

Characterization of Spinel $\text{Li}_x\text{Co}_2\text{O}_4$ -Coated LiCoO_2 Prepared with Post-Thermal Treatment as a Cathode Material for Lithium Ion Batteries

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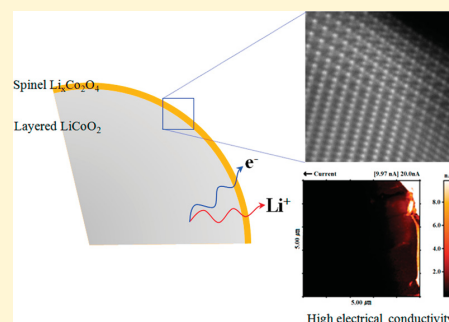
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S Supporting Information

ABSTRACT: Both the origin and mechanism of the improvement in the electrochemical performances of post-thermal treated LiCoO_2 as a cathode material for lithium ion batteries are investigated through high-quality characterization. X-ray diffraction and transmission electron microscopy measurements revealed that the high temperature sintering results in Li deficiency and the consequent formation of spinel $\text{Li}_x\text{Co}_2\text{O}_4$. The slow quenching allows the two phases of LiCoO_2 and $\text{Li}_x\text{Co}_2\text{O}_4$ to intermix, whereas the post-thermal treatment at 800 °C results in the separation of the spinel phase at the surface of LiCoO_2 . The post-thermal treated material exhibits a much better cell performance for the cycling capacity and charge rate capability than the slowly quenched material. From the conductive atomic force microscopy measurement and electrochemical impedance spectroscopy experiment, it is shown that the high electrical conductivity of the effective coating layer of the post-thermal treated LiCoO_2 performs a role in enhancing the charge transfer activity of the active material.



1. INTRODUCTION

Since its initial commercialization, the lithium-ion battery (LIB) has been the most widely used energy storage device for portable electronics. LiCoO_2 is one of the most commonly used cathode materials for LIB as a result of its relatively high energy density and good cycling performance.^{1,2} Recently, researchers have steadily investigated the effects of increasing the operation voltage (>4.4 V vs Li^+/Li) in order to improve the energy density. However, the layered structure of $\text{Li}_{1-x}\text{CoO}_2$ easily collapses at $x > 0.5$, which corresponds to operation voltages greater than 4.2 V.³ This disadvantage of LiCoO_2 is mainly attributed to the mechanical instability associated with the large lattice expansion along the c axis during delithiation.^{4–6} The mechanically vulnerable charged (delithiated) form of the material with an expanded lattice suffers from oxygen loss and chemically reacts with electrolytes at the highly oxidized surfaces.^{7–9} Consequently, many researchers have focused on modifying the surface of LiCoO_2 in order to reduce the detrimental reactions between LiCoO_2 and the electrolytes.

For surface modification, one of the simplest approaches is to introduce a coating layer composed of metal oxides, such as MgO ,^{10–17} Al_2O_3 ,^{18–22} ZrO_2 ,^{21–26} SnO_2 ,²⁷ and Co_3O_4 .²⁸ These coatings have successfully improved the discharge capacity of LiCoO_2 by ~30% compared with the bare material. Recently, spinel-structured lithium metal oxides have been proposed as a

coating material in order to minimize the capacity loss due to the coating. These composites are sometimes called core–shell materials, and the layered components are not limited to LiCoO_2 . Despite their limited capacity of ~140 mAhg^{-1} above 3 V,²⁹ spinel materials are attractive in terms of their high Li^+ ion conductivity and good thermal stability. Recently, Cho et al. reported that a shell consisting of a spinel phase surprisingly reduced the oxygen evolution of layered lithium mixed-metal (Ni, Co, and Mn) oxides during cycling.³⁰ In addition, Wu et al. synthesized an ultrathin spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ coated layered Li-rich cathode which demonstrated superior capacity, rate capability, and cycling ability.³¹ Moreover, they reported that the difficulties associated with a Li-rich cathode, such as the operation voltage decay and thermal instability, were also relieved. A similar surface modification was reported by Song et al., and they also demonstrated the improved electrochemical performance of the materials.³²

Owing to the additional process, the above-mentioned coating of the cathode materials usually results in an increase of production costs. Therefore, a more economical surface modification needs to be pursued. A few researchers reported

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that the discharge capacity and cycling performance of the post-thermal treated LiCoO_2 exhibited significant improvement.^{33–35} In particular, Pereira et al. argued that the surface passivation achieved by the post-thermal treatment at a temperature of 850 °C functions as a physical barrier and protects LiCoO_2 from contact with the electrolytes and therefore prevents cathode degradation.³⁵ Pereira et al. demonstrated that the surface layer of the post-thermal treated cathode materials consisted of a cubic spinel structure and that the oxidation states of the cobalt ions within the layer were Co^{2+} and Co^{3+} ; however, they failed to provide an exact identification.

