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Achieving Stable High-Voltage Cycling of $LiCoO_2$ Cathodes via a Layered Surface Strengthening Strategy

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Abstract. Achieving stable cycling performance of high-capacity LCO at elevated voltages, a surface coating strengthening strategy was proposed. By simply adjusting the solution concentration during AlF_3 liquid-phase treatment of LCO, a surface consisting of Al/F enrichment in the subsurface layer and an Al/F-enriched rock-salt phase on the surface was achieved. By comparing with LCO modified by conventional interface protection (N-LCO), the mechanisms by which the layered surface strengthening strategy optimizes LCO performance were systematically investigated. It is proposed that the Al/F-enriched rock-salt phase layer helps inhibit the decomposition of carbonate solvents, thereby reducing HF generation, while inducing the formation of a thin and dense inorganic CEI protective layer. Furthermore, Al/F doping in the subsurface layer modulates the electronic structure in this region, increasing the barriers for lattice oxygen redox and migration, playing a key role in mitigating detrimental L/S phase transitions. Inhibition of the structural evolution from O3 to H1-3/O1a by the coating surface strengthening strategy reduces the accumulation of strain and stress during charge/discharge, thereby minimizing crack formation.

Keywords: $LiCoO_2$, High voltage, Layered surface strengthening

1. Introduction

With the continuous development of electrolytes compatible with lithium metal anodes, in the early 1970s, primary lithium batteries were commercialized using metallic Li as the anode and MnO_2 or $SOCl_2$ as the cathode, directing attention towards secondary lithium batteries capable of reversible charge-discharge [1-3]. Building on primary lithium batteries, researchers developed new cathode materials that could reversibly intercalate/deintercalate lithium ions, promoting the development of rechargeable batteries (termed secondary batteries). In 1972, Professor Whittingham at Exxon reported a novel cathode material, TiS_2, and fabricated the world's first rechargeable secondary lithium battery. In TiS_2, Li^+ could be repeatedly intercalated and deintercalated between the layers of the transition metal sulfide. In this study, Professor Whittingham first proposed the working principle of batteries based on intercalation reactions, laying the foundation for the development of secondary lithium-ion batteries. In 1991, Sony Corporation commercialized the first lithium-ion battery using lithium cobalt oxide as the cathode paired with petroleum coke anode material. Upon its introduction, the lithium-ion battery rapidly captured the energy market due to its advantages

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such as high voltage, small size, high energy density [4-6], and environmental friendliness, promoting the miniaturization and thinning of electronic products. With the continuous innovation of portable electronic products and the rapid development of new energy vehicles, the lithium-ion battery market is expected to expand further and become an indispensable part of society. However, as energy demands increase, batteries operating at low voltages struggle to meet power supply needs. Therefore, researchers mainly focus on lithium cobalt oxide materials operating at high voltages, i.e., above 4.5 V. Increasing the cut-off voltage leads to structural degradation caused by the greater extent of delithiation.

This work proposes a layered surface strengthening strategy. By simply adjusting the solution concentration during AlF_3 liquid-phase treatment of LCO, a layered surface comprising Al/F doping in the subsurface layer and an Al/F-enriched rock-salt phase on the surface was achieved. By comparing with LCO modified by conventional interface protection (N-LCO), the mechanisms by which the layered surface strengthening strategy optimizes LCO performance were systematically investigated. The results indicate that, compared to a simple rock-salt protective layer, the Al/F-enriched rock-salt phase layer helps inhibit the decomposition of carbonate solvents, thereby reducing HF generation, while inducing the formation of a thin and dense inorganic CEI protective layer. Furthermore, Al/F doping in the subsurface layer modulates the electronic structure in this region, increasing the barriers for lattice oxygen redox and migration, playing a crucial role in mitigating detrimental layered/spinel (L/S) phase transitions [7-10]. This work highlights the critical role of subsurface elemental modulation in enhancing material structural stability and electrochemical performance, providing guidance for achieving stable cycling of high-voltage, high-capacity LCO.

