Differentiating Allotropic $\text{LiCoO}_2/\text{Li}_2\text{Co}_2\text{O}_4$: A Structural and Electrochemical Study

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ABSTRACT

In situ high-energy X-ray diffraction was carried out to investigate the structural transformation of lithium cobalt oxides during the solid-state synthesis. Two allotropic phases were observed during the synthesis process; $\text{Li}_2\text{Co}_2\text{O}_4$ with a spinel structure was formed within the temperature window between 450°C and 650°C, beyond which $\text{Li}_2\text{Co}_2\text{O}_4$ was converted to its hexagonal counterpart, layered LiCoO_2 , through a cation exchange between Li and Co. In electrochemical tests, the $\text{Li}_2\text{Co}_2\text{O}_4$ was estimated to have a very low reversible capacity, $\sim 20 \text{ mAh g}^{-1}$, and a high initial irreversible capacity loss of about 80 mAh g^{-1} . An interfacial phase between layered LiCoO_2 domain and spinel $\text{Li}_2\text{Co}_2\text{O}_4$ domain was also identified by *ex situ* high-resolution X-ray diffraction.

INTRODUCTION

Allotropic compounds are generally considered a class of chemicals with identical nominal chemical formula, but with substantial differences in their chemical and/or physical properties. Diamond and graphite are a pair of typical allotropic compounds; the former is a super hard insulator while the latter is a soft electronic conductor. Allotropic structures are also widely found in inorganic oxides like PbO ,¹⁻² TiO_2 ,³⁻⁷ MnO_2 ,⁸⁻¹² and many others.¹³ The allotropic structure has been a major barrier to establish the structure-property relationship of functional materials. Advanced structural characterization tools, like the *in situ* synchrotron probes used in this study, can provide valuable new insight for in understanding and designing complex functional materials.

For instance, lithium cobalt oxide (LiCoO_2) has been the dominant cathode material for state-of-the-art lithium-ion batteries since the early 1990s. This material is widely referred to as a “layered” material with a hexagonal structure in space group $R\bar{3}m$ (166). What is not well known is its allotropic counterpart, spinel $\text{Li}_2\text{Co}_2\text{O}_4$, which is formed by a low-temperature synthesis. The difficulty in differentiating this pair of allotropic compounds lies in their similar scattering structure factor, making it difficult to identify $\text{Li}_2\text{Co}_2\text{O}_4$ by regular X-ray diffraction techniques. However, owing to the recent development of high-quality X-ray sources from synchrotrons,¹⁴ neutron sources,¹⁵ and high-resolution transmission electron microscopes,¹⁶⁻¹⁸ the structural difference between $\text{Li}_2\text{Co}_2\text{O}_4$ and LiCoO_2 can now be easily distinguished. Using neutron diffraction, Thackeray et al.¹⁵ revealed the doping of Co atoms in lithium layers of LiCoO_2 when annealed at 400°C. Rietveld refinement suggested a small degree of Li-Co intermixing (~6%) in samples sintered at low temperatures. Using *in situ* high-energy X-ray diffraction (HEXRD), Wicker et al.¹⁴ tracked the structural evolution during the solid-state synthesis of LiCoO_2 . They reported that the layered component, LiCoO_2 , dominated the whole synthesis process, while only a small fraction of $\text{Li}_2\text{Co}_2\text{O}_4$ was observed at low temperature region.¹⁴ In this work, we employed both *in situ* HEXRD and *ex situ* high-resolution X-ray diffraction (HRXRD) for a careful characterization of the $\text{Li}_2\text{Co}_2\text{O}_4$ - LiCoO_2 system.

EXPERIMENTAL

Solid-state synthesis of cathode materials - Co_3O_4 and Li_2CO_3 with a molar ratio of 2:3.15 were mechanically mixed for 48 hours. 5% excess lithium was added to compensate potential lithium loss during synthesis. Separate batches of the mixed powder were then heated at a constant rate of 5 °C·min⁻¹ in air to selected temperatures between 450 °C and 950 °C. The

samples were then annealed at the selected temperatures for 16 hours before being naturally cooled to the room temperature (RT).