In this study, following the post-thermal procedure developed by Pereira et al., we obtained surface-modified LiCoO_2 powders, which exhibited both a highly improved rate capability and cycling performance as a cathode material for LIB. The structure of the materials was carefully characterized in atomistic detail by X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). In addition, conductive atomic force microscopy (C-AFM) was employed to investigate the surface of the LiCoO_2 powders in terms of the electrical conductivity. Density functional theory (DFT) calculations were also performed to supplement the experimental works.

2. EXPERIMENTS

LiCoO_2 powders were prepared by solid-state synthesis from stoichiometric mixtures of Li_2CO_3 and Co_3O_4 with a ratio of $\text{Li}/\text{Co} = 1:1$. Initially, the starting materials (18.66 g of Li_2CO_3 and 120.38 g of Co_3O_4) were mixed by a mechanical mixer with a rotating speed of 80 rpm for 1 h. Subsequently, the materials were synthesized in air using two different methods. Using a heating rate of 10 °C/min, the first sample was sintered in a furnace at a temperature of 1000 °C for 6 h and subsequently naturally cooled to room temperature. Hereafter, this sample will be denoted as LCO_{ref} . Meanwhile, following the sintering at 1000 °C for 6 h, the other sample was treated by an additional thermal annealing process at a temperature of 800 °C (cooling rate of 5 °C/min) for 3 h. Subsequently, the sample was naturally cooled to room temperature; this sample is denoted as $\text{LCO}_{\text{post-thermal}}$. Figure 1 shows the temperature profiles for the synthesis of the two samples. Then, the batches were crushed and subsequently sieved to obtain an average particle size of 16 μm .

The X-ray powder diffraction patterns were collected using a Philips X-PERT PRO diffractometer (Cu $K\alpha$ -ray radiation) equipped with a graphite monochromator and a PIXcel solid-state detector operated at 40 kV and 40 mA using a continuous scan mode. Diffraction patterns were obtained for $2\theta = 10\text{--}130^\circ$ with a step size of 0.013° and a scan

rate of 0.67°/min. Silicon powder (Aldrich, 99%) was added as an internal standard. The Rietveld refinement of the obtained data was performed using the GSAS suite of programs³⁶ with the EXPGUI interface.³⁷

The morphology of the particles was measured using a SEM (Magellan XHR, FEI Co., Oregon, USA) in back scattering mode. The STEM observations were performed using a Cs-corrected STEM (JEM-2100F, JEOL Co., Japan) at 200 kV, equipped with a spherical aberration corrector (CEOS GmbH, Germany), at the Korea Advanced Nano Fab Center (KANC). The smallest probe had a diameter of ~ 1 Å. The samples for the STEM measurements were prepared using the focused ion beam (FIB, Hellios FEI, USA) technique. The electrical conductivity of the materials was analyzed by an AFM (Danish Microscope Engineering, Denmark) in direct contact (DC) mode with a diamond-coated cantilever. Following the sample preparation by helium ion microscope (Carl Zeiss Microscopy GmbH), measurements were performed in an ultrahigh vacuum (10^{-8} Torr) to avoid contamination. The contact force between the tip and the samples was set as $\sim 1.6 \times 10^{-4}$ nN. The tip was connected to the AFM preamplifier in order to measure the current produced from the cross-section of the LiCoO_2 surface.

To determine the electrochemical performances of the materials, 2032 coin-type cells were fabricated. The cathode electrode was made by blending the active materials, Super-P carbon black and polyvinylidene fluoride (as a binder) in *N*-methyl-2-pyrrolidone (to a ratio of 96:2:2 in wt %). The slurry was subsequently cast onto aluminum foil and dried at a temperature of 110 °C in a vacuum oven for 10 h. The electrolyte used for the cells consisted of 1.15 M LiPF_6 in ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (30:30:40 in vol %) in addition to 5 vol % fluoroethylene carbonate (Panax etec Co., Ltd., Korea). The negative electrode consisted of lithium foil, the capacity of which was 1.5 mAh/cm². The reversible discharge capacities were measured at current rates of 0.1–3 C between 3.0 and 4.5 V. The AC-impedance measurements were performed using a Biologic VMP3 impedance analyzer over the frequency range of 500 kHz to 5 mHz with an amplitude of 10 mV. The galvanostatic intermittent titration technique (GITT) was employed using VMP3 in the voltage range of 3.0–4.5 V at a current density of 0.1 C. The cells were charged for 12 min with a rest time of 2 h.

