps. The EDX map of the Mg element shows that the Mg ions are located in the near surface of LiCoO₂ (inserted in Figure 3a). The STEM image in Figure 3b, which includes the same area as Figure 3a, shows the Moiré fringes formed by double diffraction of overlaying crystal sheets in the interfacial region between MgO layer and bulk LiCoO₂. The selected area electron diffraction (SAED) patterns of interfaces are definitely different from those of the inner area of LiCoO₂ in Figure 3b; the electron incidence was parallel to the [001]_{hex} zone-axes (the subscript "hex" represents the hexagonal structure of LiCoO₂ ($R\bar{3}m$)). As shown in the upper inset in Figure 3b, the interfacial SAED patterns exhibit the three-spot split diffractions of fundamental $(\bar{1}\bar{1}0)11\bar{2}0$ -type reflections, which are corresponding to individual different lattice plane spacing. On the contrary, there is no split SAED pattern in the internal structures (lower inset in Figure 3b). It is highly likely that substitution by Mg ions in the Co-layer induces extension of the lattice parameter. These results are consistent with the XRD results by the Rietveld method.

Figure 4 shows high angle annular dark-field (HAADF)-STEM images of the interfaces between MgO and LiCoO₂, which are recorded along the $[\bar{1}\bar{1}0]11\bar{2}0_{\text{hex}}$ zone axis. In this figure, we observe the remarkable difference of interfacial structures between the samples of 790 and 810 °C. The HAADF image of the sample of 790 °C exhibits alternate bright and dark stripes (Figure 4a); the relatively bright lines composed of gray spots (high Z) are associated with the transition-metal-rich layers whereas the dark lines (low Z) are attributed to the Li-rich layers; therefore, the typical layered-structures of LiCoO₂ are observed in the almost entire region of the sample. However, the internal structure of the sample of 810 °C (Figure 4b) is somewhat different from that of the sample of 790 °C. In the area far from the interface, the Li layers are invisible because of their low atomic weight (dark lines); hence, similarly to the sample of 790 °C, we know that the sample has ordered layered-structures. On the other hand, the stronger contrast of the layers, which are supposed to be originally occupied by Li ions, in the near interface indicates the presence of heavier elements on Li sites; that is, the Li ions are substituted by Mg ions from the MgO-layer. It is noticeable that the Mg substitutions on different sites of Co or Li are dependent on the heat-treatment temperature for the MgO coating. Chemical analysis by the EELS shows that Co and Mg are present in the surface of LiCoO₂ heat-treated at 790 and 810 °C in Figure 4c and d, respectively. The EELS spectra (single point data) were collected from the samples using a

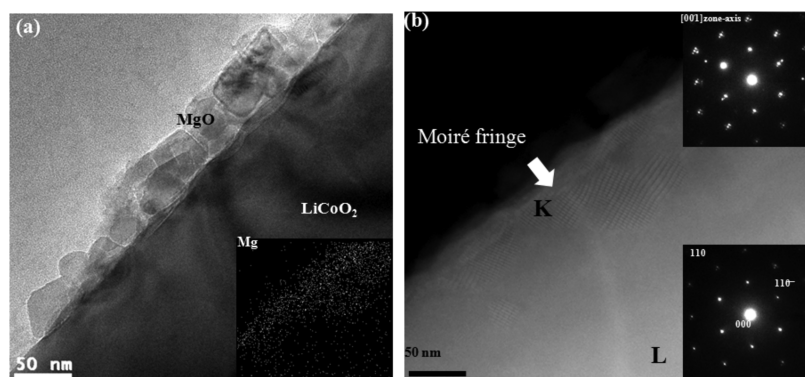


Figure 3. (a) Bright-field TEM image of MgO-coated LiCoO₂ heat-treated at 790 °C. The inset shows an EDX chemical mapping in the same area. (b) HAADF STEM image with Moiré fringes in the same area. The upper and lower insets are the SAED patterns of the interface (K) and inner (L) area, respectively.