2. Material preparation

The undoped high-capacity polycrystalline LCO material used in this experiment was purchased from TIBETAN XIANTENG INNO-SCIENCE & TECHNOLOGY CO., LTD. The samples were synthesized via a simple liquid-phase coating followed by high-temperature sintering. First, 100 mmol of LCO, x mmol of $Al(NO_3)\cdot 9H_2O$ (x = 0.25, 0.5, 1, 1.5, and 2.5), and 3x mmol of NH_4F were dispersed in deionized water and stirred for 10 h. The solution was then filtered and dried in a forced-air drying oven at 80 °C. Subsequently, the dried sample was sintered under an argon atmosphere at 500 °C for 10 h to obtain LCO treated with different Al/F concentrations via liquid-phase processing. To reveal the optimization effect of the surface modification, this chapter selects LCO treated with 1.5 wt% AlF_3 (designed according to the stoichiometric ratio) as the experimental sample, named Durable High-Capacity LCO (DH-LCO), and LCO treated with 0.25 wt% AlF_3 as the comparison sample, named Normal LCO (N-LCO).

3. Results and discussion

As shown in Figure 1, the surface morphology and elemental distribution of N-LCO and DH-LCO samples were characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). SEM images show that both materials exhibit a uniform microstructure. Corresponding EDS mapping results further indicate that cobalt (Co), aluminum (Al), and fluorine (F) elements are highly uniformly distributed on the surfaces of both materials. The uniform distribution of Co corresponds to the bulk phase of lithium cobalt oxide (LCO); while the uniform coverage of Al and F confirms the successful achievement of uniform doping or surface modification of Al and F elements through material design. This uniform elemental distribution

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helps stabilize the material's bulk structure and improve the electrode-electrolyte interface, potentially enhancing the material's cycling stability and electrochemical performance.

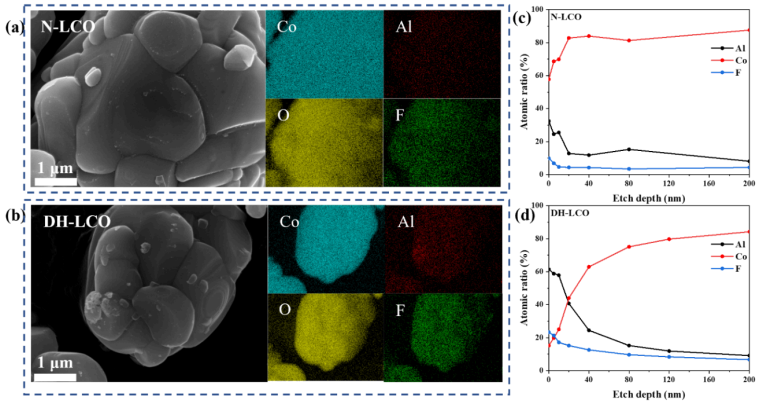

Figure 1. (a, b) SEM images and EDS results of N-LCO and DH-LCO

To elucidate the effect of aluminum/fluorine (Al/F) surface modification on the crystal structure of layered lithium cobalt oxide ($LiCoO_2$, LCO), this study performed X-ray diffraction (XRD) phase analysis and crystal structure refinement on the untreated pristine sample (N-LCO) and the Al/F-coated sample (DH-LCO). The results are shown in Figure 2, and the corresponding refined lattice parameters are listed in Table 1. The XRD patterns indicate that all diffraction peaks for N-LCO and DH-LCO are clear, sharp, and have highly consistent positions, with no impurity peaks or significant peak shifts observed. These diffraction peaks can be perfectly indexed to a hexagonal layered structure with the space group R-3m, prototype α-$NaFeO_2$ type structure. This structure is typical for high-performance layered cathode materials, where lithium ions and transition metal ions are alternately arranged in the octahedral interstices formed by oxygen atoms, creating layered channels conducive to two-dimensional lithium-ion diffusion. Both samples exhibit high intensity and good symmetry for key characteristic peaks such as (003) and (104), preliminarily indicating that the Al/F surface treatment did not alter the main crystal phase of the material or generate new phases. To further quantitatively assess subtle changes in the crystal structure, the Rietveld refinement method was employed to fit the XRD data. The refined lattice constants show that the unit cell parameters a, c, and the unit cell volume V for N-LCO and DH-LCO are very close. Specifically, the differences in a-axis and c-axis parameters between the two are on the order of 10^{-4} Å, which falls well within the experimental error and calculation error range of the XRD refinement method itself. Therefore, from a crystallographic statistical perspective, it can be concluded that DH-LCO and N-LCO possess the same bulk crystal structure.