3. RESULTS AND DISCUSSION

The outer appearance of the two samples was observed by SEM (Figure 2). Following the shape of the Co_3O_4 precursors used in this study, highly spherical particles were obtained. Concentric contours are observed in the low resolution (upper) images of both samples. It is apparent that there is no significant difference in the structures and morphologies of the LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ samples. However, in the high

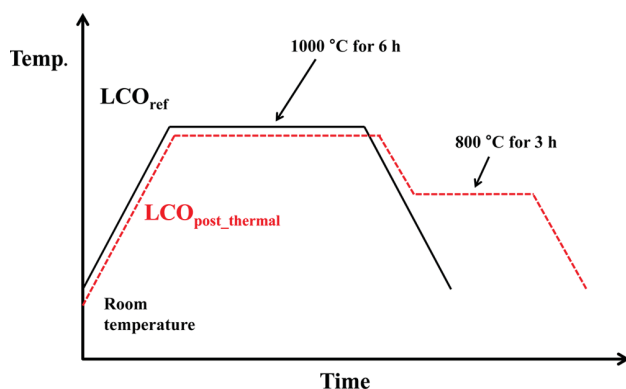


Figure 1. Temperature profiles for the synthesis of the LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ samples in this work.

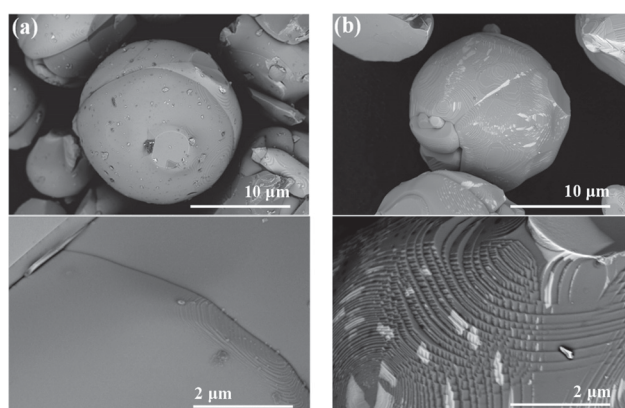


Figure 2. SEM images of (a) LCO_{ref} and (b) $\text{LCO}_{\text{post-thermal}}$ samples.

Table 1. Crystallographic Data from XRD and Rietveld Refinement

LCO _{ref}	ion	site	x	y	z	occupancy
$a = 2.81567(2) \text{ \AA}$	Li ⁺	3a	0	0	0	1
$c = 14.0526(2) \text{ \AA}$	Co ³⁺	3b	0	0	0.5	1
$R_{wp} = 2.82\%$	O ²⁻	6c	0	0	0.2399(2)	1
$R_p = 2.16\%$	Li ⁺ or Co ³⁺ ^a	6c	0	0	0.381(3)	0.22(1)
$\chi^2 = 1.553$						
LCO _{post-thermal}	ion	site	x	y	z	occupancy
$a = 2.81534(2) \text{ \AA}$	Li ⁺	3a	0	0	0	1
$c = 14.0532(2) \text{ \AA}$	Co ³⁺	3b	0	0	0.5	1
$R_{wp} = 3.01\%$	O ²⁻	6c	0	0	0.2397(3)	1
$R_p = 2.14\%$	Li ⁺ or Co ³⁺ ^a	6c	0	0	0.368(9)	0.11(2)
$\chi^2 = 2.308$						

^aWith only XRD measurements, it is unclear which ion (Li⁺ or Co³⁺) exists in this position. However, the refinement in this table was performed on the assumption that the position is occupied by Li⁺.

resolution (bottom) images, well-developed step-terrace structures can be clearly observed in the LCO_{post-thermal} sample, whereas only faint wave patterns can be observed in the LCO_{ref} sample. This difference is due to the dissimilar structural characteristics of the surfaces of the two samples. The surface of the LCO_{post-thermal} sample is largely covered by (cubic) spinel Li_xCo₂O₄, whereas that of the LCO_{ref} sample is not; this will be explained in detail in the following sections.

The laboratory X-ray powder diffraction data do not indicate the presence of any impurities in either sample. The Rietveld refinement was performed with fixed thermal parameters for all ions ($U(\text{Li}) = 0.03 \text{ \AA}^2$, $U(\text{Co}) = 0.015 \text{ \AA}^2$, $U(\text{O}) = 0.02 \text{ \AA}^2$). The refined structural parameters are provided in Table 1, and the calculated patterns are compared with the experimental results in Figure 3. The diffraction patterns of the two samples are very similar and in good agreement with the layered structure ($R\bar{3}m$) of LiCoO₂. There is no observation of cation mixing between the 3a and 3b positions within the detection limit of the XRD. However, minor additional electronic density was detected in the tetrahedral sites, even though these sites are empty in the perfect LiCoO₂ structure. This additional electronic density can be ascribed to the distribution of extra metal cations (Li or Co) in these positions, which produces the spinel phase. This phase can be obtained by the substitution of every second octahedral Li ion in the layered LiCoO₂ with two ions of Li or Co in the neighboring tetrahedral positions. As a result, it is speculated that the solid solution develops from the intergrowth of the layered LiCoO₂ and the spinel phases, as shown in Figure 4.

