Inhibiting degradation of LiCoO\textsubscript{2} cathode material by anisotropic strain during delithiation

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Abstract
Lithium cobalt oxides (LiCoO\textsubscript{2}) possess a high theoretical specific capacity of 274 mAhg\textsuperscript{-1}. However, when LiCoO\textsubscript{2} is charged at the voltage higher than 4.2 V, there exist significant structure transition and capacity fade. In this study, we used HRTEM to observe the phase evolution of LiCoO\textsubscript{2} cathode material after 100 cycles, and found that LiCoO\textsubscript{2} phase would degrade to Co\textsubscript{3}O\textsubscript{4} phase. The phase transition of Co\textsubscript{3}O\textsubscript{4} from LiCoO\textsubscript{2} gave rise to lattice expansion, by which the anisotropic strain was simultaneously impede lattice oxygen loss and structure transition of LiCoO\textsubscript{2} during delithiation at high voltage. In this case, the elongation of interplanar spacing also increases the diffusivity of Li ions in LiCoO\textsubscript{2}, contributing to rate performance.

Introduction
Lithium-ion batteries (LIBs) have been increasingly applied in mobile equipments and electric vehicles because of their high energy density [1–3]. Compared with anode materials, the performance of cathode materials is vital to the improvement on power density of LIBs [4]. Since LiCoO\textsubscript{2} was discovered by Goodenough’s group [3], a series of cathode materials, such as Li-rich [5], Mn-rich [6], Ni-rich [7] transition metal oxides, has been developed, and much progress has been made to further improve their power density and cycling stability. Nevertheless, as an archetypal cathode material, LiCoO\textsubscript{2} has been still the widely employed cathode material [8]. However, until now the commercialized LiCoO\textsubscript{2} only exhibits little more than half of its theoretical capacity. Such a large irreversible capacity is attributed mainly to the presence of an irreversible phase transition during delithiation and/or lithiation processes [9–11].

In the process of delithiation, there is an insulator-metal phase transition in the initial low-voltage region for LiCoO\textsubscript{2} [12]. While a half of the Li\textsuperscript{+} ions are removed, the material experiences an order-disorder transition [10], which drives the phase transition from hexagonal O\textsubscript{3} structure to monoclinic structure, and then back to O\textsubscript{3} structure. Furthermore, at the voltage above 4.2 V, delithiated LiCoO\textsubscript{2} tends to experience the O\textsubscript{3}-(H1-3)-O1 phase transition [10]. Along with the O\textsubscript{3}-(H1-3)-O1 phase transition, the Fermi level shifts into the valence band, and both Co 3d-t\textsubscript{2g} and O 2p states become broader and subsequently hybridized [11]. The Fermi level would reach a critical value when it touches the top of the O 2p bands, indicating that LiCoO\textsubscript{2} is exactly charged, which is the intrinsic voltage limit. With further charging, the Fermi level crosses the O 2p states, accompanying with holes migration into the O 2p states. This results in oxidation of O\textsuperscript{2–} and oxygen loss from the lattice, hence leading to degradation of LiCoO\textsubscript{2} material [13–15]. It is evident that the energy proximity of the Fermi level and the O 2p bands determines the intrinsic voltage limit of LiCoO\textsubscript{2} cathode material. Therefore, in order to increase the capacity of LiCoO\textsubscript{2}, the phase transition during delithiation should be suppressed and the top of O 2p states in valence band should be lower.
Many efforts have been made to maintain the structural stability and improve the electrochemical performance of LiCoO₂, in which cations doping have been proved to be efficient, including Mg [16, 17], Zr [18], Al [19], Ni [20], Fe [21], Cr [22], Mn [23], and Ti [24], et al. Although through doping the specific capacity of LiCoO₂ has been improved, it is still far below the theoretical value of 273 mAh g⁻¹. As aforementioned, it is phase transition or structure degradation at high charging voltage that decreases the capacity of LiCoO₂ cathode material. In this study, we used HRTEM to observe the microstructure evolution of LiCoO₂ material after charge/discharge cycling. The degradation mechanism of LiCoO₂ was discussed. Moreover, an approach was proposed by anisotropic strain to inhibit LiCoO₂ degradation during delithiation.

