

Article Electrochemically Driven Phase Transition in LiCoO₂ Cathode

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Abstract: Lithium cobalt oxide (LiCoO₂), which has been successfully applied in commercial lithiumion batteries for portable devices, possesses a theoretical specific capacity of 274 mAh g⁻¹. However, its actual capacity is only half of the theoretical specific capacity, because the charging voltage is restricted below 4.2 V. If a higher charging voltage is applied, an irreversible phase transition of LiCoO₂ during delithiation would occur, resulting in severe capacity fading. Therefore, it is essential to investigate the electrochemically driven phase transition of LiCoO₂ cathode material to approach its theoretical capacity. In this work, it was observed that LiCoO₂ partially degraded to Co₃O₄ after 150 charging-discharging cycles. From the perspective of crystallography, the conventional cell of LiCoO₂ to cubic Co₃O₄ proposed. The theoretical analysis indicated that the electrochemically driven phase transition from LiCoO₂ to Co₃O₄ underwent several stages. Based on this, an experimental verification was made by doping LiCoO₂ with Al, In, Mg, and Zr, respectively. The doped samples theoretically predicted behavior. The findings in this study provide insights into the electrochemically driven phase transition in LiCoO₂, and the phase transition can be eliminated to improve the capacity of LiCoO₂ to its theoretical value.

Keywords: LiCoO₂; degradation; Co₃O₄; phase transition

1. Introduction

Lithium-ion batteries (LIBs) are widely implemented in mobile equipment and electric vehicles to provide power because of their high power density and cycle stability [1-4]. In general, cathode materials are the major factor for the performance of LIBs, and higher energy density and better cycle stability are pursued [5-10]. Layered lithium cobalt oxide $(LiCoO_2)$ is considered as one of the most important cathode materials due to its large theoretical capacity of 274 mAh g^{-1} [11,12]. LiCoO₂ operates by reversible de-intercalation (charge) and intercalation (discharge) of lithium ions, without the irreversible phase transition of crystal structures [13–15]. The charging voltage of LiCoO₂ cathode is restricted to 4.2 V to avoid the irreversible phase transition. Due to this limitation, commercial LiCoO₂ only exhibits a little more than half of its theoretical value [1,16]. The irreversible phase transition arising from over charging voltage would cause the cathode capacity to fade quickly [17–19]. Therefore, to further improve the performance of LiCoO₂, e.g., charging voltage, capacity, and cycling stability, great efforts should be made to inhibit the irreversible phase transition during charge/discharge cycles [20]. Although various beneficial modifications have been reported in recent years [21–23], there is a lack of insight into the origin of electrochemically driven phase transition in LiCoO₂. Hence, currently,



Citation: Tan, J.; Wang, Z.; Li, G.; Hu, H.; Li, J.; Han, R.; Zhang, D. Electrochemically Driven Phase Transition in LiCoO₂ Cathode. *Materials* **2021**, *14*, 242. https://doi.org/10.3390/ ma14020242

Received: 10 November 2020 Accepted: 29 December 2020 Published: 6 January 2021

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LiCoO₂ is still unable to be charged to a higher voltage and its capacity is much less than its theoretical value.

Van der Ven et al [24] theoretically studied the phase stability in Li_xCoO₂ with different lithium contents and predicted that Li_xCoO₂ went through a phase transition from O3 to H1-3 symmetries as lithium content decreased. Chen et al [25] verified the phase transition in Li_xCoO₂ with decreasing lithium content by in-situ XRD. Dahéron et al [26] and Ohnishi et al [27] found the degraded product of CoxOy from LiCoO₂ due to the irreversible electrochemically driven phase transition. However, the phase of Co_xO_y is still controversial. Electrochemically driven phase transition path in LiCoO₂ is still unclear. It is widely acknowledged that an effective strategy to improve the capacity of LiCoO₂ to 190 mAh g⁻¹ with 96% capacity retention over 50 cycles by inhibiting the order-disorder transition and H1-3 transition. Therefore, it is of utmost significance to determine the mechanism of the electrochemically driven phase transition phase transition in LiCoO₂ during charge/discharge cycles, to further improve the cycling stability and practical capacity of LiCoO₂.