TEM measurements were employed to investigate the internal structures of the materials in detail. In Figure 5a and c, the bright field TEM images and the selected area electron diffraction (SAED) patterns of the LCO_{ref} and LCO_{post-thermal} samples are shown, respectively; the electron incidence was parallel to the $[100]_{\text{hex}}$ zone axis. The SAED patterns of both samples confirm the layered structure of $R\bar{3}m$ (indexed by dark letters in Figure 5a). In addition, weak reflections (indexed by blue letters) are also observed, which correspond to the spinel structure of Li_xCo₂O₄ ($Fd\bar{3}m$).³⁸ It is known that the formation of the spinel phase is owed to a lack of lithium supply because it is relatively volatile. The dark field TEM images of the LCO_{ref} and LCO_{post-thermal} samples are shown in Figure 5b and d, respectively. The direct beam was blocked by the aperture in the TEM operating system, and only a diffracted beam (marked by a red circle (spinel Li_xCo₂O₄)) was allowed to pass the objective aperture. Hence, the dark field images show the

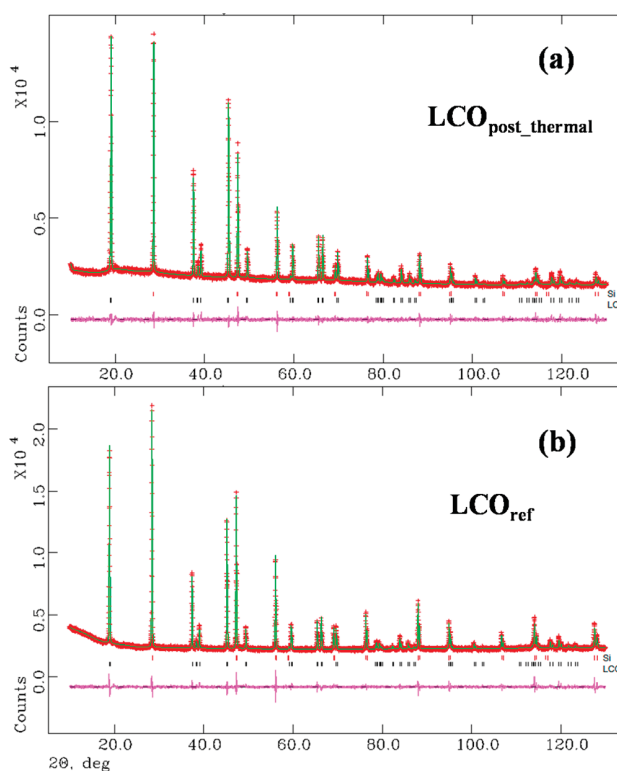


Figure 3. Rietveld plots of (a) LCO_{ref} and (b) LCO_{post-thermal} samples (red dots, experimental pattern; green line, calculated pattern; purple line, difference; black and red ticks, reflection positions of LiCoO₂ and Si standard, respectively).

distribution of the spinel Li_xCo₂O₄ phase. In the LCO_{ref} sample, it is observed that the spinel Li_xCo₂O₄ phase is distributed throughout the crystal (Figure 5b), whereas that in the LCO_{post-thermal} sample is located near the surface (yellow ellipse in Figure 5d). This result indicates that slow quenching (natural cooling) from a high temperature (1000 °C) allows the intergrowth of the layered phase of LiCoO₂ and the spinel phase of Li_xCo₂O₄, i.e., the formation of a solid solution, whereas the post-thermal treatment at 800 °C induces the segregation of the spinel phase at the surface because the solubility range reduces as the temperature decreases.

Figure 6 shows the aberration-corrected high angle annular dark-field (HAADF) STEM images of the LCO_{ref} and LCO_{post-thermal} samples, which are viewed along the $[100]$

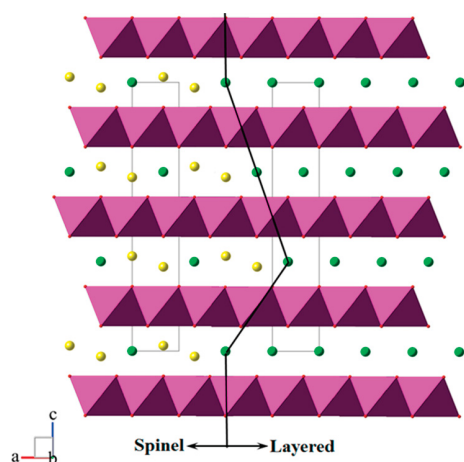


Figure 4. Intergrowth of the layer-structured LiCoO_2 ($R\bar{3}m$, right side) and spinel-structured $\text{Li}_x\text{Co}_2\text{O}_4$ ($Fd\bar{3}m$, left side). Red purple polyhedron, Co; green sphere at octahedral site, Li; and yellow sphere at tetrahedral site, Li or Co.