Experimental

In this study, LiCoO₂ cathode powder was synthesized by solid-state reaction at 1 000 °C [25]. Co₃O₄ and Li₂CO₃ were used as starting materials, as the sources of Li and Co, respectively. The mixture of the starting materials with the stoichiometric ratio of LiCoO₂, where 5% excess lithium carbonate was added to compensate for the volatilization of lithium during calcination. The mixed starting materials were then heat-treated in the air at 1 000 °C for 12 h. To assess the electrochemical performance, the synthesized LiCoO₂ powders was mixed with 10 wt% acetylene black, 10 wt% PVDF binder and N-methyl-2-pyrrolidene (NMP) to prepare a homogenous slurry, which was pasted at Al foil, dried at 120 °C and employed as a cathode in 2032-type coin-cell Li-ion batteries. The coin-cells were assembled by using Cellgrad 2300 as a separator, metallic lithium foil as a counter electrode, and 1 M LiPF₆ dissolved in water as the electrolyte. After 100 charging-discharging cycles under 4.3-2.0 V, the battery was disassembled in an insert Ar atmosphere. The electrode was clean with dimethyl carbonate, and cathode materials were stripped from the electrode of disassembled batteries and were dispersed in ethanol to prepare samples for TEM observation. The microstructure of LiCoO₂ cathode particle was observed by transmission electron microscopy (TEM, JEM 2100 F).

A first-principles calculation was performed by using the Vienna ab initio simulation package (VASP) [26] within the density functional (DFT) theory frame with the supplied PAW pseudopotentials [27, 28] and Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) [29]. The cut-off energy for the plane wave basis was set as 570 eV, and the Monkhorst-Pack k grid was set as 6 × 6 × 6 for sampling Brillouin zone.

Results and discussion

Figure 1(a) shows the HRTEM image of degraded LiCoO₂ particles. As can be seen, there are two regions with different phases, respectively. Comparing to the HRTEM images of LiCoO₂ before assembled into battery as shown in figure S1 is available online at stacks.iop.org/MRX/7/025501/mmedia, which demonstrated uniform LiCoO₂ phase in the particle, degraded LiCoO₂ particles consist of regions with different phases. Figure S2 also shows the HRTEM image of degraded LiCoO₂ particles. Similarly, the surface region of the degraded LiCoO₂ particles consist of regions with different phases. Significantly, figure S2b shows the FFT result of the marked
Fourier transformation of the area marked by the square in figure 1(a), this region was a phase of Co$_3$O$_4$ with Fd-3m symmetry. Figure 1(b) is the FFT result of the marked the square in figure 1(a). The angle between the (003) orientation of LiCoO$_2$ and the (0-22) orientation of Co$_3$O$_4$ is approximately 37°, which is approximately equal to the angle between the c-axis of the traditional cell of LiCoO$_2$ and the face diagonal of the rebuild cell LiCoO$_2$, as shown in figure 2. Therefore, TEM analysis demonstrates that the degradation of LiCoO$_2$ cathode material is attributed to the phase transition from LiCoO$_2$ to Co$_3$O$_4$ after delithiation.

To further discern the phase transition pathway from LiCoO$_2$ to Co$_3$O$_4$, the crystal cell of LiCoO$_2$ was rebuilt to a rhombohedral presentation for comparing with the conventional cell of Co$_3$O$_4$, as seen in figure 2. Figure 2(a) shows the conventional cell of LiCoO$_2$ and the rebuilt cell. The rebuilt cell has the lattice parameters $a = b = c = 8.01 \, \text{Å}$ and $\alpha = \beta = \gamma = 89^\circ$. Figure 2(b) shows the conventional cell of Co$_3$O$_4$ with lattice parameters $a = b = c = 8.12 \, \text{Å}$ and $\alpha = \beta = \gamma = 90^\circ$. Through comparing the crystal structures and lattice parameters of LiCoO$_2$ with Co$_3$O$_4$, one can see that lattice expansion and oxygen loss occurs during the phase transition from LiCoO$_2$ to Co$_3$O$_4$. Thus, lattice expansion and oxygen loss should be inhibited during delithiation to improve the capacity and stability of LiCoO$_2$ cathode materials.

One effective method to suppress the lattice expansion is compression, and this is equivalent to doping by elements with smaller radii. Meanwhile, lattice compression would reduce interlayer space of crystal, which leads to the decrease in Li$^+$ diffusivity. In addition, to avoid the oxidation of O$^{2-}$ caused by the overlap of Fermi level and the O 2p states, the strain from lattice compression/expansion should change the band structure and make the O 2p states lower. Therefore, we calculated the band structure of LiCoO$_2$ under different strain conditions using first-principles calculations.

Figure 3 shows the band structures of LiCoO$_2$ crystal under different strain conditions. Significant splitting of the Co 3d states is observed and covalent interaction results in hybridization of Co 3d and O 2p [30]. According to the band structure, an intrinsic voltage limit regarding the decomposition potentials of cathode materials was proposed [14]. At the intrinsic voltage, Co 3d states cross the top of O 2p states. For further charging, the Fermi level falls below the top of O 2p states and holes form in the bonded O 2p states, resulting in oxidation of O$^{2-}$. Thus, for inhibiting oxygen loss, the cross point of Co 3d states and O 2p states should move far away from the Fermi level. As shown in figure 3, the cross point of Co 3d states and O 2p states was marked in dash. As can be seen, four different strain types are applied to LiCoO$_2$ via changing the lattice parameters. The calculated partial density of states indicates that the strain conditions of (a) and (c) would give rise to the decline in the cross point of Co 3d states and O 2p states. This inhibits the oxidation of O$^{2-}$ when LiCoO$_2$ cathode is charged to higher voltage. Contrarily, the strain conditions of (b) and (d) increase the cross point of Co 3d states and O 2p states, which would make the oxidation of O$^{2-}$ easier.