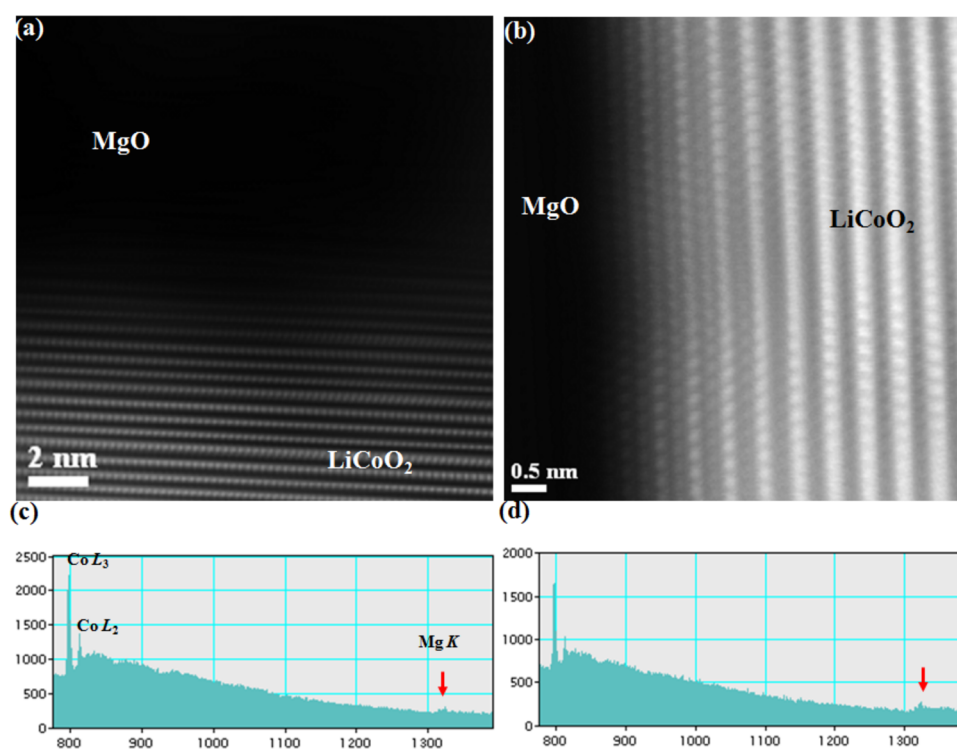


Figure 4. High-resolution aberration-corrected HAADF (Z-contrast) images in interface between MgO layer and LiCoO₂ of MgO-coated LiCoO₂ heat-treated at (a) 790 °C and (b) 810 °C, respectively. EELS spectra acquired at the surface of MgO-coated LiCoO₂ heat-treated at (c) 790 °C and (d) 810 °C, respectively.

probe size of 0.2 nm. The shape, position, and intensity of Co $L_{2,3}$ -edge and Mg K -edge data are very similar for both samples heat-treated at 790 and 810 °C. From the DFT calculations, a Mg substitution on a Co site is more favorable than unsubstituted LiCoO₂ by -0.222 eV per formula unit, whereas that on a Li site is slightly less stable by 0.006 eV. We can suppose that the Mg replacement for Co ions is energetically favorable; however, the slight unfavorability of the Mg substitution on Li sites in enthalpy can be overcome at high temperatures. Consequently, the heat-treatment temperature has influence on substitution of Mg ions in the MgO-coated LiCoO₂ samples.

3.2. Cycling Stability of MgO-Coated LiCoO₂. The first charge–discharge curves, which were obtained after first three cycles for formation, of the pristine and MgO-coated LiCoO₂ heat-treated at different temperatures are shown in Figure 5a.