***In situ* HEXRD** - The powder mixture of Co_3O_4 and Li_2CO_3 was compressed into a pellet of about 2-mm in thickness. The pellet was then vertically placed in a programmable furnace (Linkam TS 1500) with the X-ray beam aimed at the center of the pellet. The sample was then heated from RT to 1050 °C with a constant heating rate of 1 °C·min⁻¹. The *in situ* HEXRD experiment was carried out at sector 11-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory. The wavelength of the X-ray beam was pre-fixed at 0.10804 Å. During the *in situ* solid-state synthesis, a 2D X-ray detector was used to collect the XRD patterns at a rate of one spectrum per minute. The details of the experimental setup can be found in our previous report.¹⁹

***Ex situ* HRXRD** - The HRXRD patterns of cathode samples synthesized at various temperatures were collected at sector 11-BM of the APS. The wavelength of the X-ray beam used was 0.413326 Å.

Electrochemical characterization - The electrochemical performance of the cathode powders was tested in 2032 coin cells using a lithium foil as the anode. The cathode was fabricated with a mixture of cathode powder (80 wt%), Super P (10 wt%), and polyvinylidene fluoride (PVDF) (10 wt%) in N-methyl-2-pyrrolidone (NMP). The slurry was coated onto the aluminum foil and dried in a vacuum oven at 75 °C. The electrolyte was 1.2 M LiPF_6 in a mixture solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a mass ratio of 3:7. The half

cells were charged/discharged between 3.0 V and 4.2 V at a constant current of 0.08 mA (C/10) at the room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of HEXRD profiles during the solid-state synthesis of LiCoO₂ using Co₃O₄ and Li₂CO₃ as the starting materials. During the *in situ* experiment, the starting materials were heated from the room temperature to 1050°C with a constant rate of 1°C·min⁻¹. The characteristic diffraction peak positions for both Co₃O₄ (spinel, PDF card # 74-2120) and Li₂CO₃ (PDF card # 72-1216) are labeled at the bottom of Figure 1. Thermal expansion of the lattice was observed, and the continuous shift of the diffraction peaks toward smaller 2θ values was observed up to 400°C, beyond which the peak intensity for both Co₃O₄ and Li₂CO₃ decreased quickly. To further analyze the reaction between Co₃O₄ and Li₂CO₃, we used the peak area of the (110) peak for Li₂CO₃ (2θ = 1.49°) to estimate the relative content of Li₂CO₃ during the solid-state reaction and the (422) peak for Co₃O₄ (2θ = 3.78°) to estimate the Co₃O₄ content. Figure 2a shows the evolution of peak areas as a function of the temperature. From RT to 400°C, the peak area remained stable for Li₂CO₃ but slowly decreased for Co₃O₄. It is speculated that this change is related to the loss of moisture from Co₃O₄. Above 400°C, the peak areas for both Li₂CO₃ and Co₃O₄ dropped dramatically at roughly the same rate. The strong correlation between the two starting materials is also illustrated in Figure 2b, which indicates a strong linear relationship between Li₂CO₃ and Co₃O₄ content. This suggests that the solid-state reaction is a one-step reaction:

In the above reaction, the products of layered LiCoO_2 and spinel $\text{Li}_2\text{Co}_2\text{O}_4$ were identified from the *in situ* HEXRD data. Figure 1 clearly shows the emergence of a new set of diffraction peaks when the temperature is above 400°C . At the plotting scale of Figure 1, the new peaks could be assigned to layered LiCoO_2 (R-3m, space group 166). However, the zoom-in view of the data between 3.9° and 4.05° in Figure 3a shows that the new peaks were dominated by the spinel $\text{Li}_2\text{Co}_2\text{O}_4$ (Fd-3m, space group 227). This figure clearly shows three characteristic diffraction peaks: the (511) peak for Co_3O_4 at the bottom; the (511)_s peak for $\text{Li}_2\text{Co}_2\text{O}_4$ at the right, between 620°C and 760°C ; and the characteristic (107)_L peak for layered LiCoO_2 at the left. Figure 3b shows that, within the temperature window between 620°C and 760°C , the (107)_L and (551)_s peaks are well separated from each other. The initial decrease in the peak intensity of (107)_L is an artifact of the residual Co_3O_4 whose (551) peak overlaps with the (107)_L peak. Other than that, the content of LiCoO_2 increases while that of $\text{Li}_2\text{Co}_2\text{O}_4$ decreases steadily with the heating temperature. This indicates that $\text{Li}_2\text{Co}_2\text{O}_4$ was the dominant product when the temperature was below 620°C , beyond which $\text{Li}_2\text{Co}_2\text{O}_4$ converted to layered LiCoO_2 . Figure 3a shows that this conversion process finished at about 820°C . The formed LiCoO_2 crystallized at a temperature above 820°C , as indicated by the sharpening of the (107)_L peak in Figure 3a.

