Understanding the Irreversible Reaction Pathway of the Sacrificial Cathode Additive Li_6CoO_4

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The use of a sacrificial cathode additive that contains a large amount of lithium is one potential solution to compensate for the irreversible capacity loss associated with next-generation anodes such as silicon. Antifluorite-type Li_cCoO₄ has attracted attention as a potential cathode additive owing to its remarkably high theoretical lithium extraction capacity. However, the complex mechanism of lithium extraction as well as the oxygen loss from $Li_{c}CoO_{4}$ is not well understood. A generalizable computational thermodynamics and experimental framework is presented to understand the lithium-extraction pathway of Li_6CoO_4 . It is found that one lithium per formula unit can be topotactically extracted from Li₆CoO₄, followed by an irreversible and nontopotactic phase transformation to Li₂CoO₃ or LiCoO₂ depending on the temperature. The results show that peroxide species may form to charge-compensate for Li extraction which is undesirable as this can lead to gas release during battery operation. It is suggested that charging Li_6CoO_4 at an elevated temperature that the electrolyte can withstand, redirects the reaction pathway and prevents the formation of intermediate peroxide species making it an effective and stable sacrificial cathode additive.

example, a significant amount of irreversible lithium loss has been reported^[1] in the formation of a Li-rich solid electrolyte interphase on Si-based anodes. Chemical and electrochemical prelithiation of Si-based anodes have been used to compensate for this irreversible loss.^[2–4] Although these approaches have resulted in significant improvement in the reversible capacity of lab-scale cells with Si anodes, they are less practical in largescale manufacturing because of the need for additional processing after electrode preparation. This is particularly problematic because of the high reactivity and handling challenge with lithiated anodes. The most practical method to tackle lithium loss is the use of sacrificial cathode additives,^[5] which can serve as a drop-in solution for current lithium-ion battery manufacturing. The idea of these sacrificial additives is to release most of their capacity irreversibly during the

1. Introduction

Lithium loss from the cathode during the first charging process is a serious issue for next-generation lithium–ion batteries. For

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first charge to compensate for the irreversible capacity loss in these systems.

A sacrificial cathode additive has the following requirements:^[5] 1) it must be electrochemically oxidizable within the potential window of the cathode to release a large

L. Kaufman, B. D. McCloskey Department of Chemical and Biological Engineering University of California Berkeley, CA 94720, USA W. Jung, B. Park, C. Jo, T. Yoo, D. Lee Battery R&D Center LG Energy Solution Daejeon 34122, Republic of Korea B. Lee Computational Science Research Center Korea Institute of Science and Technology (KIST) Seoul 02792, Republic of Korea amount of lithium during the first charge (or activation); 2) it must possess a high irreversible capacity such that a small amount of the additive can compensate for the overall capacity loss; and 3) after activation, any residue must remain stable and not cause adverse side reactions. The first two requirements require almost certainly conversion reactions to take place as topotactic Li removal is typically limited to one Li per transition metal. The third requirement is challenging since high voltage and the presence of unstable conversion products in which oxygen is poorly hybridized^[6,7] may lead to oxygen-oxidation, either as O₂ gas or as peroxide species. Any peroxide species that forms may lead to O₂ release or other gaseous reaction products during battery operation which will induce swelling of the battery pouch. Li₅FeO₄ with the antifluorite structure has been proposed as a sacrificial cathode additive due to its high irreversible capacity, low cost, and environmental friendliness.^[8,9] However, poor air stability remains its biggest challenge for scaling.^[10] Other examples of sacrificial cathode additives include Li₂NiO₂, Li₃N, and organic lithium salts.^[11–13] Li_6CoO_4 is also a promising candidate because of its remarkably high theoretical capacity^[14-16] of 977.11 mAh g^{-1} when extracting six lithium per formula unit. Li_6CoO_4 crystallizes in the antifluorite structure, where O^{2-} anions form a face-centered cubic (fcc) sublattice and cations occupy 87.5% of the tetrahedral sites. To control its behavior as a sacrificial cathode additive, understanding the reaction pathway during the activation process is crucial. Although various computational^[14] and experimental techniques^[14-17] have been used to elucidate the behavior of Li₆CoO₄ during the first charge (i.e., activation), the capacity limit of the topotactic reaction and the onset of nontopotactic reactions, the identification of each phase that appears during the activation process, and the chemical and electrochemical stability of the residue during long-term storage and cycling remain uncertain.

In this work, we employ a suite of computational methodologies to predict the irreversible lithium extraction pathway of Li_6CoO_4 . We compare these predictions with experimental results obtained from in situ X-ray diffraction (XRD), differential electrochemical mass spectrometry (DEMS), ex situ gas chromatography (GC), and galvanostatic intermittent titration (GITT) to provide a comprehensive understanding of Li_6CoO_4 as a sacrificial cathode additive.