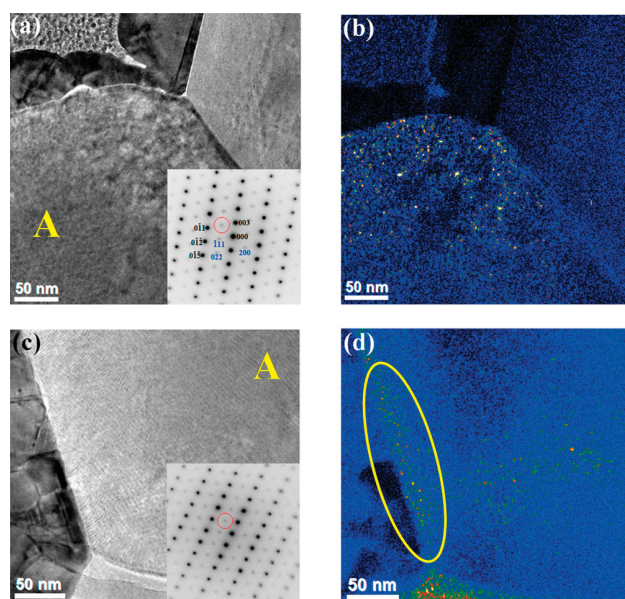


Figure 5. Bright field TEM images of (a) LCO_{ref} and (c) $\text{LCO}_{\text{post-thermal}}$ samples. The inset figures show the SAED patterns of area “A”. The dark field TEM images of (b) LCO_{ref} and (d) $\text{LCO}_{\text{post-thermal}}$ samples. To obtain these dark field TEM images, only a diffracted beam marked by a red circle (spinel $\text{Li}_x\text{Co}_2\text{O}_4$) in the SAED pattern was allowed to pass the objective aperture.

zone axis. As shown in Figure 6a, the overall structure of the LCO_{ref} sample correlates well with the trigonal lattice of $R\bar{3}m$. Meanwhile, the structure of the surface of the $\text{LCO}_{\text{post-thermal}}$ sample corresponds to the spinel lattice of $Fd\bar{3}m$, as shown in Figure 6b. Co and Li ions occupy the 16d and 16c octahedral sites, respectively. The relatively bright columns of the Li layers located within the interior of $\text{LCO}_{\text{post-thermal}}$ indicate that “cation-mixing” of the Li and Co ions has occurred. Meanwhile, the HRTEM (high resolution TEM) image clearly demonstrates the segregation of the spinel phase at the surface of the $\text{LCO}_{\text{post-thermal}}$ sample. In Figure 7, a spinel structure with a thickness of ~ 10 nm can be observed; it exhibits a similar appearance to the coating layer on the layered LiCoO_2 , which is

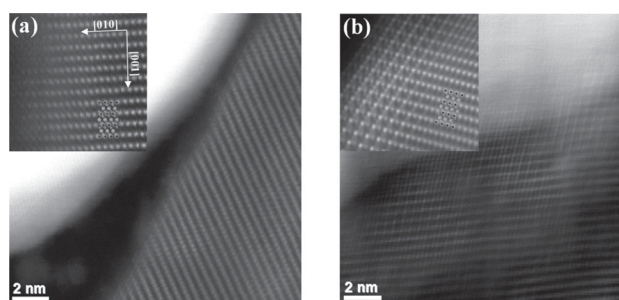


Figure 6. HAADF STEM images of (a) LCO_{ref} and (b) $\text{LCO}_{\text{post-thermal}}$ samples.

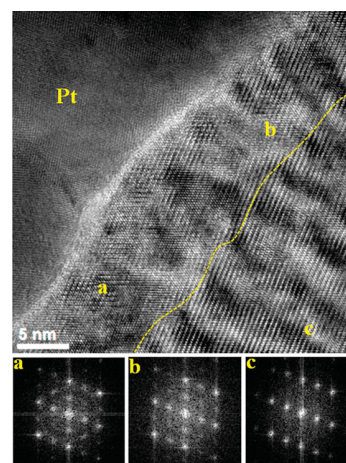


Figure 7. HRTEM image of the $\text{LCO}_{\text{post-thermal}}$ sample. The bottom figures (a, b, and c) exhibit the FFT patterns of the corresponding areas.

confirmed by FFT (fast Fourier transform) analysis. The FFT pattern of the inner area (area c in Figure 7) clearly demonstrates that it consists of a layered structure, whereas those of the areas near the surface (areas a and b) indicate that they consist of a spinel phase.

Figure 8 shows the cycling performance and rate capability of the LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ samples. At a rate of 0.5 C, the $\text{LCO}_{\text{post-thermal}}$ sample exhibits a marked improvement in the capacity retention compared with the LCO_{ref} sample, even though an initial capacity fade during the early 10 cycles is still inevitable. It is speculated that the spinel phase in the $\text{LCO}_{\text{post-thermal}}$ sample functions as a protection layer in order to prevent electrolytes from reacting with the LiCoO_2 materials. Therefore, the oxygen loss as a result of the side reactions is considerably reduced; specifically, the stability is significantly enhanced.³⁹ Figure 8b shows the cycling results for the incremental charging/discharging rates from 0.1 to 3.0 C. The initial capacity fade is not shown because of the low C rates during the early cycles; this is noticeable in the cycling performance measurements in Figure 8a. Meanwhile, the rate capability of the $\text{LCO}_{\text{post-thermal}}$ sample was significantly improved, particularly at a rate of 3.0 C compared with that of the LCO_{ref} sample.