The structure transition should be forbidden, while the oxidation of O$^{2-}$ is suppressed during delithiation for LiCoO$_2$. It is known that structural transition at the high charging voltage is driven by electrochemical potential, so the transition could be impeded as the transition potential barrier increases. Furthermore, for
practical application of LiCoO$_2$, the diffusivity of Li ions significantly affects the performance of LIBs. LiCoO$_2$ is a typical layered structural cathode material, and the reduced lattice parameter makes the interplanar spacing smaller, resulting in the decrease in Li$^+$ diffusivity. Hence, the strain condition (a) enables to inhibit oxygen loss during delithiation, but the shrinkage of lattice parameter causes less diffusivity of Li ions. By contrast, it is desired for the strain condition (c) to achieve the intention inhibiting oxygen loss and structural transition.

During delithiation, LixCoO$_2$ ($x < 0.5$) lost Li$^+$ and preferably transformed to Co$_3$O$_4$ because the free energy of Co$_3$O$_4$ was lower than that of the LixCoO$_2$ ($x < 0.5$) [15]. Figure 4 shows the change in the free energy along the proposed transition pathway for the LiCoO$_2$ with and without strain. As shown in figure 4, Li ions deinsertion from LiCoO$_2$ is described by transition steps 1-2-3, and transition steps 3-4-5 demonstrate the lattice expansion from $a = b = c = 8.01$ Å to $a = b = c = 8.12$ Å, and transition steps 5-6-7 indicate the oxygen loss. The free energy for each transition step was calculated by using a first-principles calculation method. For LiCoO$_2$ cathode material, although the system free energy increases due to the delithiation, the potential barrier is surmounted by an applied electric filed. The oxygen loss was energetically preferred after lattice expansion. The potential barriers of lattice expansion for strain condition (c) and without strain were calculated. Clearly, potential barrier is 5.57 eV under the strain condition (c), higher than the unstrain condition. Thus, the anisotropic strain i.e. lattice parameter $c$ extension and $a$ compression, enables to simultaneously inhibit oxygen

Figure 3. Band structures of LiCoO$_2$ crystal under different strain conditions: (a) lattice parameters of both $a$ and $c$ were compressed; (b) lattice parameter $a$ was extended and $c$ was compressed; (c) lattice parameter $a$ was compressed and $c$ was extended; (d) both $a$ and $c$ were extended.
loss and structural transition during delithiation at high voltage. Also, the increased in interplanar spacing enhances the diffusivity of Li ions, which is available on the rate performance of Li\textsubscript{x}CoO\textsubscript{2}.

As above theoretical analysis, the structural stability of LiCoO\textsubscript{2} could be improved by lattice strain. The lattice strain could be achieved by doping ions with different radius with Li\textsuperscript{+} or Co\textsuperscript{3+}. For example, doping ions with smaller radius such as Al, Ga would compress the lattice, conversely, doping ions with larger radius such as In, Sc would stretch the lattice. However, the lattice strain arising from doping ions with different radius would not be isotropic. Hence, co doping would realize the anisotropic strain.

Conclusion

In conclusion, we used HRTEM to observe the structure evolvement of LiCoO\textsubscript{2} material after 100 charging-discharging cycles, and found that the degradation compound of LiCoO\textsubscript{2} is Co\textsubscript{3}O\textsubscript{4}. The conventional cell of LiCoO\textsubscript{2} was rebuilt to exhibit what is the atoms correspondence between LiCoO\textsubscript{2} and Co\textsubscript{3}O\textsubscript{4}. Accordingly, a structural transition pathway was proposed, containing delithiation of Li ions, lattice expansion, and oxidation of O\textsuperscript{2−}. Hence, to improve the capacity and charging voltage of LiCoO\textsubscript{2}, the lattice expansion and oxidation of O\textsuperscript{2−} should be inhibited. The first-principles calculation was employed to obtain the band structure of LiCoO\textsubscript{2} crystal under different strain conditions. Results show that anisotropic strain, i.e. lattice parameter c extension and a compression, inhibits oxygen loss and structural transition without reducing Li\textsuperscript{+} diffusivity during delithiation.