2. Results and Discussion

2.1. Approach

As lithium is removed from Li_6CoO_4 , competition arises between topotactic extraction ($\text{Li}_{6-x}\text{CoO}_4$), which maintains the crystal structural framework, and nontopotactic reactions, which induce transformations into a different structure. We use density functional theory (DFT) and add entropic terms (see the Experimental Section) to compute the relevant free energies of all the topotactic and possible nontopotactic reaction products.

Because the reaction pathway of $\text{Li}_{6-x}\text{CoO}_4$ is complicated by the participation of oxygen in the oxidation process, we include in our analysis nontopotactic reactions that involve oxygen oxidation (delithiating $\text{Li}_{6-x}\text{CoO}_4$ to x > 2). Oxygen anions (O^{2-}) can be oxidized directly into released O_2 gas or a multistep oxidation can occur in which oxygen anions first become partially oxidized to a peroxide species in the structure, and then eventually become fully oxidized as O_2 gas that leaves the compound. To account for the competition between oxygen oxidation via direct O_2 gas evolution (namely O_2 reaction) and the formation of an intermediate peroxide species (namely *peroxide reaction*), we consider both scenarios in our computations (see Note S1, Supporting Information). As it is challenging to distinguish the formation of a peroxide phase such as Li_2O_2 from the formation of peroxide species in the host, we take the formation of a Li_2O_2 phase as a proxy for any *peroxide reaction* because the reaction potential for the formation of Li_2O_2 phase is always lower than that of peroxide species in the host (see Note S1, Supporting Information).

With the reaction boundaries set by these thermodynamic calculations, we combine various experimental techniques to reach a comprehensive understanding of the activation behavior of Li_6CoO_4 . We measure the equilibrium potential as a function of Li content in Li_6CoO_4 using GITT and compare with the computed voltage profiles for different reaction hypothesis. In addition, in situ XRD and DEMS experiments are performed to track the phase evolution and quantify the gas release during the electrochemical Li extraction. Ex situ GC experiments are performed at various state of charge (SOC) as well as after long-term storage and cycling to provide further information on gas evolution of the activated material.

2.2. Results

2.2.1. Limit of Topotactic Delithiation of Li_6CoO_4

The computed thermodynamic stability of topotactically delithiated $\text{Li}_{6-x}\text{CoO}_4$ phases at various temperatures from 0 to 1500 K is shown in **Figure 1**a as energy above the convex hull (see the Experimental Section for computational details). Energy above the hull is the driving force to react to the lowest energy phases in the Li–Co–O chemical space. We find that the topotactically delithiated Li_5CoO_4 is metastable with 32 meV per atom above the hull at 0 K and 20 meV per atom above the hull at 300 K. This phase becomes stable above 800 K (Figure 1a). As more lithium is extracted topotactically from $\text{Li}_{6-x}\text{CoO}_4$, the energy above the hull increases, indicating that additional topotactic lithium extraction may be difficult to achieve.

We expect that further topotactic lithium extraction from Li_5CoO_4 to generate Co^{4+} is difficult in the close-packed oxide framework of $\text{Li}_{6-x}\text{CoO}_4$. Co^{4+} is not stable in tetrahedral sites based on crystal field theory^[18] and prefers octahedral sites. Thus, the oxidation of Co^{3+} to Co^{4+} would require the migration of Co to an octahedral site which cannot occur at the high cation to anion ratio (cation/anion > 1) of this compound without creating a high-energy face-sharing environment between occupied tetrahedral and octahedral sites. Consistent with this, we observe a significant collapse of the antifluorite framework as a result of the DFT structural relaxation for x > 2. Structure-mapping of the Co–O framework of these delithiated structures indicates that the collapsed Co–O frameworks can no longer be mapped back to the antifluorite structure. Therefore, we expect that topotatic delithiation from $\text{Li}_{6-x}\text{CoO}_4$ will end before *x* reaches 2.

Figure 1b shows the predicted voltage profile of Li_6CoO_4 assuming topotactic delithiation at various temperatures from 0





Figure 1. Topotactic delithiation reaction of Li_6CoO_4 . a) Energy above the convex hull of Li-extracted $Li_{6-x}CoO_4$ structures at various temperatures. b) Computed voltage profile for topotactic lithium extraction from Li_6CoO_4 at various temperatures. The GITT results are shown as black lines. In the GITT experiments, Li_6CoO_4 was charged at 5 mA g⁻¹ and the cell was allowed to rest for 90 h after each 5 h of charging. The shaded area shows the region where the antifluorite framework of Co–O is expected to collapse.

