

Approaching the capacity limit of lithium cobalt oxide in lithium ion batteries via lanthanum and aluminium doping

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Lithium cobalt oxides (LiCoO₂) possess a high theoretical specific capacity of 274 mAh g⁻¹. However, cycling LiCoO₂-based batteries to voltages greater than 4.35 V versus Li/Li⁺ causes significant structural instability and severe capacity fade. Consequently, commercial LiCoO₂ exhibits a maximum capacity of only ~165 mAh g⁻¹. Here, we develop a doping technique to tackle this long-standing issue of instability and thus increase the capacity of LiCoO₂. La and Al are concurrently doped into Co-containing precursors, followed by high-temperature calcination with lithium carbonate. The dopants are found to reside in the crystal lattice of LiCoO₂, where La works as a pillar to increase the *c* axis distance and Al as a positively charged centre, facilitating Li⁺ diffusion, stabilizing the structure and suppressing the phase transition during cycling, even at a high cut-off voltage of 4.5 V. This doped LiCoO₂ displays an exceptionally high capacity of 190 mAh g⁻¹, cyclability with 96% capacity retention over 50 cycles and significantly enhanced rate capability.

Because of their high energy density, lithium ion batteries (LIBs) have become a rapidly growing energy storage technology with wide applications in mobile phones, portable electronics and electric cars^{1–5}. Cathode materials are one major performance-limiting factor for cell energy and power density. There are many advanced cathode materials such as Li, Mn-rich and Ni-rich transition metal oxides, and much progress has been made to improve their performance^{6–8}. However, these materials face significant issues such as voltage and capacity fading as well as structural and thermodynamic instability, which have so far prevented their commercialization^{8,9}.

Among the commercialized cathode materials, LiCoO₂ is the most successful for portable devices; for example, it is used in the majority of smart phones. However, commercial LiCoO₂-based batteries generally utilize little more than half their theoretical capacity. Such a large irreversible capacity is mainly attributed the presence of phase transitions. Studies have shown that LiCoO₂ experiences a series of phase transitions during the lithium insertion/deinsertion processes^{10–12}. Initially, there is an insulator–metal phase transition in the low-voltage region. Then, when charging to 4.2 V, approximately 50% of the Li⁺ ions are removed and the material experiences an order–disorder transition from the hexagonal structure (O3 phase in the *R*[−]3*m* space group in which three CoO₂ slabs are in a unit cell and both Li⁺ and Co⁺ occupy the octahedral sites) to a monoclinic structure (C2/m phase in which Li, Co and O ions occupy 2a and 4c, 2b and 4c and 4c sites, respectively), and then back to the O3 phase. When charging to above 4.5 V, the cathode undergoes another transition from the O3 phase to a H1-3 phase or O6 phase (*R*[−]3*m* group in which six CoO₂ slabs are in a unit cell, and Li, Co and O occupy 3a, 6c and 6c sites, respectively) before the

emergence of an O1 phase (one CoO₂ slab in a unit cell)¹¹. These phase transitions are quite reversible, but the order–disorder transition substantially lowers the Li⁺ diffusivity and the transition to the H1-3 phase severely stresses the structure, generating mechanical strains and micro-cracks between and within the particles. These phase transitions, coupled with the decreased Li⁺ diffusivity and increased mechanical stress, lead to dramatic capacity fading in the deeply charged Li_xCoO₂. Accordingly, the charging voltage was restricted to 4.2 V in the early development stage of commercial LiCoO₂-based batteries¹³.

To maintain structural integrity and stable electrochemical performance, substantial efforts towards improving the capacity of LiCoO₂ have been made via various techniques such as doping with various metals and surface modification by coating with MgO (ref. ¹⁴), Al₂O₃ (ref. ¹⁵), TiO₂ (ref. ¹⁵), ZrO₂ (refs ^{15,16}) and so on. Among these techniques, doping with different elements including Mg (refs ^{17–19}), Zr (refs ^{19,20}), Al (refs ^{21,22}), Ni (ref. ²³), Fe (ref. ²⁴), Cr (ref. ²⁵), Mn (ref. ²⁶) and Ti (ref. ²⁷) has been employed to suppress the order–disorder transition, with varying degrees of success. This has led to an improvement of LiCoO₂-based commercial LIBs from 4.2 V in the 1990s to 4.35 V at present, achieving a delivered capacity of 165 mAh g⁻¹. However, this is still far below the capacity limit. For higher capacity, one has to utilize more lithium in the insertion/deinsertion processes by pushing LiCoO₂ to work at higher voltages, where it is more challenging to maintain the structural integrity and improve Li⁺ diffusivity.