In general, the C-rate property of a lithium coin cell strongly depends on the Li^+ ion diffusion behavior of its cathode materials. As shown in Figure 9a, it can be observed from the GITT data that the chemical diffusion coefficient of the Li^+ ions in the $\text{LCO}_{\text{post-thermal}}$ sample is much higher than that in the

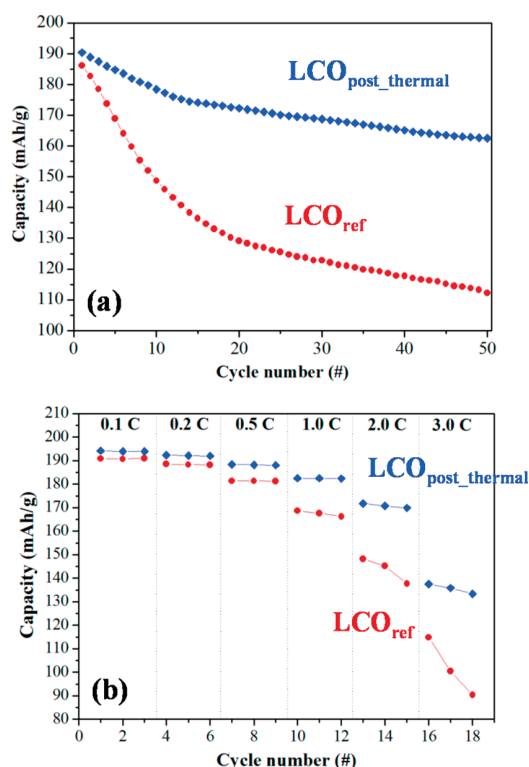


Figure 8. Cycling performances of the half-coin cells with LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ cathodes at (a) 0.5 C rate and (b) incremental charging/discharging rates from 0.1 to 3.0 C in the voltage range of 3.0 to 4.5 V.

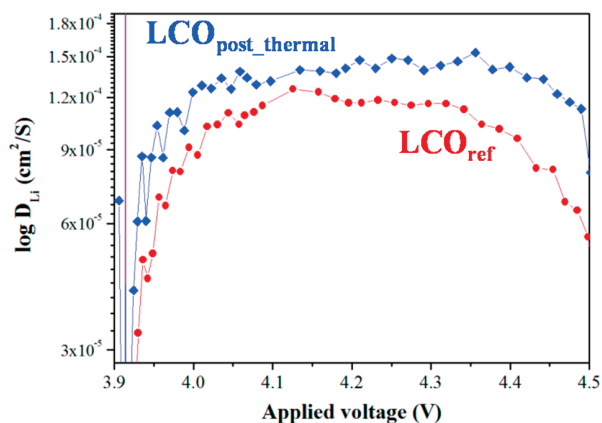


Figure 9. Lithium diffusion coefficients of LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ electrodes calculated from GITT curves as a function of the applied cell voltage.

LCO_{ref} sample. Two possible explanations can be provided for the difference in the Li^+ ion conductivity. The first is that the $\text{LCO}_{\text{post-thermal}}$ sample possesses relatively more crystalline LiCoO_2 than the LCO_{ref} sample. Following sintering, the additional thermal annealing treatment often results in high crystallinity and consequent fast lithium diffusion.⁴⁰ The second explanation refers to the difference in the ionic diffusion of the Li^+ ion in the layered LiCoO_2 and in the spinel $\text{Li}_x\text{Co}_2\text{O}_4$. We do not have any experimental evidence; however, computational studies that calculate the diffusion barriers of Li^+ ions have been reported. The calculated Li^+ ion migration barrier in the layered LiCoO_2 is 0.6–0.2 eV (depending on the lithium

content),⁴¹ this value is greater than that in the spinel LiCo_2O_4 (<0.1 eV).⁴² These calculations are consistent with the GITT data in the present study; this is because the $\text{LCO}_{\text{post-thermal}}$ cathode is partially coated by the spinel $\text{Li}_x\text{Co}_2\text{O}_4$ while the LCO_{ref} cathode is not.