to 1500 K. The black line in Figure 1b shows the experimental GITT result, in which the relaxed potential or the so-called quasi-equilibrium potential was obtained after 90 h of relaxation after each 5 h of charging at 5 mA g^{-1} . The computed topotactic Li-extraction potential starts at 2.52 V versus Li/Li⁺ at 300 K (2.59 V at 0 K), with Co^{2+}/Co^{3+} redox via a two-phase reaction between Li_6CoO_4 and Li_5CoO_4 . This is followed by $\text{Co}^{3+}/\text{Co}^{4+}$ redox at 3.43 V at 300 K (3.51 V at 0 K) for $1 \le x \le 2$. Our predicted voltages for the topotactic delithation reactions are much lower than those reported in some earlier experimental work, particularly for 0 < x < 1 in Li_{6-x} CoO₄.^[14,15,17] This can be rationalized by our finding from the relaxed potential obtained in the GITT experiment (black line in Figure 1a) that significant overpotentials $(\approx 1 \text{ V})$ exist in this material during the initial charge (between x = 0 to x = 1 in Li_{6-x}CoO₄). The measured open-circuit voltage after relaxation is in excellent agreement with our computational result up to x = 2. Interestingly, the unrelaxed potentials have no distinct steps at x = 1 in $\text{Li}_{6-x}\text{CoO}_4$, similar to previous reports in the literature;^[14,15,17] however, the relaxed potentials exhibit a clear voltage step near x = 1 in Li_{6-x}CoO₄, indicating that the

delithiation process from x = 0 to x = 2 is not a one-step topotactic reaction, consistent with our computational prediction.

2.2.2. Identifying the Onset of Nontopotactic Reaction and Its Reaction Product

To determine which phase may form after the antifluorite framework can no longer be retained for $x \ge 1$ in Li₆ "CoO₄, we weigh the competition between the topotactic reaction and all the possible nontopotactic decomposition reactions of Li_{6-x}CoO₄. Figure 2 and Figures S1-S6 in the Supporting Information show the voltage of the topotactic reaction as a black dashed line. The voltages for the nontopotactic decomposition reactions evaluated are shown as colored solid lines. All ground states identified on the Materials Project^[19] Li-Co-O phase diagram are included in this analysis. These include Co, CoO, CoO₂, Li₁₀Co₄O₉, Co₃O₄, Co₂₃O₃₂, LiCoO₂, Li_{0.5}CoO₂, and Li₂CoO₃. Pathways that involve the release of gaseous O_2 (denoted as an O_2 reaction) and the formation of intermediate Li₂O₂ peroxide (O⁻) (denoted as a peroxide reaction) (Note S1, Supporting Information) are distinguished. The reaction free-energies of both types of pathways were computed at various x following Equation (1). A is the possible reaction-product and a, b, and c are the reaction coefficients. The reaction free energies were converted into the reaction potential (V_{rxn}) versus lithium metal following the Nernst equation in Equation (2). The reactions for extraction of Li from Li_6CoO_4 are shown in Figure 2a,b and the reaction for extraction from Li₅CoO₄ in Figure 2c,d. From a purely thermodynamic perspective one would expect the reaction with lowest voltage to proceed.

 $\text{Li}_{6-x}\text{CoO}_4 \text{ (antifluorite)} \rightarrow a A + b \text{Li}^+ + b e^-$

+ $c \left(O_2 \text{ or } \text{Li}_2 O_2 \right)$ (1)

$$V_{rxn} = -\frac{\Delta G_{rxn}}{zF} \tag{2}$$

Reaction stage 1: $\text{Li}_6\text{CoO}_4 \rightarrow \text{Li}_5\text{CoO}_4 + \text{Li}^+ + e^-$

In the first stage of the reaction in Figure 2a,b, we find that the topotactic reaction potential (black dashed line) is lower than any decomposition reactions in the entire relevant temperature regime. Therefore, we can conclude that a topotactic reaction occurs up to x = 1, and no O_2 or Li₂ O_2 is expected to form.

Reaction stage 2: $\text{Li}_5\text{CoO}_4 \rightarrow \text{Li}_4\text{CoO}_4 + \text{Li}^+ + \text{e}^-$

This stage involves competition between the topotactic and decomposition reactions, as shown in Figure 2c,d. At 0 K, the Li_2O_2 -forming reaction (Figure 2d) has a lower reaction potential (forming Li_2CoO_3 as the first nontopotactic product) than the O_2 -forming reaction (Figure 2c) or the topotactic Li-extraction. We find that up to 300 K, the Li_2O_2 -peroxide forming reaction with Li_2CoO_3 as the reaction product is thermodynamically most favored. At temperatures from 400 K, the entropic effect of O_2 formation makes the O_2 reaction (with the formation of Li_2CoO_3) thermodynamically more favored than the Li_2O_2 -peroxide formation. Therefore, we predict that the decomposition reaction that generates the peroxide species (peroxide reactions) is likely to occur at low temperature (<400 K), and direct O_2 formation (O_2 reactions) is likely to occur at high temperature (>400 K).