When the sample was heated to a temperature beyond 960°C , LiCoO_2 was partially decomposed into CoO (see Figure 1) by losing both Li_2O and O_2 . During the cooling process, CoO was converted back to the stable form Co_3O_4 (XRD data during the cooling process are not shown). As a precaution, the annealing temperature for the *ex situ* syntheses was limited to 950°C .

The above results were obtained during a dynamic heating process with continuously changing temperature. It is of interest to determine whether the same reaction mechanism can be

applied to steady-state synthesis. The *ex situ* experiments were thus carried out by annealing the cathode materials for 16 hours at temperatures ranging from 450°C to 950°C. Figure 4 shows the normalized HRXRD patterns of the samples annealed at these temperatures. Note that the wavelength of the HRXRD was 0.413 Å, which is much longer than that for HEXRD. It is common that the peak intensity increased rapidly with the annealing temperature because of the increase in crystallinity. It is of our interest to determine the relationship between different phases. Hence, the HRXRD patterns were normalized by rescaling the (003)_L peak at 5.05°, for layered LiCoO₂, to unity (see Figure 4). One can see that the peak width of the (003)_L decreases steadily with the annealing temperature, but the peak position remains constant. More importantly, a big broad peak, which can be assigned to the (111)_S peak for spinel Li₂Co₂O₄, appears at a slightly higher 2θ value, about 5.13°. Figure 4 indicates that the spinel form Li₂Co₂O₄ was the major product when the annealing temperature is below 550°C. This finding is not consistent with the report of Wicker and Walker¹⁴ that the content of Li₂Co₂O₄ is low throughout the whole synthesis process. Figure 4 also shows that the Li₂Co₂O₄ content decreases rapidly with the annealing temperature. At annealing temperature above 750°C, the (111)_S peak for Li₂Co₂O₄ completely disappeared from the HRXRD patterns in Figure 4. This finding agrees with the *in situ* experiment, except that the finishing temperature for the conversion was higher for the *in situ* experiment.

Rietveld refinement was also carried out to fit the HRXRD data for the samples annealed at different temperatures. A two-phase model, involving layered LiCoO₂ and spinel Li₂Co₂O₄, was used to fit the data for samples annealed at 450°C, 550°C, and 650°C. For annealing temperature higher than 650°C, a single-phase model, layered LiCoO₂, was used. Table 1 shows the cell parameters obtained from the Rietveld refinement. The *a* and *b* values of layered

LiCoO₂ slightly decrease (~0.04%) with the annealing temperature, while the *c* values increase slightly (~0.1%). Since the variation of the cell parameters are at the detecting limit of the instrument, the cell parameters can be considered constant regardless of the annealing temperature. Figure 5a shows a typical good fit for samples annealed at a high temperature, while Figure 5b shows a typical poor fit for samples annealed at lower temperatures. The fitting residue in Figure 5b suggests the existence of a third set of weak diffraction peaks. Therefore, we performed a simple peak deconvolution using a type 2 pseudo-Voigt peak to identify the number of components in area around 5.1° and 16.8°. As a reference, the HRXRD pattern for the sample annealed at 850°C was also included to help in peak assignment. The diffraction data in the 2θ window between 4.8° and 5.3° were successfully decomposed into three independent peaks, whose peak positions remained constant regardless of the annealing temperature (left panel in Figure 6). We assigned the sharp peak at the left to the (003)_L peak of layered LiCoO₂, the right peak at about 5.15° to the (111)_S peak of the spinel Li₂Co₂O₄, and the broad, weak peak in the middle to the (111)_{S'} peak of a strained spinel phase. The diffraction data in the 2θ window between 16.5° and 17.0° were de-convoluted into four peaks (right panel in Figure 6). The (107)_L and (110)_L peaks for layered LiCoO₂ were assigned to two sharp peaks at 16.63° and 16.88°, respectively. The one at 16.82° was assigned to the (551)_S peak of the spinel Li₂Co₂O₄. Similar to the results shown in the left panel of Figure 6, a broad, low intensity peak was identified (at about 16.74°). In general, layered LiCoO₂ deviates from the standard cubic structure (*c/a*=2√6), leading to the splitting between the (107)_L and (110)_L peaks. Hence, the minor phase is more likely a spinel phase due to the lack of another peak. In addition, the minor phase should have a crystal structure between the layered and the spinel structures based on the

relative peak positions. More than likely, the minor phase was a strained spinel phase that bridged the crystalline LiCoO_2 and $\text{Li}_2\text{Co}_2\text{O}_4$.