In this work, the electrochemically driven phase transition of $LiCoO_2$ during charge/ discharge cycles was investigated. The microstructure change of $LiCoO_2$ after 150 cycles at charging voltage of 4.3 V was observed by high resolution transmission electron microscope (HRTEM). From the perspective of crystallography, the conventional cell of $LiCoO_2$ was rebuilt to an orthonormal coordinate, the Co and O sites in $LiCoO_2$ and Co_3O_4 were compared, and the electrochemically driven phase transition route was proposed. Both experimental observation and theoretical analysis indicated that the electrochemically driven phase transition occurred at the surface of $LiCoO_2$ particle. Furthermore, relevant experiments were designed to verify the proposed transition mechanism.

2. Experimental Procedure and Computational Method

2.1. Samples Preparation

In this study, LiCoO₂ powders were synthesized by sintering the oxide mixture of Li_2CO_3 and Co_3O_4 at 1000 °C for 12 h. Then, the as-prepared $LiCoO_2$ was used as cathode in the Li-ion coin-cell, in which the counter electrode was metallic lithium foil, 1M LiPF₆ was electrolyte, and Celgard 2300 was separator. After 150 charging-discharging cycles under 2.8–4.3 V at 0.5C, the cell was disassembled, and the electrode was removed. Then, the cathode powder was stripped and washed by alcohol for microstructure characterization by HRTEM.

The doped LiCoO₂ powders were synthesized by the same procedure, using Al₂O₃, In₂O₃, MgO, and ZrO₂ as dopants. The doping content was controlled at 1 mol% in all samples. To characterize the electrochemical performance, the doped or undoped LiCoO₂ powders were mixed with the solvent system including 10 wt% acetylene black, 10wt% PVDF and N-methyl-2-pyrrolidine (NMP) to prepare a homogenous slurry. The slurry was casted on Al foil, dried at 120 °C and employed as a cathode in 2032-type Li-ion coin-cell. The coin-cells were assembled by using Celgard 2300 as a separator, a counter electrode of metallic lithium foil, and LiPF₆ dissolved in the mixed organic solvent of ethylene carbonate, dimethyl carbonate, and diethyl carbonate to obtain 1M solution as the electrolyte.

2.2. Characterization

The microstructure was observed by transmission electron microscopy (TEM, JEM 2100F, JEOL, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS, Thermo Fisher ES-CALAB Xi+, Waltham, MA, USA) analysis was performed to determine the elemental valence states. The crystalline phase of as-prepared powders was identified by X-ray diffraction (XRD, Bruker D8 Advanced, Hamburg, Germany) in standard θ –2 θ configuration, using Cu K α radiation. The galvanostatic charge-discharge performance was

measured in the potential range of 2.0–4.3 V (vs. Li/Li⁺) at room temperature by using a battery test system (Land CT2001A, Wuhan Jinnuo Electronic Co. Ltd., Wuhan, China).

2.3. Density Functional Theory Calculations

A first-principles calculation was performed by using the Vienna ab initio simulation package (VASP) [29] within the density functional theory (DFT) using the supplied PAW pseudopotentials [30,31] and the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) [32]. Cut-off energy for the plane wave basis was chosen as 570 eV and $6 \times 6 \times 6$ Monkhorst-Pack k grid was used for sampling the Brillouin zone. Structure optimization was performed with the convergence criteria that energy change was less than 1×10^{-4} eV before calculating the energy at each transition step.

3. Results and Discussion

3.1. Microstructure Characterization

The as-prepared coin-cell was operated under 2.8-4.3 V (vs. Li/Li⁺) and was then disassembled to evaluate the degradation of LiCoO₂ cathode. Figure 1 shows the Coulombic efficiency of the as-prepared Li-ion coin-cell with LiCoO₂ as cathode. At the beginning, the Coulombic efficiency was low because the high charging voltage caused the phase transition of $LiCoO_2$ cathode material. As a result, Li ions failed to re-intercalate into the cathode. In order to investigate the electrochemically driven phase transition of LiCoO₂ cathode, the degradation of LiCoO2 cathode from disassembled cell was observed by HRTEM, and the obtained images are shown in Figure 2. Three different phase regions were observed on the LiCoO₂ particle surface, namely LiCoO₂ crystal, Co_3O_4 crystal and amorphous, respectively, as shown in Figure 2a,b. Also, Figure 2b shows a very small crystallite inclusion indicated by the yellow dash circle which is considered to be Co_3O_4 crystal nucleus. Figure 2c shows the corresponding fast Fourier transformation (FFT) of the square selected area in Figure 2a. Analysis of FFT pattern indicates that the phase constitution of the square selected area in Figure 2a is Co_3O_4 (PDF#80-1540) with Fd-3m symmetry. Figure 2d, e are inverse FFT of Figure 2b and atomic configuration of Co_3O_4 (112) surface, respectively. Microstructure analysis of the degradation of LiCoO₂ cathode revealed that a phase transition occurred from layered $LiCoO_2$ to cubic Co_3O_4 in the surface zone of LiCoO₂ cathode.