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Figure 2. Competition of topotactic and nontopotactic lithium extraction reactions computed at various possible stages of topotactic reactions. Delithiation reaction of Li_6CoO_4 in antifluorite structure releasing a) O_2 or b) Li_2O_2 , Li_5CoO_4 in antifluorite structure releasing c) O_2 or d) Li_2O_2 . In each figure, the black dashed line refers to the topotactic reaction maintaining the antifluorite structure. The legend in (a) applies to all the subfigures.



Figure 3. Lithium extraction from the first reaction product Li_2CoO_3 or Li_2O_2 . a) The reaction potentials to extract lithium from Li_2CoO_3 with O_2 release were computed at various temperatures. b) The reaction potentials to extract lithium from Li_2CoO_3 accompanied by Li_2O_2 formation were computed at various temperatures. The black line represents the potential to decompose Li_2O_2 to extract lithium and release O_2 gas. The legend in (a) also applies to (b).

At even higher temperatures (>600 K), the formation of $LiCoO_2$ becomes more energetically preferred than Li_2CoO_3 among the possible O_2 reactions (Figure 2c) consistent with the more reducing conditions of elevated temperature. In contrast, among peroxide-producing reactions, Li_2CoO_3 formation is always preferred at all temperatures (Figure 2d). We note that although the Li_2CoO_3 phase has not yet been experimentally observed, it is computationally predicted to be a ground-state phase on the phase diagram and is isostructural to the thoroughly studied close-packed layered Li_2MnO_3 .^[20,21]

We now consider how Li₂CoO₃ that formed in the first conversion reaction can be further delithiated. The reaction potentials in **Figure 3**a indicate that extracting additional lithium from Li₂CoO₃ with O₂ gas evolution to form LiCoO₂ is most likely to occur. On the other hand, the data in Figure 3b show that Li extraction from Li₂CoO₃ to form additional Li₂O₂ is energetically unfavorable as the potentials for this reaction are significantly higher than the potential to decompose Li₂O₂ with release of O₂. From any Li₂O₂ that formed in the previous step, additional delithiation can occur following the reaction Li₂O₂ \rightarrow 2 Li⁺ + 2 e⁻ + O₂ at 2.81 V (300 K) as plotted in Figure 3b.

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Figure 4. Overall proposed lithium extraction scenario of Li_6COQ_4 at a) 300 K and b) 400 K. The upper plots in each subfigure show the reaction potentials throughout the entire lithium extraction reaction and the lower plots in each subfigures show the amount of reaction products normalized per unit of Li_6COQ_4 as function of the lithium extraction reactions. a) At 300 K, the O_2 reaction (red) and peroxide reaction (blue) are both shown as they compete with each other. b) At 400 K, only the O_2 reaction is shown because the peroxide reaction has a higher reaction potential than the lithium extraction reaction from Li_2O_2 .

2.2.3. Overall Reaction Scenario

Combining all of our analysis, the computationally predicted delithiation pathways of Li_6CoO_4 as well as the amount of reaction products at each point of the lithium extraction are plotted in **Figure 4**. At all of the considered temperatures, the first lithium is extracted topotactically. The further lithium extraction scenario depends on the temperature regime: 300 K or lower (Figure 4a), 400 to 500 K (Figure 4b), and 600 K or higher (Figure S7, Supporting Information).

At temperatures up to 300 K (Figure 4a), we predict a competition between the O₂ reaction and peroxide reaction to start at x = 1 in Li_{6-x}CoO₄. Lithium can be further extracted by forming Li_2CoO_3 with either O_2 gas release (red line) or peroxide formation (blue line). Subsequently, in case Li₂O₂ forms, additional lithium can be extracted from Li₂O₂ by releasing O₂ gas. The final stage of the reaction is the extraction of one lithium from Li_2CoO_3 accompanied by O_2 gas to form the final reaction product LiCoO₂. In this temperature regime, the reaction pathway that forms an intermediate Li2O2 peroxide (blue) is slightly more favored than the direct O₂ formation reaction (red). At 400 K (Figure 4b) and 500 K, the reaction pathway with direct O₂ formation is the only possible route as intermediate Li₂O₂ can no longer form. We show in Figure S7 in the Supporting Information that at 600 K or higher, Li_5CoO_4 is expected to directly form the final product LiCoO₂ with O₂ gas evolution in a single step reaction. The total amount of O2 gas release or extracted lithium is not dependent on the temperature or reaction pathway because the final conversion product is LiCoO₂ in all scenarios. However, the reaction temperature directly affects which intermediate phases appear and hence, at what stage of Li removal, O2 is being released. We do not consider further lithium extraction from the final conversion product LiCoO_2 as its average lithium extraction voltage with respect to Li is higher than 4.0 V.^[22–24]

2.2.4. In Situ XRD and DEMS during the First Charging Process

To evaluate the phase evolution during the charging of Li_6CoO_4 , in situ XRD was performed with the results shown in **Figure 5**a,b. The in situ XRD experiment was conducted in a full-cell configuration with graphite as the counter electrode. In Figure 5a, the intensities of the (101), (201), and (211) peaks of $\text{Li}_{6-x}\text{CoO}_4$ fade gradually and completely disappear at x = 2 (Figure 5a), suggesting that nontopotactic decomposition reactions start for x < 2, in excellent agreement with our computational predictions. The peak near 11.8° originates from the lithiated graphite.