Half cells using the cathode materials annealed at 450-950°C were cycled between 3.0 V and 4.2 V vs. Li^+/Li for two cycles. Figure 7 shows the voltage profiles of these cells, and the corresponding differential capacity profiles (dQ/dV) are plotted in Figure 8. For the materials annealed at 750°C and above, the cells delivered a high reversible specific capacity of 141 mAh g^{-1} with a small potential hysteresis between the charge and discharge profiles (see Figures 7d-f). The pair of sharp dQ/dV peaks at about 3.9 V vs. Li^+/Li was assigned to the redox reaction between LiCoO_2 and $\text{Li}_{0.5}\text{CoO}_2$ (see Figures 8d-f). When the materials were annealed at 650°C and below, we observed a huge initial irreversible capacity loss (IICL), which decreased dramatically with the annealing temperature (Figures 7a-c). After the initial cycle, the cells still retained small portion of their initial capacity; the dQ/dV profiles of the second cycle agreed well with that of the redox reaction between LiCoO_2 and $\text{Li}_{0.5}\text{CoO}_2$ (Figures 8a-c). The potential hysteresis for the cathode materials annealed at low temperatures was substantially greater than that of materials annealed at high temperatures. As evidenced from both the electrochemical and the HRXRD data (Figure 4), the potential hysteresis and the large IICL were caused by the existence of the spinel $\text{Li}_2\text{Co}_2\text{O}_4$.

Figure 9 shows a strong linear relationship between the discharge capacities of the cathode materials treated at different annealing temperatures and their initial charge capacities. Assuming that the samples were physical mixtures of two independent phases and taking into consideration that LiCoO_2 has a very small IICL and $\text{Li}_2\text{Co}_2\text{O}_4$ a large IICL, one can easily predict the linear relationship shown in Figure 9, as well as a large IICL of about 80 mAh g^{-1} for $\text{Li}_2\text{Co}_2\text{O}_4$. This two-phase model also predicts that the samples annealed at 750°C and above

would be mostly LiCoO_2 while the sample annealed at 650°C would be a mixture of about 70% LiCoO_2 and 30% $\text{Li}_2\text{Co}_2\text{O}_4$. If the peak areas of $(003)_\text{L}$ and $(111)_\text{S}$ are used to estimate the ratio between LiCoO_2 and $\text{Li}_2\text{Co}_2\text{O}_4$, the sample annealed at 650°C is composed of about 95% LiCoO_2 and 5% $\text{Li}_2\text{Co}_2\text{O}_4$. This discrepancy indicates that the real mechanism might be more than the simple two-phase mixture.

Figure 10 schematically shows the atomic ordering in both layered LiCoO_2 and spinel $\text{Li}_2\text{Co}_2\text{O}_4$. The serious overlapping of diffraction peaks between LiCoO_2 and $\text{Li}_2\text{Co}_2\text{O}_4$ suggests similar spacing between diffraction planes, as shown in Figure 10. The striking difference between LiCoO_2 and $\text{Li}_2\text{Co}_2\text{O}_4$ lies in the systematic Li/Co intermixing in $\text{Li}_2\text{Co}_2\text{O}_4$. In the layered framework, both lithium and cobalt columns line up to form separated lithium and cobalt layers. However, in the $\text{Li}_2\text{Co}_2\text{O}_4$ framework, every other lithium column (or cobalt column) is doped with 50% cobalt (or lithium), resulting in the loss of the lithium diffusion channel. Figure 10 suggests that the conversion reaction from the spinel $\text{Li}_2\text{Co}_2\text{O}_4$ to the layered LiCoO_2 can be accomplished by the Li/Co exchange between adjunct slabs. The *in situ* HEXRD results show that $\text{Li}_2\text{Co}_2\text{O}_4$ was converted to LiCoO_2 at elevated temperatures, but LiCoO_2 was not converted back to $\text{Li}_2\text{Co}_2\text{O}_4$ during the slow cooling process. This finding indicates that LiCoO_2 is the overall stable form within the temperature window explored in this work, and the appearance of the transitional metastable $\text{Li}_2\text{Co}_2\text{O}_4$ originates from the pre-occupation of cobalt atoms in the precursor, spinel Co_3O_4 .¹⁴ The HRXRD profiles in Figure 4 also show a small mismatch in lattice parameters between the spinel $\text{Li}_2\text{Co}_2\text{O}_4$ and the layered LiCoO_2 ; thus, one can anticipate the existence of an interfacial phase to bridge the LiCoO_2 and the $\text{Li}_2\text{Co}_2\text{O}_4$ domain. We believe that this interfacial phase is a strained spinel framework, matching the minor phase shown in Figure 5; the small dislocation of atoms caused by the strain can also help to reduce the energy