In comparison with the pristine one (~ 150 mAh/g), the discharge capacity of MgO-coated samples is slightly increased (~ 156 mAh/g), regardless of the heat-treatment temperature. However, the MgO coating effect becomes conspicuous after repeated charge/discharge cycling. After 60 cycles, the discharge capacities of MgO-coated LiCoO₂ samples are 126.0, 122.5, 129, and 132.5 mAh/g, which are varied with the heat-treatment temperatures of 750, 770, 790, and 810 °C, respectively, whereas that of the pristine LiCoO₂ is 110 mAh/g as shown in Figure 5b. In Figure 5c, the discharge capacity of each sample is plotted as a function of cycles. As the heat-treatment temperature increases, the capacity retention improves from 72.8% (the pristine sample) to 85% (the MgO-coated sample heat-treated at 810 °C). In Figure 5d, dQ/dV plots of the first and sixtieth cycles of the pristine and 810 °C heat-treated samples are shown. From the first cycle plots,

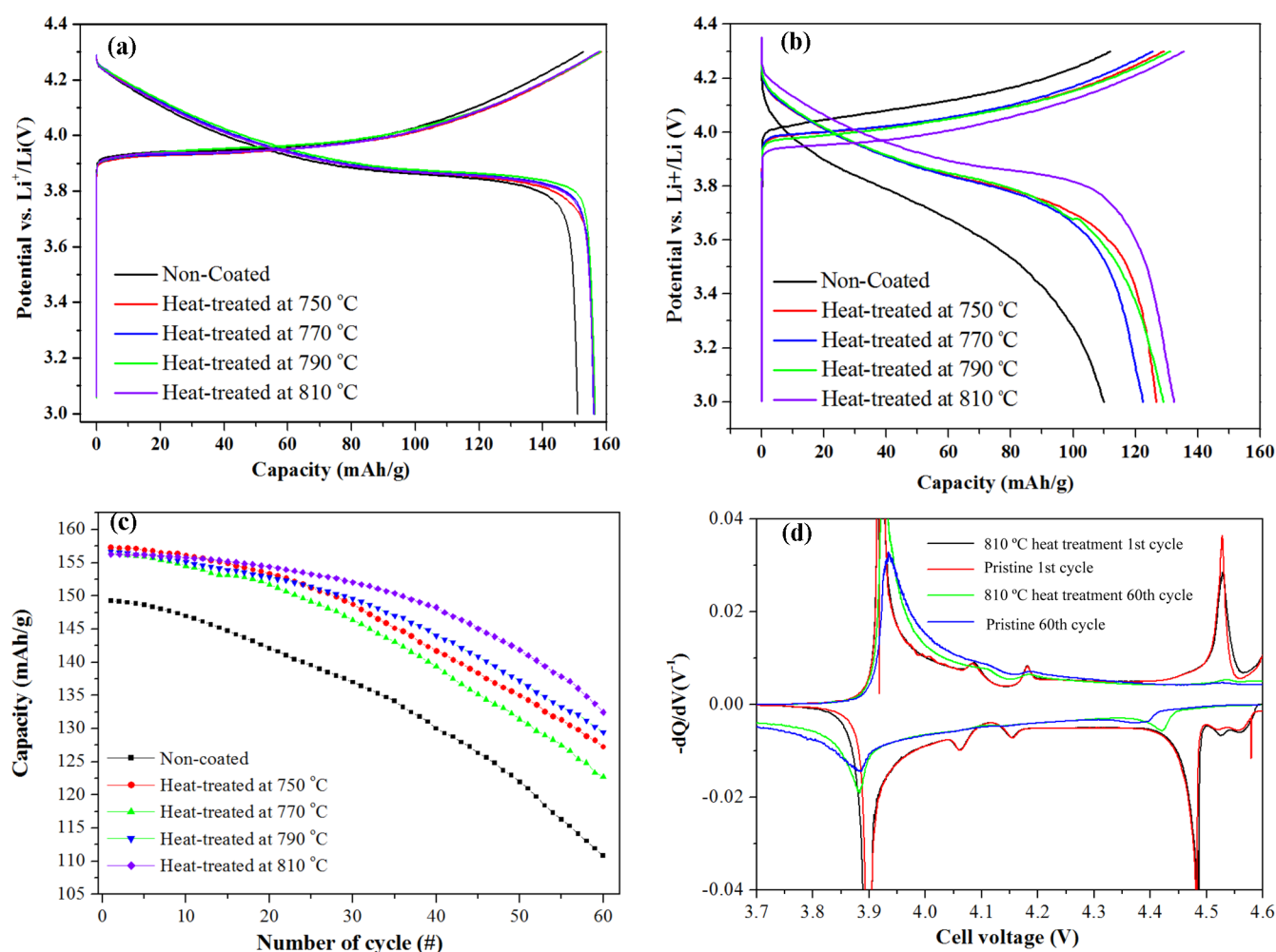


Figure 5. Charge/discharge profiles of MgO-coated LiCoO₂ with various heat-treatment temperature: (a) first and (b) sixtieth cycles. (c) Discharge capacity vs. cycle. (d) dQ/dV plots of the first and 60th cycles of pristine and MgO-coated LiCoO₂ heat-treated at 810 °C.

we find no significant differences between the pristine and MgO-coated samples. However, after 60 cycles, the peak of the pristine sample (3.9–4.0 V) is strongly diminished compared to that of the MgO-coated sample, which shows clearly the effect of MgO-coating layer for improvement in cyclability. In the case of the MgO-coated sample heat-treated at 810 °C, the Mg ions in the Li