Our results are consistent with previous work by Takeda et al.,^[15] where they argued that after x = 1, $\text{Li}_{6-x}\text{CoO}_4$ starts to decompose, and our computational predictions. While they reported the growth of new peaks (indexed with the same space group but smaller lattice constant than Li_6CoO_4) in the range $0 \le x \le 1$ indicating a two-phase reaction, our in situ XRD did not show any new peak evolution. This discrepancy might come from the different experimental condition: in situ versus ex situ. In contrast, previous work by Park et al.^[14] argued that the $\text{Li}_{6-x}\text{CoO}_4$ framework is thermodynamically stable without structural collapse from x = 0 to x = 4. However, our in situ XRD findings (Figure 5a) and DFT-based thermodynamic analysis (Figure 1a) indicate that it may be challenging to retain the antifluorite framework up to x = 4. Work by Cho et al.^[17] suggested the formation of the CoO₂ phase. However, we do not identify

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Figure 5. Characterizing $\text{Li}_{6-x}\text{CoO}_4$ during the charging process with in situ XRD and DEMS. a) In situ XRD result measured during charging process of Li_6CoO_4 , b) its corresponding voltage profile during in situ XRD, c) in situ DEMS result measured during charging process of Li_6CoO_4 , and d) its corresponding voltage profile during DEMS experiment. X = 2 in $\text{Li}_{6-x}\text{CoO}_4$ corresponds to ≈ 325.7 mAh g⁻¹.

any peak related to CoO_2 in our in situ XRD experiments and CoO_2 is identified as one of the least stable reaction products in Figure 2, making it unlikely that CoO_2 forms in the delithiation of Li_6CoO_4 .

Figure 5c,d shows data from the DEMS experiments conducted at room temperature. Technical details can be found in the Experimental Section. As shown in Figure 5c,d, oxygen gas evolution starts for x slightly lower than 2, indicating that near x = 2, oxygen oxidation and O2 gas evolution are clearly responsible for the charge compensation of the lithium extraction reaction. The cumulative amount of O₂ gas evolved during lithium extraction is $0.503 \text{ mol } O_2 \text{ per Li}_6 \text{CoO}_4$, resulting in $\approx 1 \text{ O per Li}_6 \text{CoO}_4$ released as O₂ gas. The O₂ evolution from the DEMS experiment (1 O per Li_6CoO_4) is much smaller than our prediction (2 O per Li_6CoO_4) in Figure 4). This finding indirectly indicates that instead of O²⁻ being oxidized straight into O₂ gas, some intermediate peroxides within the structure may form, leading to delayed O_2 evolution. Another possibility is that some intermediate peroxides may have been released as CO₂/CO gas by reacting with electrolytes and/or conductive carbon additives. As the nucleation and growth of the Li₂O₂ phase would require the segregation of lithium and cobalt, and we do not observe peaks matched to Li₂O₂ in in situ XRD experiments, we suspect that lattice peroxides in the host form instead of as a separate Li_2O_2 phase.

2.2.5. Ex Situ Gas Chromatography of Charged Samples

After collecting the gas released during the charging of three pouch cells up to SOC 30, 60, and 100, respectively, we performed ex situ GC experiments to understand the species and amount of gas evolution as shown in **Figure 6**a,b. Here, SOC 100 corresponds to lithium extraction to x = 5, as illustrated in Figure 4. This ex situ experiment is conducted because we suspect that some O₂ evolution may be delayed due to oxidized oxygen species

remaining in the system as an intermediate. The nominal compositions at each SOC were estimated from the capacity and the amount of evolved O_2 gas from GC measurements.

When charging up to SOC 30, achieving a nominal composition of Li₄₅CoO₄, a negligible amount of gas is detected (Figure 6b). This result indicates that up to this point, all of the oxidation occurs via lattice oxygen oxidation (O^{2-}/O^{-}) or $Co^{2+}/Co^{3+}/Co^{4+}$ oxidation, which is in good agreement with the DEMS result (Figure 5c) as well as our prediction (Figure 4a). When charging up to SOC 60, mostly O_2 gas was observed with a small amount of hydrocarbon species, resulting in a nominal composition of Li₃CoO₃₅, in agreement with our prediction that O oxidation dominates. Finally at SOC 100, more O₂ was released (with a negligible amount of non-O₂ gas), resulting in a final composition of LiCoO2.5. We note that these nominal compositions estimated from GC only take into account the O₂ gas. However, as some oxygen can be lost via side reactions with the electrolyte, releasing CO or CO_2 , the oxygen concentration of the final product may actually be lower, being closer to the predicted LiCoO₂.