The electronic conductivity is another factor which influences the C-rate performance. Therefore, C-AFM measurements were performed to investigate the electronic conductivity of the LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ samples. Cross sections of the areas near the surfaces of the cleaved particles were characterized. The surface topographies and the corresponding current images were simultaneously obtained by applying an electrical bias of 3 V. Both the samples were prepared by helium ion FIB and maintained a relatively uniform height throughout the entire area, as shown in Figure 10a and d. Meanwhile, the electrical behavior exhibited in the current images was quite different. In the case of the LCO_{ref} sample, there was no remarkable contrast observed for the entire region (Figure 10b); this indicates that the sample is almost electrically nonconducting (Figure 10c). Conversely, a bright contrast which indicates high conductivity was observed in the $\text{LCO}_{\text{post-thermal}}$ sample (Figure 10e). The conductive area is located on the surface of the $\text{LCO}_{\text{post-thermal}}$ particle, and the current level reaches at ~ 2.0 nA (Figure 10f). It is known that the partially delithiated spinel lithium cobalt oxide ($\text{Li}_x\text{Co}_2\text{O}_4$), which is often called low temperature LiCoO_2 (LT- LiCoO_2), exhibits much higher electrical conductivity than the layered LiCoO_2 , i.e., high temperature (HT)- LiCoO_2 (layer-structured LiCoO_2). A recent study by Maiyalagan et al. demonstrated that the high electrical conductivity of the partially delithiated spinel $\text{Li}_x\text{Co}_2\text{O}_4$ results in its strong bifunctional electrocatalytic activity for the oxygen evolution and oxygen reduction reactions required for lithium–air batteries.⁴³ Using the DFT calculations, we compared the band gap energies of the LiCoO_2 and LiCo_2O_4 materials. The former exhibits a considerably large band gap energy of 1.15 eV, whereas the latter demonstrates almost metallic conduction behavior. The detailed results, which include the density of states, are available in the Supporting Information.

Electrochemical impedance spectroscopy (EIS) provides useful information, such as the transport properties of lithium ions in the electrolyte, the characteristics of the charge transfer across the electrode/electrolyte interfaces, and the absorption of lithium ions into the solid matrix.^{44,45} The Nyquist plots of the cells produced from the LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ materials for the first and the 50th cycle are compared in Figure 11. The plots can be explained with an equivalent circuit, as shown in the figure inset. The high frequency intercept of the real impedance (Z') axis corresponds to the impedance related to the ion diffusion in the electrolyte solution (solution resistance, R_s). The high frequency semicircle is assigned to the solid electrolyte interface (SEI) resistance (R_{SEI}), while the low frequency semicircle reflects the charge transfer resistance at the interface of the cathode/electrolyte (R_{ct}). The Warburg tail, i.e., the sloping line at low frequency, indicates the lithium ion diffusion in the solid electrodes. The respective impedance components (R_s , R_{SEI} , and R_{ct}) are summarized in Table 2. From the plot of the first cycle (Figure 11a), we know that the $\text{LCO}_{\text{post-thermal}}$ cathode exhibits a smaller resistance, particularly R_{ct} , than the LCO_{ref} cathode; however, this difference is insignificant. Meanwhile, during the 50th cycle, the resistances of both cells greatly increase as a result of cycling degradation. The majority of the increased resistance originates from R_{ct}