sites have a role of “pillars” to preserve the layered structure, particularly, in the charged (delithiated) state, which is a main reason it has enhanced cycling ability. The similar “pillar effect” of Ni ions in the mixed metal oxides of the layered structure with the excellent structural stability has recently been reported by Cho et al.³⁵

We employed the TEM measurements and SAED patterns to investigate the phase transformation during cycling and the MgO-coating effect in detail. In Figure 6, the TEM image of fresh (uncycled) sample of MgO-coated LiCoO₂ heat-treated at 810 °C (left, large figure) and the SAED patterns (right, small figures) of region A (interfacial area), B (middle area), and C (area distant from the interface, i.e., bulk LiCoO₂) are shown; the electron incidence were parallel to the [010]_{hex} zone axes. For the sake of simplicity, the typical diffraction spots were indexed in terms of the $R\bar{3}m$ structure with the hexagonal notation. All three areas exhibit the same diffraction pattern of $R\bar{3}m$. In Figure 7, the TEM image and the SAED patterns of the same sample after 60 cycles and then recharged at 4.35 V

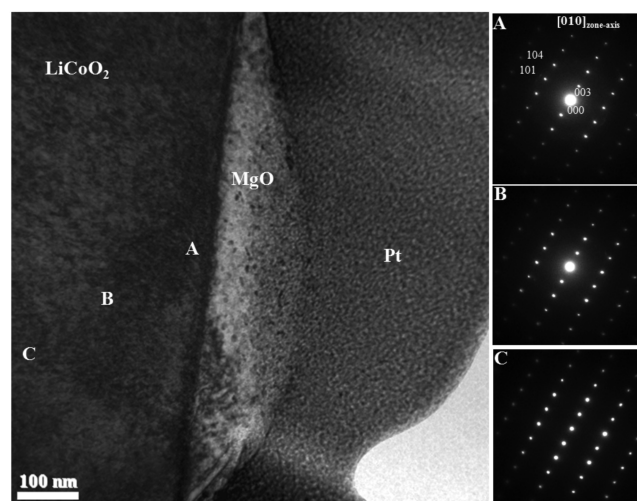


Figure 6. Bright-field TEM image in the interface of fresh (uncycled) MgO-coated LiCoO₂ heat-treated at 810 °C between MgO layer and LiCoO₂. The SAED patterns are obtained from interfacial area (A), middle area (B), and area distant from interface (C), respectively.

are shown. The TEM image (upper large figure) shows the MgO-coating layer of which thickness is ~50 nm. The SAED patterns of interfacial area, which is denoted as A, prove that