We note an important discrepancy in the amount of O_2 evolution determined from the ex situ GC (Figure 6b) and in situ DEMS experiments (Figure 5c). The amount of O_2 measured from the in situ DEMS experiment (\approx 1 O per f.u.) is smaller than that measured from ex situ GC (\approx 1.5 O per f.u.). While the DEMS measurement was conducted in situ, the GC measurements were taken one day after reaching the SOC. This delay may have given the reacted samples more time for the peroxide species to decompose and release O_2 gas, which is the lower free-energy state. We expect that during the charging process, peroxides within the structure form first (therefore, less O_2 evolution is observed for in situ DEMS). Ex situ GC measures the additional O_2 gas produced from the disproportionation of the peroxide species. We note here that the larger amount of CO_2 evolution observed for DEMS analysis compared with ex situ GC analysis is likely due

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Figure 6. First charge profile, ex situ GC result at three distinct states of charge and after the storage and cycling process. a) Voltage profile of Li_6CoO_4 pouch cell indicating the points where ex situ GC was performed, and their nominal compositions. b) GC results at SOC30, 60, and 100. c) GC results of Li_6CoO_4 after the storage and cycling processes, where a negligible amount of O_2 gas yet a significant amount of H_2 and CO_2 were detected, suggesting the decomposition of the electrolytes.

to the different electrode composition and cell configuration (see the Experimental section).

2.2.6. Stability of Li_6CoO_4 as a Sacrificial Cathode Additive in a Practical Cell during Cycling and Storage

To serve as a sacrificial cathode additive, the chemical and electrochemical stability of the additive during full-cell operation and storage in the charged state are important. Any remnant peroxide species that are not fully oxidized into O_2 gas after the initial activation can slowly react to release O_2 gas or react with the carbonate electrolyte and evolve gaseous species during operation of the battery.^[25] which results in swelling of the battery.

To understand the chemical and electrochemical stability of Li_6CoO_4 after activation, we measured the type and amount of gaseous species released after 1) long-term storage (4 weeks) of activated Li₆CoO₄ and 2) cycling (50 cycles between 4.2 and 2.5 V vs graphite) of cell including activated Li₆CoO₄ using GC as shown in Figure 6c. In contrast to the initial charging process where O_2 is the majority gas released, we observe that the gas evolved during storage and cycling consists of CO₂ or carbohydrates, not O2, which we suspect to originate from the decomposition of carbonate electrolytes. We suggest that peroxide-like species within the sample may be dissolved into the electrolyte during storage and cycling to either react with the carbonate electrolyte or catalyze the decomposition of them. Another possibility is that singlet oxygen may evolve by oxygen oxidation and react with the electrolyte to form CO₂. Similar reactions where these oxygen radical and singlet oxygen^[26] degrade the carbonate electrolytes^[27,28] are widely reported in the Li-O₂ battery field.

2.3. Discussion

Our prediction of a topotactic two-phase reaction between x = 0and x = 1 of $\text{Li}_{6-x}\text{CoO}_4$ agrees well with previous experimental work^[15] that shows the gradual growth of new peaks between x = 0 and x = 1. Our experimental data (Figure S8 and S9, Supporting Information) also supports that when charging beyond x > 1, a significant portion of the capacity cannot be retrieved upon discharge, supporting our suggested topotactic limit of x = 1. Similarly, Cho et al.^[17] reported that when charging to x = 2 and discharging in the voltage window of 1.0 to 4.4 V, the discharge capacity (10 mAh g⁻¹) was drastically lower than the charge capacity (318 mAh g⁻¹, $x \cong 2$), indicating high irreversibility and low coulombic efficiency. In contrast, when they limited the charge of Li_6CoO_4 to 3.2 V (160 mAh g⁻¹, 1 Li per f.u.), the discharge capacity (145 mAh g⁻¹) was much more reversible, further providing support for the finding that the first lithium extraction is topotactic. Guo et al.^[16] similarly reported an extremely low first cycle coulombic efficiency of 3.19% when charging up to 4.3 V. These observations are in good agreement with our computational prediction that the antifluorite frameworks should start to disappear after x = 1, and with our experimentally measured charge-discharge curves for various SOC (Figure S8, Supporting Information). The high irreversibility of Li₆CoO₄ indeed makes this material a viable sacrificial cathode additive.