Figure 1. The Coulombic efficiency of Li-ion coin-cell with LiCoO₂ as cathode materials.



Figure 2. High resolution transmission electron microscope (HRTEM) images and structure analysis of LiCoO₂ after 150 charging-discharging cycles under 4.3 V. (**a**) HRTEM image consists of LiCoO₂, Co₃O4 and amorphous region, (**b**) HRTEM image consist of LiCoO₂, Co₃O₄, Co₃O₄ crystal nucleus and amorphous region, (**c**) FFT of the blue square selected region in (**a**); (**d**) inverse FFT of (**c**); (**e**) the atomic model of Co₃O₄ ($\overline{112}$) surface.

XPS analysis was employed to determine the valence state of Co element during the degradation of LiCoO₂ cathode, as shown in Figure 3. The surface of degraded LiCoO₂ particles contained Co²⁺ and Co³⁺ ions, with more Co²⁺ than Co³⁺. In contrast, pristine LiCoO₂ before charge-discharge cycling only contained Co³⁺ ions. Apparently, Co²⁺ ions were produced from the phase transition of LiCoO₂ during the process of delithiation-lithiation, and originated from electrochemically driven phase transition product, Co₃O₄. This result further indicated the surface phase transition from layered LiCoO₂ to cubic Co₃O₄.



Figure 3. XPS of LiCoO₂ after 150 charging-discharging cycles under 4.2 V.

3.2. Modeling and Density Functional Theory Calculations:

According to the TEM analysis, surface composition of as-prepared $LiCoO_2$ particles degraded into Co_3O_4 after 150 cycles in the potential range of 2.8~4.3 V. During the charge process, de-intercalation of Li-ions occurred as follows:

$$\operatorname{LiCoO_2} \underset{\text{discharging}}{\overset{\text{charging}}{\leftarrow}} x \operatorname{Li}^+ + \operatorname{Li}_{1-x}(\operatorname{CoO_2})^-$$
(1)

During the discharge process, an inverse reaction of Equation (1) occurred. However, some Li-ions failed to be intercalated into the layered structure of cathode, resulting in capacity fading, as shown in Figure 2. The failure of Li-ions to re-intercalate was attributed to the structural transformation of layered $(CoO_2)^-$ during delithiation, which is an irreversible phase transition causing degradation.

$$\text{LiCoO}_2 \xrightarrow{\text{charging(high voltage)}} \text{Li}^+ + \frac{1}{3}\text{O}_2 \uparrow + \frac{1}{3}\text{Co}_3\text{O}_4 \tag{2}$$

Comparing the structure of layered $(CoO_2)^-$ lacking lithium ion with that of Co_3O_4 , it was inferred that the following two steps likely occurred: (1) Li-ions were released from cathode under external field, and the lattice of $(CoO_2)^-$ expanded; (2) lattice oxygen escaped from the layered $(CoO_2)^-$, forming amorphous Co_xO and then transforming to Co_3O_4 . Figure 4 schematically shows the de-intercalation of Li-ions from LiCoO₂ and the electrochemically driven phase transition from LiCoO2 to Co3O4, DFT calculation was performed according to the proposed transition path. In order to provide insights into the mechanism of degradation of LiCoO₂ to Co_3O_4 , the crystal cell of layered LiCoO₂ was rebuilt from a hexagonal presentation to an orthogonal coordination, as shown in Figure 4a. After comparing each atom position in $(CoO_2)^-$ and Co_3O_4 , a first principles calculation was performed based on DFT [33,34]. In the rebuilt LiCoO₂ cell, 64 atoms were employed to perform the DFT calculation. The occupancy and displacement of atoms in rebuilt $LiCoO_2$ cell were gradually changed to approach Co_3O_4 structure in order to simulate the transition path and to calculate the potential barrier during transition. Figure 4b shows the calculated total energy along the transition path from $LiCoO_2$ to Co_3O_4 . Under an external electric field, LiCoO₂ overcame the potential barrier at transition steps 1 and 2 to release Li-ions. Accompanying the release of Li-ions, partial loss of lattice oxygen and lattice expansion occurred. The oxygen escaped from lattice because the applied voltage made the Fermi level touch O 2p level. Due to the existence of the potential barrier, this reaction was driven by an external electric field.