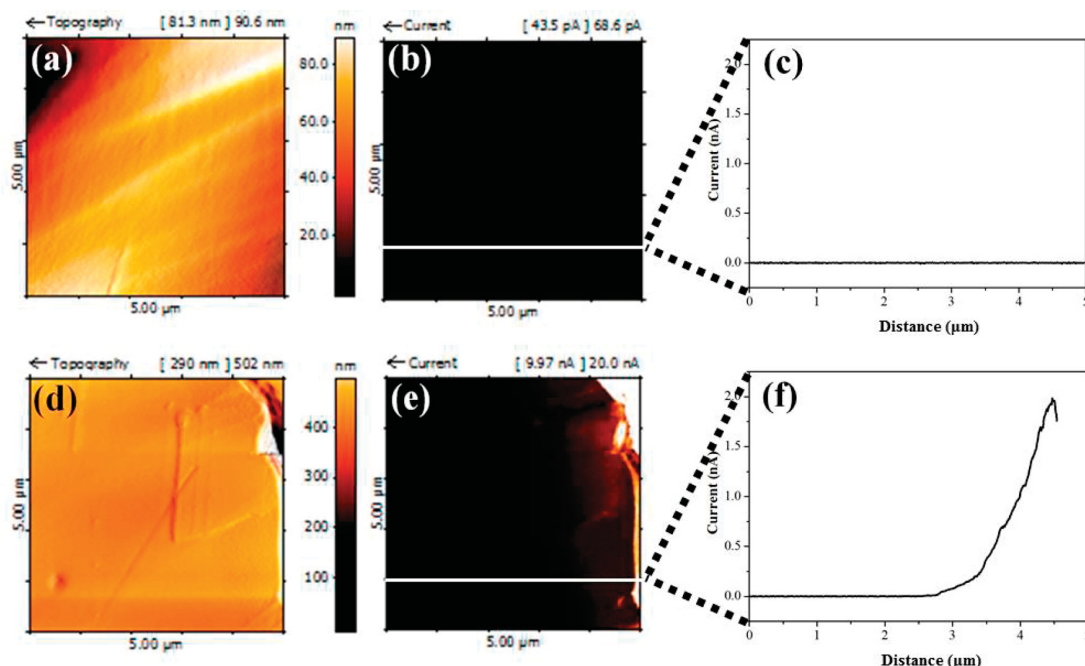


Figure 10. Topographic images ((a) LCO_{ref} and (d) $\text{LCO}_{\text{post-thermal}}$) and current maps ((b) LCO_{ref} and (e) $\text{LCO}_{\text{post-thermal}}$) from C-AFM measurements. Current profiles of (c) LCO_{ref} and (f) $\text{LCO}_{\text{post-thermal}}$ collected at positions indicated by the white lines in b and e, respectively.

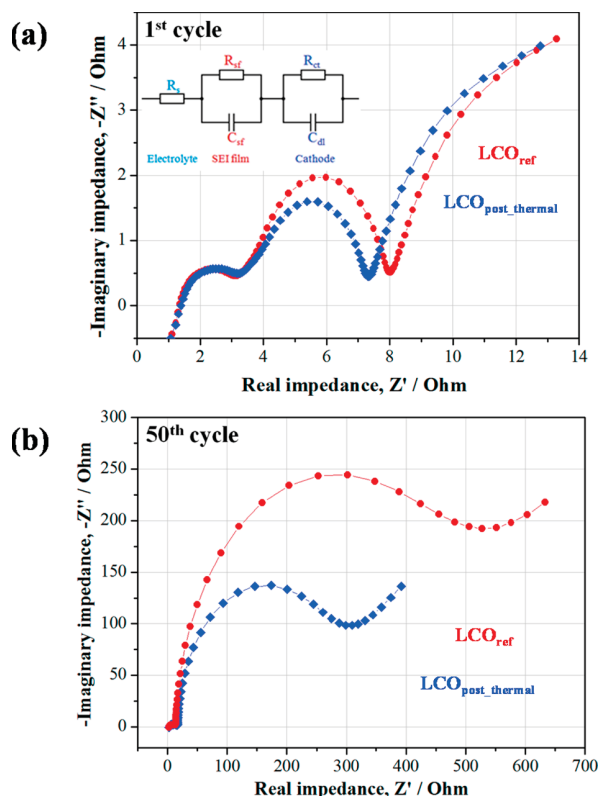


Figure 11. Nyquist plots of the half-coin cells with LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ cathodes at the (a) first and (b) 50th cycle. The inset diagram is an equivalent circuit.

which implies that the charge transfer at the interface of cathode/electrode becomes difficult. However, there is a significant difference in the extent of the increase of R_{ct}

Table 2. Resistances Obtained from Equivalent Circuit Fitting of Experimental Data for the LCO_{ref} and $\text{LCO}_{\text{post-thermal}}$ samples

resistance (Ω)	first cycle		50th cycle	
	LCO_{ref}	$\text{LCO}_{\text{post-thermal}}$	LCO_{ref}	$\text{LCO}_{\text{post-thermal}}$
R_s	1.37	1.40	3.19	3.21
R_{ct}	4.73	4.23	445.8	251.2
R_{sf}	1.98	1.92	10.36	11.67

between the samples. The R_{ct} of the cell with the $\text{LCO}_{\text{post-thermal}}$ material is nearly half of that with the LCO_{ref} materials, while the other impedance components (R_s and R_{sf}) exhibit relatively similar values. The $\text{LCO}_{\text{post-thermal}}$ material exhibits relatively higher electrical conductivity than the LCO_{ref} material as a result of the conductive spinel phase at the surface of the cathode materials, and this may attenuate the cycling deterioration and the consequent rapid rise of R_{ct} . In addition, though it is considered to be a minor effect, the higher ionic conductivity of the $\text{LCO}_{\text{post-thermal}}$ material also positively influences the cycling performance. This is because the rapid Li^+ ionic diffusion does not result in the accumulation of Li^+ ions at the surface of the cathode materials.

4. CONCLUSION

Thin spinel ($\text{Li}_x\text{Co}_2\text{O}_4$)-coated LiCoO_2 material prepared by post-thermal treatment was thoroughly characterized by various experiments to determine the origin of its excellent performance as a cathode material for LIB. The structural features of the spinel phase on the surface of the material were characterized on an atomistic scale by TEM measurements with the aid of XRD. From the C-AFM and the EIS experiments, it was revealed that the spinel $\text{Li}_x\text{Co}_2\text{O}_4$ phase on the surface of the active materials was strongly conductive. Hence, we conclude that the enhanced electrochemical performances of the post-thermal treated material exist because

the effective coating layer exhibits a dual role. It prevents side reactions as a protection layer and functions as a conductive agent, thus improving the electrical behavior.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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