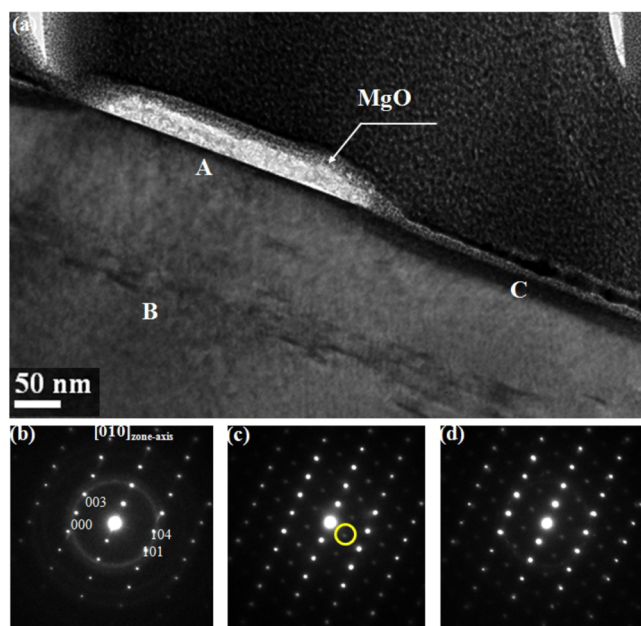


Figure 7. Bright-field TEM image in the interface of MgO-coated LiCoO₂ heat-treated at 810 °C after 60 cycles between MgO layer and LiCoO₂. The SAED patterns are obtained from interfacial area (A), inner area (B), and noncoated area (C), respectively.

the interfacial area retains its original structure of LiCoO₂ in the [010]_{hex} zone-axis. Meanwhile, the SAED patterns of inner region of LiCoO₂ (denoted as B) represent structural alterations from the $R\bar{3}m$ structure, which indicates that the inner region undergoes structural transformation during delithiation (charging). It is noticeable that the similar transformation is also observed in the surface region of noncoated LiCoO₂ (denoted as C). Note that new spots of weak reflections are appeared in the middle of the (000) and (101) reflections from lithium and vacancy ordering (marked in a yellow circle).³⁶ In Figure 8, a dark-field TEM image of the

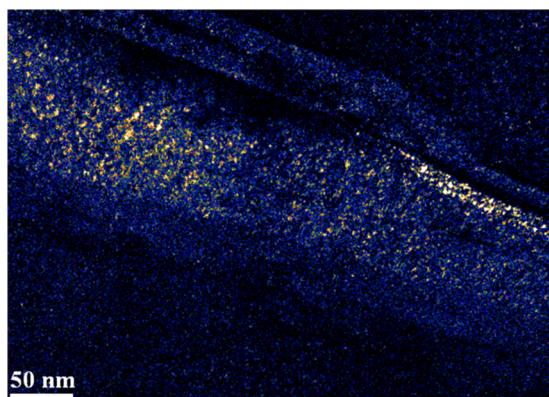


Figure 8. Dark-field image from a weak reflection showing lithium and vacancy ordering. See the text for details.

MgO-coated sample heat-treated at 810 °C is shown, which is from the same area as in Figure 7; the direct beam is blocked by the aperture while one diffracted beam, marked in a yellow circle (Figure 7c), is allowed to pass the objective aperture in TEM operating system. A dark field image shows the distribution of lithium and vacancy ordering area formed by weak reflection in the SAED pattern. In this figure, it is

observed that the lithium and vacancy phases are located in the interior (B in Figure 7) and noncoated surface area (C in Figure 7) of LiCoO₂, but they do not exist in the interfacial area between MgO-layer and LiCoO₂ (A in Figure 7). Combining this result and the high resolution TEM images in Figures 6 and 7, we suppose that the interfacial area with Mg substitution on Li sites does not undergo phase transformation during cycling; as a result, it would improve the structural stability of MgO-coated sample heat-treated at the high temperature of 810 °C. It is important to note that this effect from MgO-coating is strongly dependent on the heating temperature. Therefore, it is believed that lithium and vacancy ordering could have a detrimental effect on the structural integrity of LiCoO₂ crystals, which would lead to structural degradation and gradual capacity fading during electrochemical cycling.