The experimentally measured and computationally predicted reaction pathways are compared on top of the r2-SCAN + U





Figure 7. Comparison of experimental and thermodynamic phase evolution of Li_6CoO_4 during charging process on Li–Co–O phase diagram. The yellow circle denotes the initial Li_6CoO_4 compound. The red points denote the experimentally observed phases from GC experiments and the blue points denote the thermodynamically predicted reaction pathway. The gray dashed line indicates the topotactic lithium extraction line and the orange dashed lines indicate the Co⁴⁺, Co³⁺, Co²⁺ isovalent line. All of the 0 K stable compounds from the r2-SCAN + U phase diagram are shown as circles (green, blue, and yellow).

computed phase diagram in **Figure 7**. The topotactic delithiation line from Li_6CoO_4 (yellow circle) are shown in gray dashed line. The predicted reaction pathways are plotted in blue for low and high temperature. The experimentally measured reaction pathway determined from ex situ GC is shown in red line. We find that the experimentally measured compositions of the reaction product estimated by ex situ GC (red line) have a slightly higher oxygen amount compared with the thermodynamic predictions (blue line). This discrepancy appears as the skewing of the experimental reaction pathway toward the oxygen-rich region in the phase diagram. The deviation of experimental final composition (LiCoO_{2.5}) from prediction (LiCoO₂) may originate from the existence of peroxide oxygen species in the residue of the charge product.

Any kind of gas evolution during battery operation is a critical issue. While the gas evolved during the initial activation of Li₆CoO₄ is not problematic as it can be purged, any delayed gas evolution during the battery operation must be avoided. The formation of peroxide species can lead to gas evolution in two ways: peroxide decomposing the carbonate electrolyte to release carbohydrates and CO₂, or peroxide disproportionation to release O₂ gas, both of which are detrimental to the battery operation. As all of our experiments were performed near room temperature (30 or 45 °C), the thermodynamically most stable reaction pathway always involves the formation of intermediate peroxide species, as shown in Figure 4a. We suggest that charging Li₆CoO₄ at slightly elevated temperature at the activation stage will help inhibit the formation of peroxide species and allow the composition of the final product to be closer to the thermodynamic prediction (LiCoO₂) with less oxygen excess. However, excessively high temperatures above 400 K may not be practically compatible with liquid-electrolyte systems.

3. Conclusion

In this work, we investigated the thermodynamics of irreversible lithium extraction from a promising sacrificial cathode additive Li_6CoO_4 . Based on our calculations and experiments, a topotactic reaction is predicted to proceed up to x = 1. Subsequently, sequential structural evolution to release oxidized oxygen species accompanied by the formation of Li_2CoO_3 or LiCoO_2 , depending

on the reaction temperature, is expected. Experimentally, most of the oxidized oxygen species are removed from the structure as O_2 gas, in line with our thermodynamic predictions. However, it is likely that a certain amount of oxidized oxygen species remain within the material to result in degradation of the electrolyte releasing carbohydrate and CO_2 gas during storage and cycling. By charging Li_6CoO_4 at a slightly elevated temperature, we may steer the reaction pathway away from the formation of intermediate peroxide species to direct O_2 gas evolution during the activation cycle. This will drive the composition of the final product to be closer to the thermodynamic prediction (LiCoO₂) with less oxygen excess remaining. Our computational workflow to understand the complex reaction pathways involving gas evolution can be further generalized to other potential candidates for sacrificial cathode additives.

4. Experimental Section

Density Functional Theory Calculations: The DFT calculations were performed within the projector augmented wave formalism,^[29] as implemented in the Vienna ab initio simulation package.^[30] The r2-SCAN exchange correlation functional was employed,^[31] which was recently developed as one of the meta generalized gradient approximation (meta-GGA) functionals. This functional has been reported to significantly reduce the computational cost of meta-GGA calculations while retaining the improved chemical accuracy of the SCAN^[32] exchange correlation functional.^[31] Meta-GGA based exchange correlation functionals are employed in this work as they have been reported to overcome the oxygen overbinding issue of the conventional GGA-based functionals and therefore more accurately describe the cohesive energy of oxygen.^[33] A Hubbard U parameter of 3.0 eV was applied to cobalt because it was reported to accurately predict the energies of redox reactions of binary transitionmetal oxide systems.^[34]

Computing Free Energies to Construct Phase Diagrams: The phase diagrams were generated using a sequential multistep process. Preliminary ternary Li–Co–O phase diagram was generated using all of the GGA/GGA + U-computed entries spanning the corresponding chemical space from the Materials Project database^[19] after applying the mixing scheme of GGA/GGA + U^[35] proposed by Jain et al. Then, the stable entries on the GGA/GGA + U convex hull were recalculated using the r2-SCAN + U functional to generate the r2-SCAN + U based phase diagram.

To predict the reaction potential at finite temperatures, a free-energy estimation scheme was employed using the sure independence screening and sparsifying operator proposed by Bartel et al.^[36] to include machine-learned vibrational entropies of solid phases and the experimental entropy of O₂ gas. It is noted that the configurational entropies are not included in this free-energy estimation.

Computing Topotactic Reactions: The topotactic delithiation reaction of Li_6COQ_4 was computed by enumerating a maximum of 20 distinct lithium-vacancy configurations with the lowest Ewald energies^[37] and calculating their r2-SCAN + U DFT energies. All of the enumerations were performed in a (1, 1, 2) supercell with a total of 16 O²⁻ anions.