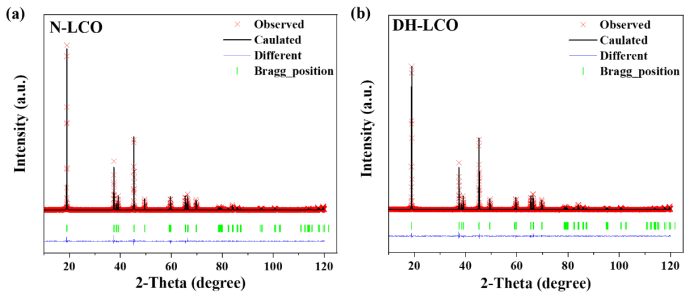

Figure 2. XRD patterns and refinement fits of N-LCO and DH-LCO

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Table 1. Rietveld refined lattice parameters for N-LCO and DH-LCO

Sample	Space Group	a (Å)	b (Å)	c (Å)	R_{wp} (%)
N-LCO	R-3m	2.8147	2.8147	14.0509	3.76
DH-LCO	R-3m	2.8146	2.8146	14.0517	3.63

Figure 3 shows the changes in cycling stability and rate capability of LCO after treatment with different concentrations of AlF_3. Figure 3a shows that untreated LCO delivers only an initial specific capacity of 213 mAh/g at a 0.2 C current density and exhibits very poor cycling stability and rate capability. However, upon simple interface treatment (0.25 wt%, i.e., N-LCO), the initial specific capacity of N-LCO reaches as high as 233 mAh g^{-1}, and its cycling stability and rate capability are significantly improved. As the AlF_3 content increases from 0.25 wt% to 1.5 wt%, the capacity retention of LCO continuously increases, and it also exhibits similar specific capacities at high rates. However, when the AlF_3 content is further increased to 2.5 wt%, the cycling stability does not show significant improvement compared to 1.5 wt%, but the excessively thick interface protective layer hinders capacity delivery. The research results indicate that the interface of LCO treated with 1.5 wt% AlF_3 exhibits a special structure, achieving the best balance between high capacity and high stability.

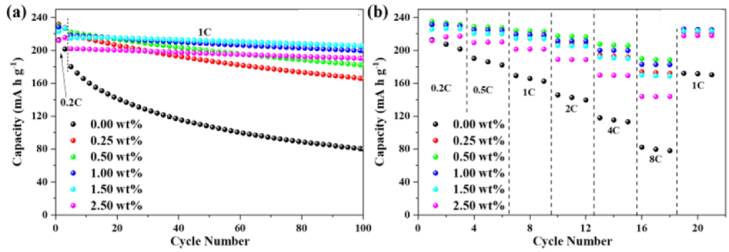

Figure 3. Comparison of (a) cycling stability and (b) rate capability of LCO after treatment with different AlF_3 concentrations

To investigate the electrochemical behavior characteristics of N-LCO and DH-LCO, charge-discharge tests were first conducted. Figure 4 shows the first three cycles of charge-discharge curves and corresponding Cyclic Voltammetry (CV) curves for N-LCO and DH-LCO. From Figures 4a and 4b, it can be seen that N-LCO exhibits a discharge specific capacity of 233 mAh g^{-1} in the first cycle but also shows slow capacity decay in subsequent cycles. DH-LCO, on the other hand, exhibits only 223 mAh g^{-1} discharge specific capacity in the first cycle, and the charging plateau voltage is as high as 4.27 V. Since the Al/F-induced rock-salt phase on the N-LCO surface still contains a certain amount of Li^+, it allows for rapid Li^+ intercalation/deintercalation. In contrast, the Al/F-enriched surface rock-salt phase layer of DH-LCO exhibits a certain degree of lithium deficiency; this lithium-poor rock-salt phase hinders Li^+ intercalation/deintercalation, so DH-LCO shows greater impedance during the first charge-discharge cycle. However, in the subsequent two cycles, DH-LCO undergoes an activation process, with decreased polarization and gradually increased capacity. The CV curves in Figures 4c and 4d show similar results. The main redox peak positions in the CV curve of N-LCO stabilize at 3.99 V/3.87 V from the second cycle onwards, corresponding to the phase transition between O3(I) and O3(II). However, the redox peaks in the CV curve of DH-LCO undergo a significant shift process and only stabilize at 4.04 V/3.85 V by the fourth cycle. The larger

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polarization of the redox peaks for DH-LCO implies that the surface of DH-LCO possesses greater impedance.