4. CONCLUSION

We have prepared MgO-coated LiCoO₂ with thermal treatment at various temperatures by the solid state reaction method. The annealing condition controls the structure of LiCoO₂ surface. The fabricated coin cell demonstrates that the capacities are dependent on the MgO-coating layer. Interestingly, the MgO-coated LiCoO₂ annealed at 810 °C shows the highest initial (at the first cycle) and retention capacity (at the sixtieth cycle) in the voltage range of 3.0–4.35 V at 0.2 C rate. Its surface layer rarely suffers from phase transformation during charge/discharge cycling. The characteristics of interfaces between MgO layer and bulk LiCoO₂, which seem apparently similar at the μm scale regardless of the thermal treatment temperature, are probed by TEM at the nanometer scale. The results confirmed that diffusion of Mg²⁺ ions from the MgO-coating layer into the interfacial area is accompanied by competitive substitution on the Co or Li sites depending on the thermal treatment temperature. This study provides the direct evidence associated with lithium and vacancy ordering in the delithiated state, which was highly related to the cycling performances.

■ ASSOCIATED CONTENT

Supporting Information

SEM images of MgO-coated LiCoO₂ thermally treated at various temperatures and computational details of DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*S. Lee. E-mail: sanghunlee@gachon.ac.kr.

*S. S. Park. E-mail: sung.s.park@samsung.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partly supported by the Korea Research Foundation (KRF) Grant funded by the Korean Government (KRF-2009-352-D00138). The authors also thank Prof. W.-S. Yoon (Sungkyunkwan University) for thoughtful comments on the XRD data.

■ REFERENCES

- (1) Nagaura, T.; Tozawa, K. *Prog. Batteries Sol. Cells* **1990**, 9, 209–214.