barrier for Li/Co exchange. Before the completion of the conversion reaction from $\text{Li}_2\text{Co}_2\text{O}_4$ to LiCoO_2 , the strained interfacial spinel phase covers the outer boundary of the LiCoO_2 domains, acting as a percolation barrier for the lithium diffusion. This leads to the increase of the potential hysteresis (see Figures 7a-c) and a significant reduction of lithium utilization in the cathode materials annealed at a low temperature, such as 650°C (see Figure 9).

CONCLUSION

The allotropic structures LiCoO_2 and $\text{Li}_2\text{Co}_2\text{O}_4$ are difficult to distinguish using a regular lab-scale X-ray diffractometer. Both *in situ* high-energy X-ray diffraction and *ex situ* high-resolution X-ray diffraction were applied to investigate the formation of $\text{Li}_2\text{Co}_2\text{O}_4$ and LiCoO_2 during solid-state reaction. Compared to $\text{Li}_2\text{Co}_2\text{O}_4$, layered LiCoO_2 is energetically favored, and $\text{Li}_2\text{Co}_2\text{O}_4$ is formed as an intermediate phase during the solid-state synthesis due to the pre-occupation of cobalt atoms in the oxygen framework in the precursor, spinel Co_3O_4 . A strained spinel phase was also identified as the interfacial phase, which bridges the layered LiCoO_2 and spinel $\text{Li}_2\text{Co}_2\text{O}_4$. It was speculated that the strained spinel phase helps to facilitate Li/Co exchange during the conversion reaction from $\text{Li}_2\text{Co}_2\text{O}_4$ to LiCoO_2 .

Notes

The authors declare no competing financial interest.

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Table 1. Rietveld refinement for HRXRD data^a

T, °C	LiCoO ₂		Li ₂ Co ₂ O ₄	wRp	CHI**2
	<i>a=b</i>	<i>c</i>	<i>a=b=c</i>		
450	2.8175(4)	14.040(6)	7.9982(4)	0.092	3.50
550	2.8163(9)	14.046(1)	7.9980(2)	0.111	4.59
650	2.8164(9)	14.045(0)	7.9989(0)	0.119	6.96
750	2.8160(9)	14.053(4)	-	0.133	7.94
850	2.8163(6)	14.054(3)	-	0.141	9.10
950	2.8162(7)	14.053(0)	-	0.155	10.8

a. Based on two-phase model for temperatures $\leq 650^\circ\text{C}$ and single-phase model for $>650^\circ\text{C}$.

Figure 1. HEXRD patterns during the solid-state synthesis of LiCoO_2 using Co_3O_4 and LiCO_3 as the starting materials.

Figure 2. Peak area for (110) peak of Li_2CO_3 and (422) peak of Co_3O_4 during solid-state reaction.

Figure 3. (a) Zoomed view of HEXRD pattern within the 2θ range of 3.90° and 4.05° , and (b) the variation of peak area for (107) peak for layered LiCoO_2 and (511) peak for spinel $\text{Li}_2\text{Co}_2\text{O}_4$ as functions of the temperature.

Figure 4. Normalized HRXRD patterns of samples annealed at different temperatures showing the coexistence of $\text{Li}_2\text{Co}_2\text{O}_4$ and LiCoO_2 at a low temperature.

Figure 5. Typical Rietveld refinement results for materials annealed at (a) 850°C and (b) 550°C.

Figure 6. Peak deconvolution of HRXRD profiles.

Figure 7. Voltage profiles of half cells using the cathode materials annealed at different temperature. The cells were cycled between 3.0 V and 4.2 V at a constant current of C/10.

Figure 8. Differential capacity profiles of half cells whose voltage profiles are shown in Figure

7.

Figure 9. Discharge capacity versus initial charge capacity for cathode materials with different annealing temperatures.

Figure 10. Schematic showing the conversion mechanism from $\text{Li}_2\text{Co}_2\text{O}_4$ to LiCoO_2 .