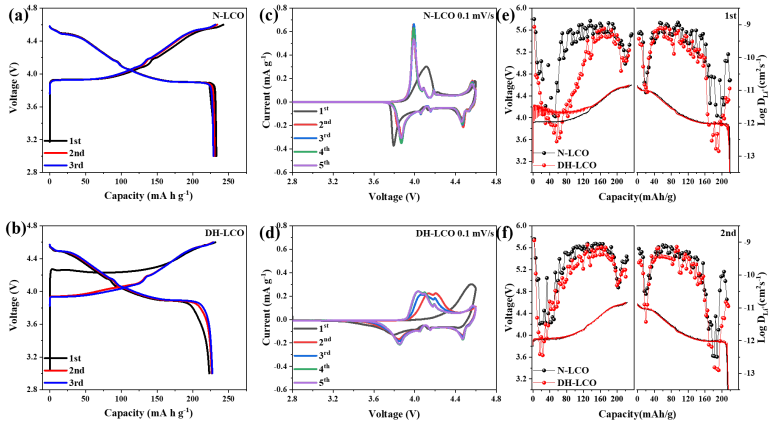

Figure 4. (a,b) Voltage-capacity hysteresis loops for the first three cycles of (a) N-LCO and (b) DH-LCO (c,d) The corresponding cyclic voltammograms (first three cycles, 0.1 mV s^{-1})

Lithium cobalt oxide (LCO) has become an extremely important cathode material in consumer electronics applications due to its high energy density, high tap density, excellent conductivity, and cycling stability. However, when the voltage exceeds 4.5 V, irreversible phase transitions in the LCO bulk and interfacial side reactions increase, leading to deteriorated cycling stability. Even with surface coating, detrimental "layered/spinel" phase transitions in the subsurface are difficult to avoid, and aluminum/fluorine doping plays a positive role in suppressing these detrimental subsurface transitions. Simultaneously, the layered strengthening structure comprising the Al/F-rich surface rock-salt phase and the Al/F-doped subsurface effectively inhibits surface side reactions and optimizes the cathode-electrolyte interphase (CEI). In this work, we report a lithium cobalt oxide with a reinforced layered structure. It delivers a high reversible capacity of 235 mAh/g at 4.7 V and retains 81.2% of its initial capacity after 1000 cycles at 800 mA/g.

4. Conclusion

Lithium-ion batteries are now widely used in consumer electronics and new energy vehicles. To meet the demand for longer endurance times/ranges in products, the industry has placed higher requirements on both the volumetric and gravimetric energy densities of lithium-ion batteries. Currently, efforts are focused on achieving higher specific capacity and energy density by increasing the charge cut-off voltage of lithium cobalt oxide. When the operating voltage of lithium cobalt oxide exceeds 4.5 V, detrimental phase transitions in the bulk increase, and interfacial side reactions between the material and electrolyte also intensify, leading to reduced cycling stability. This hinders the commercialization of high-voltage lithium cobalt oxide. To address these issues, researchers propose enhancing the electrochemical performance of high-voltage LCO through bulk and interface structure optimization. Targeting the detrimental phase transitions caused by excessive delithiation of LCO and the interfacial side reactions at high voltages, a layered surface strengthening structure for LCO was designed, consisting of an Al/F-rich surface rock-salt phase and Al/F-doped subsurface. The doping of Al/F elements optimizes the electronic structure near the lattice oxygen in the subsurface, significantly inhibiting detrimental phase transitions in LCO during high-voltage cycling. Meanwhile, the Al/F-enriched rock-salt phase layer helps inhibit the decomposition of

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carbonate solvents, thereby reducing HF generation, and induces the formation of a thin, dense inorganic CEI protective layer, greatly mitigating surface side reactions.

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