Figure 5 shows the calculated density of states (DOS) and integrated DOS of LiCoO₂. First principles calculation indicates that LiCoO₂ is a compound with significant covalent character [35]. The interaction of Co 3d-electrons with O 2p-electrons resulted in a splitting of the 3d levels and a hybridization of Co 3d and O 2p levels. Under an external field, Li-ions deintercalated from layered LiCoO₂ cathode, which lowered the Fermi level to touch O 2p level. This led to the generation of holes in the bonding anion p-state. Thus, oxidation reaction of anions occurred, causing the decomposition of $(CoO_2)^-$ by oxygen loss. In LiCoO₂ cathode, oxygen atoms form an interstitial octahedron, and cobalt atoms occupy the center. Li-ions take positive electricity, and Co-O octahedrons take negative electricity. When Li-ions were released from LiCoO₂ cathode, the lattice expanded due to the electrostatic repulsion between Co-O octahedrons. Hence, partial oxygen loss and lattice expansion led to degradation of LiCoO₂ into amorphous Co_xO_y which was observed in Figure 2e. Besides, CoxO eventually formed Co_3O_4 which contributed to the capacity fading. As can be seen, in the integrated DOS for O atoms, the hybridization part of O-2p orbitals with Co-3d orbitals above -1.5 eV was less than one electron per unit cell. This indicated that an appropriate applied voltage would not lead to oxygen loss. The experimental results also confirmed that LiCoO2 cathode exhibited good cycling stability

when the charge voltage was at 4.2 eV. The calculated energy barrier along transition path indicated that the degradation process should overcome a potential barrier to finally form Co_3O_4 . Consequently, in order to maintain the layered structure of $LiCoO_2$ and to improve its charge voltage and capacity, its lattice should be compressed by doping ions with smaller radius and the hole capture level should be introduced by doping ions with lower valence, which was confirmed by our previous work [36].



Figure 4. (a) Schematic diagram of electrochemically driven phase transition path from $LiCoO_2$ to Co_3O_4 ; (b) calculated potential barrier along the proposed electrochemically driven phase transition path from $LiCoO_2$ to Co_3O_4 .



Figure 5. Calculated density of states (DOS) and integrated DOS of LiCoO₂.

3.3. Experimental Verification

From the aforementioned microstructure analysis and first principle calculation, it can be inferred that two key issues prompt the irreversible transition of $LiCoO_2$ after releasing lithium. One is lattice expansion, and the other is O^{2-} oxidation. If these two factors are inhibited, the cycling stability of $LiCoO_2$ cathode material will be improved. Doping ions with smaller radius would inhibit the lattice expansion, while doping ions with lower valence would trap more holes. Therefore, through doping, the performance of LIBs would be improved or deteriorated at charge voltage above 4.2 V. To verify the theoretical analysis, $LiCoO_2$ was doped with 1 mol% of Al, In, Mg, and Zr, respectively.

The experimental result based on the theoretical prediction are listed in Table 1. Among the doping ions, Al and In ions have the same valence state of +3 as Co ions in

LiCoO₂, but the radius of Al³⁺ ions is smaller than that of Co³⁺ and the radius of In³⁺ ions is larger than that of Co³⁺. Hence, Al doping can compress the LiCoO₂ lattice and inhibit the phase transition. In doping will expand the LiCoO₂ lattice, promoting the phase transition which would cause performance deterioration. Mg²⁺ and Zr⁴⁺ have similar ionic radius compared to Co³⁺, but different valence state. Mg doping will introduce the acceptor level which will enable trapping of holes, and thus inhibit O²⁻ oxidation. Zr doping will form donor level due to higher valence, which will compensate the intrinsic acceptor level to promote the O²⁻ oxidation [36]. Figure 6 shows the XRD patterns of doped and undoped LiCoO₂ samples. As can be seen, doping with 1% Al, In, Mg and Zr did not change the phase of LiCoO₂. The inset is the enlarged view of (003) and (104) peaks of Al and In doped samples. It can be seen that both the (003) and (104) peaks of Al doped sample shifted towards higher angles, which indicated that the lattice shrunk according to the Bragg equation, while the In doped sample showed the effect of lattice expansion. The calculated lattice parameters and their variation are shown in Table 2.