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References

[1] Goodenough J B and Park K-S 2013 The li-ion rechargeable battery: a perspective J. Am. Chem. Soc. 135 1167–76
[2] Jaguemont J, Boulon L and Dubé Y 2016 A comprehensive review of lithium-ion batteries used in hybrid and electric vehicles at cold temperatures Appl. Energy 164 99–114
[3] Mizushima K, Jones P C, Wiseman P J and Goodenough J B 1980 Li\textsubscript{x}CoO\textsubscript{2} (0 < x < −1): a new cathode material for batteries of high energy density Mater. Res. Bull. 15 783–9
[4] Koksbang R, Barker J, Shi H and Saïdi M Y 1996 Cathode materials for lithium rocking chair batteries Solid State Ionics 84 1–21
[5] Thackeray M M et al 2007 Li2MnO2-stabilized LiMO2 (M = Mn, Ni, Co) electrodes for lithium-ion batteries J. Mater. Chem. 17 3112–25
[6] Zhang S et al 2018 A novel strategy to significantly enhance the initial voltage and suppress voltage fading of a Li- and Mn-rich layered oxide cathode material for lithium-ion batteries J. Mater. Chem. A 6 3610–24
[7] Myung S-T et al 2017 Nickel-rich layered cathode materials for automotive lithium-ion batteries: achievements and perspectives ACS Energy Lett. 2 196–223
[8] Cherrouk G and Nestler T 2014 Cathodes-technological review AIP Conf. Proc 1597, 134–45
[9] Chen Z, Lu Z and Dahn J R 2002 Staging phase transitions in Li1.2CoO2 J. Electrochem. Soc. 149 A1604–9
[10] Van der Ven A, Aydinol M K, Ceder G, Kresse G and Hafner J 1998 First-principles investigation of phase stability in LixCoO2 Phys. Rev. B 58 2975–87
[11] Hausbrand R et al 2015 Fundamental degradation mechanisms of layered oxide Li-ion battery cathode materials: methodology, insights and novel approaches Mater. Sci. Eng. B 192 3–25
[12] Ménétrier M, Saadoune I, Levasseur S and Delmas C 1999 The insulator-metal transition upon lithium deintercalation from LiCoO2: electronic properties and 7Li NMR study J. Mater. Chem. 9 1135–40
[13] Ensling D et al 2014 Nonrigid band behavior of the electronic structure of LiCoO2 thin film during electrochemical Li deintercalation Chem. Mater. 26 3948–56
[14] Goodenough J B and Kim Y 2010 Challenges for rechargeable Li batteries Chem. Mater. 22 587–603
[15] Laubach S et al 2009 Changes in the crystal and electronic structure of LiCoO2 and LiNiO2 upon Li intercalation and de-intercalation Phys. Chem. Chem. Phys. 11 3278–89
[16] Mladenov M, Stoyanova R, Zhecheva E and Vassilev S 2001 Effect of Mg doping and MgO-surface modification on the cycling stability of LiCoO2 electrodes Electrochim. Commun. 3 410–6
[17] Luo W, Li X and Dahn J R 2010 Synthesis and Characterization of Mg Substituted LiCoO2 J. Electrochem. Soc. 157 A782
[18] Kim S H and Kim C-S 2008 Improving the rate performance of LiCoO2 by Zr doping J. Electroceramics 23 254
[19] Xie M, Hu T, Yang L and Zhou Y 2016 Synthesis of high-voltage (4.7 V) LiCoO2 cathode materials with Al doping and conformal Al2O3 coating by atomic layer deposition RSC Adv. 6 63250–5
[20] Jin Y et al 2018 The influence of Ni doping on the structure and electrochemical properties of LiCoO2 materials J. Electrochem. Soc. 165 A2267
[21] Zhu Y, Zhou W, Chen Y, Yu J, Liu M and Shao Z 2015 A high-performance electrocatalyst for oxygen evolution reaction: LiCo0.8Fe0.2O2 Adv. Mater. 27 7150–5
[22] Madhavi S, Subba Rao G V, Chowdari B V R and Li S F Y 2002 Effect of Cr dopant on the cathodic behavior of LiCoO2 Electrochim. Acta 48 219–26
[23] Waki S et al 2002 High-Speed voltammetry of Mn-doped LiCoO2 using a microelectrode technique J. Solid State Electrochem. 4 205–9
[24] Sivajee Ganesh K et al 2015 Microstructural and electrochemical properties of Li1+yCo1-yO2 film cathodes prepared by RF sputtering J. Solid State Electrochem. 19 3621–7
[25] Nakamura T and Kajiyama A 1999 Synthesis of LiCoO2 particles with uniform size distribution J. Eur. Ceram. Soc. 19 871–4
[26] Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86
[27] Blöchl P E 1994 Projector augmented-wave method Phys. Rev. B 50 17953–79
[28] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758–75
[29] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8
[30] Melot B C and Tarascon J-M 2013 Design and preparation of materials for advanced electrochemical storage Acc. Chem. Res. 46 1226–38