- (2) Reimers, J. N.; Dahn, J. R. *J. Electrochem. Soc.* **1992**, *139*, 2091–2097.
- (3) Menetrier, M.; Saadoune, I.; Levasseur, S.; Delmas, C. *J. Mater. Chem.* **1999**, *9*, 1135–1140.
- (4) Kim, H.-J.; Jeong, Y. U.; Lee, J.-H.; Kim, J.-J. *J. Power Sources* **2006**, *159*, 233–236.
- (5) Tukamoto, H.; West, A. R. *J. Electrochem. Soc.* **1997**, *144*, 3164–3168.
- (6) Nobili, F.; Dsoke, S.; Croce, F.; Marassi, R. *Electrochim. Acta* **2005**, *50*, 2307–2313.
- (7) Levasseur, S.; Menetrier, M.; Delmas, C. *Chem. Mater.* **2002**, *14*, 3584–3590.
- (8) Nobili, F.; Croce, F.; Tossici, R.; Meschini, I.; Reale, P.; Marassi, R. *J. Power Sources* **2012**, *197*, 276–284.
- (9) Yin, R.-Z.; Kim, Y.-S.; Shin, S.-J.; Jung, I.; Kim, J.-S.; Jeong, S.-K. *J. Electrochem. Soc.* **2012**, *159*, A253–A258.
- (10) Zhou, F.; Luo, W.; Zhao, X.; Dahn, J. R. *J. Electrochem. Soc.* **2009**, *156*, A917–A920.
- (11) Mladenov, M.; Stoyanova, R.; Zhecheva, E.; Vassilev, S. *Electrochem. Commun.* **2001**, *3*, 410–416.
- (12) Kim, H.-S.; Ko, T.-K.; Na, B.-K.; Cho, W. I.; Chao, B. W. *J. Power Sources* **2004**, *138*, 232–239.
- (13) Valanarasu, S.; Chandramohan, R. *Cryst. Res. Technol.* **2010**, *45*, 835–839.
- (14) Zhou, M.; Yoshio, M.; Gopukumar, S.; Yamaki, J. *Chem. Mater.* **2003**, *15*, 4699–4702.
- (15) Aurbach, D.; Markovsky, B.; Rodkin, A.; Levi, E.; Cohen, Y.; Kim, H.-J.; Schmidt, M. *Electrochim. Acta* **2002**, *47*, 4291–4306.
- (16) Wang, Z.; Huang, X.; Chen, L. *J. Electrochem. Soc.* **2003**, *150*, A199–A208.
- (17) Wang, Z.; Wu, C.; Liu, L.; Wu, F.; Chen, L.; Huang, X. *J. Electrochem. Soc.* **2002**, *149*, A466–A471.
- (18) Zhao, H.; Gao, L.; Qiu, W.; Zhang, X. *J. Power Sources* **2004**, *132*, 195–200.
- (19) Iriyama, Y.; Kurita, H.; Yamada, I.; Abe, T.; Ogumi, Z. *J. Power Sources* **2004**, *137*, 111–116.
- (20) Kweon, H.-J.; Park, J. J.; Seo, J. W.; Kim, G. B.; Jung, B. H.; Lim, H. S. *J. Power Sources* **2004**, *126*, 156–162.
- (21) Wang, Z.; Liu, L.; Chen, L.; Huang, X. *Solid State Ionics* **2002**, *148*, 335–342.
- (22) Cho, J.; Kim, Y. J.; Park, B. *J. Electrochem. Soc.* **2001**, *148*, A1110–A1115.
- (23) Cho, J.; Kim, Y. J.; Park, B. *Chem. Mater.* **2000**, *12*, 3788–3791.
- (24) Liu, L.; Chen, L.; Huang, X.; Yang, X.-Q.; Yoon, W.-S.; Lee, H. S.; McBreen, J. *J. Electrochem. Soc.* **2004**, *151*, A1344–A1351.
- (25) Cho, J.; Kim, Y. J.; Kim, T.-J.; Park, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3367–3369.
- (26) Chen, Z.; Dahn, J. R. *Electrochem. Solid-State Lett.* **2003**, *6*, A221–A224.
- (27) Chen, Z.; Dahn, J. R. *Electrochem. Solid-State Lett.* **2002**, *5*, A213–A216.
- (28) Miyashiro, H.; Yamanaka, A.; Tabuchi, M.; Seki, S.; Nakayama, M.; Ohno, Y.; Kobayashi, Y.; Mita, Y.; Usami, A.; Wakihara, M. *J. Electrochem. Soc.* **2006**, *153*, A348–A353.
- (29) Kim, Y. J.; Cho, J.; Kim, T.-J.; Park, B. *J. Electrochem. Soc.* **2003**, *150*, A1723–A1725.
- (30) Chung, K. Y.; Yoon, W.-S.; McBreen, J.; Yang, X.-Q.; Oh, S. H.; Shin, H. C.; Cho, W. I.; Cho, B. W. *J. Electrochem. Soc.* **2006**, *153*, A2152–A2157.
- (31) Cho, J.; Kim, C.-S.; Yoo, S.-I. *Electrochem. Solid-State Lett.* **2000**, *3*, 362–365.
- (32) Amatucci, G. G.; Tarascon, J. M.; Klein, L. C. *J. Electrochem. Soc.* **1996**, *143*, 1114–1123.
- (33) Madhavi, S.; Subba Rao, G. V.; Chowdari, B. V. R.; Lia, S. F. Y. *J. Electrochem. Soc.* **2001**, *148*, A1279–A1286.
- (34) Akimoto, J.; Gotoh, Y.; Oosawa, Y. *J. Solid State Chem.* **1998**, *141*, 298–302.
- (35) Cho, Y.; Oh, P.; Cho, J. *Nano Lett.* **2013**, *13*, 1145–1152.
- (36) Shao-Horn, Y.; Levasseur, S.; Weill, F.; Delmas, C. *J. Electrochem. Soc.* **2003**, *150*, A366–A373.