Synthesis of Li_6CoO_4 : Li_6CoO_4 was synthesized by a conventional solid-state synthesis reaction using Li_2O and CoO as precursors. Li_2O (Sigma-Aldrich, 97%) and CoO (Sigma-Aldrich, 99.99%) precursors were homogeneously mixed by dry ball milling. Excess Li_2O (16%) was used to compensate for any potential Li loss during heating at high temperatures. To avoid contaminations from the exposure to air, powders were added to the ball-milling jar and sealed in an Ar-filled glovebox. The mixed powders were pelletized in 6 mm diameter form and calcinated at 700 °C under continuous Ar flow. When the dwelling time at 700 °C was greater than 12 min, the LiCoO₂ impurity phase was detected, as shown in Figure S10 in the Supporting Information.

Electrochemical Measurements and In Situ X-Ray Diffraction: For the GITT experiment, Li₆CoO₄ electrodes were prepared by mixing Li₆CoO₄ (active material, 70 wt%), super P carbon (20 wt%), and polytetrafluoroethylene (PTFE) binder (10 wt%) in an Ar-filled glovebox. Cathodes with a loading density of \approx 4.0 mg cm⁻² were assembled in a two-electrode configuration using a Li-metal anode and a glass-fiber separator (Whatman, GF/F) in a 2032 coin cell. 1 M LiPF₆ was used in ethylene carbonate (EC)/dimethyl carbonate. Electrochemical tests were performed on a battery testing station (Arbin Instruments) at room temperature. The GITT experiment (performed at 25 $^\circ\text{C})$ was conducted at 5 mA g^{-1} with 5 h of charging and 90 h of relaxation for each step to reach quasi-equilibrium potentials. An in situ XRD experiment was conducted with pouch cell with a graphite anode at 45 °C. The cathode was prepared by mixing Li₆CoO₄ (97.5 wt%), conductive carbon (1.0 wt%), and a polyvinylidene fluoride (PVDF) binder (1.5 wt%). An Empyrean X-ray diffractometer using a Mo target X-ray was used for the in situ experiments.

Differential Electrochemical Mass Spectroscopy: DEMS was used to detect the gases evolved from the battery during cycling at room temperature and has been used extensively by Kaufman, McCloskey, and colleagues to quantify gas evolution from a variety of Li-ion cathode materials and metal-air batteries.^[25,38,39] The DEMS setup and calibration is extensively described in the appendix of Renfrew's thesis.^[40] The DEMS cell was designed to be hermetically sealed (confirmed with a helium leak check), with inlet and outlet capillaries connecting the DEMS gas handling system to the cell headspace. Every few minutes, the cell outlet was opened, allowing accumulated gases to flow to a mass spectrometer, and the cell headspace was concomitantly refilled through the inlet with a carrier gas such as argon. To achieve quantifiable results, calibrations were performed to relate the ion current detected by the mass spectrometer to the partial pressure of the gas of interest $(CO_2 \text{ and } O_2)$ in argon. The total volume of gas (carrier plus evolved gas) sent to the mass spectrometer was also calibrated (\approx 0.5 mL), allowing a simple ideal gas law calculation to obtain the molar generation rate of gas between each pulse.

Swagelok-type cells were assembled for the DEMS experiments with cathodes composed of 50 wt% Li_6CoO_4 , 35 wt% carbon black (Super P), and 15 wt% PTFE binder coated onto stainless-steel mesh. The electrolyte used was 1 m LiPF₆ in a 1:1 mixture by weight of ethylene carbonate and diethyl carbonate (Gotion). Cells were assembled with two separators, one polypropylene (Celgard 2500) and one glass fiber (Whatman), with the Celgard in direct contact with the cathode. Lithium metal (FMC corporation) was used as the anode.

Ex Situ Gas Chromatography: An ex situ GC experiment (GC Instrument: Agilent 7890/8890, Column: Shin carbon, Gaspro) was conducted using a pouch cell with a graphite anode. The cell was charged at a current rate of 1.025 mA at 45 °C. The cathode was prepared by mixing Li₆CoO₄ (97.5 wt%), conductive carbon (1.0 wt%), and PVDF binder (1.5 wt%). The gas evolved was collected at three points of SOC30, SOC60, and SOC100. The gas was collected by vacuum from the cell at each SOC. The injection volume was \approx 10 µL. GC experiment was performed at 0 °C on the collected gas.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Author Contributions

K.J., H.K., and G.C. conceived the project idea. K.J. performed all of the calculations based on discussions with B.L. H.K. conducted the synthesis and experimental characterization. L.K. and B.D.M. performed the DEMS measurements. W.J., B.P., C.J., D.L., and T.Y. performed the in situ XRD and ex situ GC experiments and discussed the data. H.K. and G.C. supervised all aspects of the research. K.J. wrote the paper with assistance from all of the authors.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

computational thermodynamics, density functional theory, lithium-ion batteries, sacrificial cathode additive, silicon anodes

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