Table 1. The theoretical prediction, experimental results, and literature results of the cycling performance for doped LiCoO₂.

Doping Ion	Ion Radius (Å)	Effect	Theoretical Prediction	Experimental Results	Literature Results
Al ³⁺	0.50	Inhibit lattice expansion	Improved	Better	Better [37,38]
In ³⁺	0.81	Promote lattice expansion	Deteriorated	Worse	-
Mg^{2+}	0.72	Inhibit oxidation	Improved	Better	Better [20]
Zr^{4+}	0.72	Promote oxidation	Deteriorated	Worse	Worse [39]
Co ³⁺ (Reference)	0.745	Reference			



Figure 6. (a) XRD patterns of doped and undoped LiCoO₂. (b) Enlarged view of (003) peak. (c) Enlarged view of (104) peak.

Doped Element	Lattice a (Å)	Δa	Lattice c	Δc (Å)
Al	2.8147(4)	-0.051%	14.0458(5)	-0.042%
In	2.8169(7)	0.028%	14.0569(3)	0.037%
Mg	2.8160(4)	-0.005%	14.0535(9)	0.013%
Zr	2.8159(6)	-0.005%	14.0493(5)	-0.018%
undoped (Reference)	2.8161(8)	-	14.0517(8)	-

Table 2. Calculated lattice parameters of doped LiCoO₂, and their variation compared to the undoped LiCoO₂.

Figure 7 shows the cycling performance and charge-discharge profiles of doped and undoped LiCoO₂ samples. The galvanostatic charge-discharge performance was measured at 0.5 C by charging to 4.3 V. After 100 cycles, Al and Mg doped LiCoO₂ exhibited better capacities, while In and Zr doped LiCoO₂ exhibited worse capacities, in agreement with the theoretical prediction. This verifies the theoretical analysis on the electrochemically driven phase transition from LiCoO₂ to Co₃O₄. Notably, Al doped LiCoO₂ demonstrated good cycling stability under 0.5 C after 100 cycles, and a specific capacity as high as 180 mAh g⁻¹ during the initial cycles. Therefore, the capacity and cycling stability can be effectively improved through our proposed mechanism. Namely, the electrochemically driven phase transition can be inhibited by doping elements with smaller radius or lower valence.



Figure 7. (a) Cycling performance comparison; (b) The charge-discharge profiles of doped and undoped LiCoO₂.

4. Conclusions

In this study, HRTEM observations of LiCoO₂ cathode particle were performed after 150 charging-discharging cycles under 2.8–4.3 V. It was found that the surface of LiCoO₂ particle consisted of LiCoO₂ crystal, Co_3O_4 crystal, Co_3O_4 crystal nucleus, and an amorphous region. According to the degradation product Co_3O_4 from LiCoO₂, DFT calculations were performed to investigate the electrochemically driven phase transition path. Theoretical analysis indicated that the electrochemically driven phase transition undergoes two stages, lattice expansion, and oxygen escape. Through doping, the electrochemically driven phase transition of LiCoO₂ could be inhibited and the electrochemical performance could be improved. The experimental verification was made by doping LiCoO₂ with Al, In, Mg, and Zr to confirm the proposed electrochemically driven phase transition mechanism. Al or Mg doping significantly improved the cycling stability of LiCoO₂ cathode materials by inhibiting the lattice expansion or oxygen escape, respectively.

Author Contributions: Conceptualization, R.H. and D.Z.; methodology, J.T., Z.W., H.H., J.L., and R.H.; software, G.L., J.T. and D.Z.; validation, Z.W., R.H. and D.Z.; investigation, J.T., R.H. and D.Z.; writing—original draft preparation, J.T.; writing—review and editing, R.H. and D.Z.; visualization, H.H. and J.L.; funding acquisition, J.L., Z.W., and D.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (Grant Nos. 51703182 & 51701147), Sichuan Science and Technology Program (2017JY0137 & 2019JDTD0024), and "Young Scholars" Program of Xihua University.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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