In this work, we dope the LiCoO₂ cathode with two elements concurrently, lanthanum and aluminium, to address the above-mentioned issues. The larger-diameter La cations function as a pillar and effectively increase the *c*-axis spacing, leading to a significant

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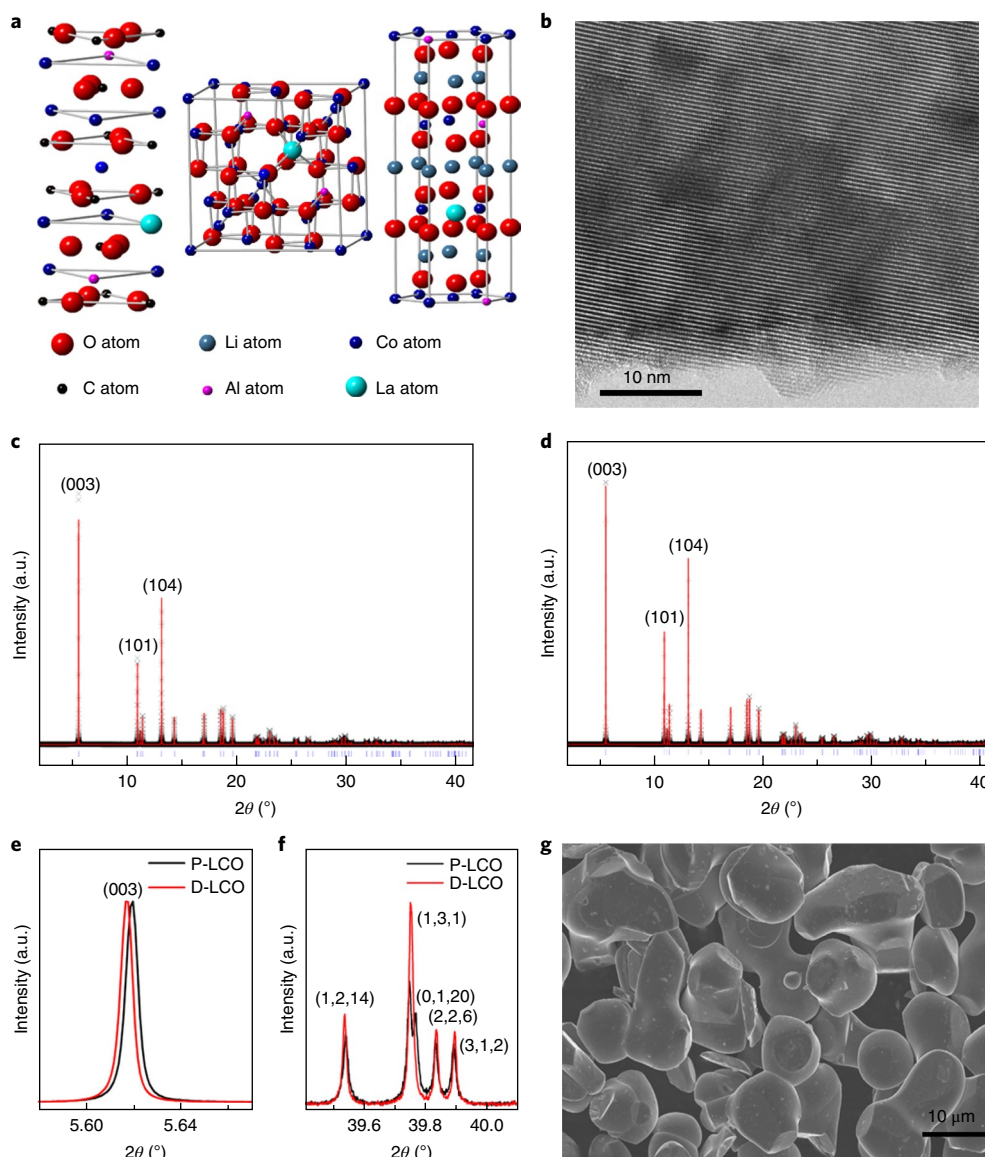


Fig. 1 | Ex situ characterization of D-LCO and P-LCO. **a**, Schematic structures of doped CoCO_3 and Co_3O_4 , and the final product D-LCO. **b**, The high-resolution TEM image of D-LCO. **c**, The HRXRD pattern of P-LCO. **d**, The HRXRD pattern of D-LCO: $\lambda = 0.4593 \text{ \AA}$. **e**, Comparison of the (003) peak in P-LCO and D-LCO. **f**, Comparison of the characteristic peaks in the HRXRD patterns between 39.4° and 40.2° . **g**, The SEM image of D-LCO.

increase in Li^+ diffusivity. The smaller-diameter Al cations serve as positively charged centres that disrupt and suspend the order-disorder transitions and H1-3 phase transition during cycling. Compared with pristine LiCoO_2 , the co-doped LiCoO_2 can work at cut-off voltages as high as 4.5 V versus Li/Li^+ , significantly improving its capacity retention from 84% to 96% with an exceptionally high capacity of 190 mAh g^{-1} at C/3.

Characterization of the cathode materials

The co-doping approach starts with the preparation of La- and Al-co-doped cobalt carbonate (CoCO_3) via a controlled liquid-state crystallization. In a subsequent annealing, co-doped Co_3O_4 is formed as a precursor of the doped LiCoO_2 in which the occupation of La and Al in Co sites is inherited. Finally, the co-doped LiCoO_2 (D-LCO) is synthesized by calcinating this precursor with Li_2CO_3 at $1,050^\circ\text{C}$ for 12 h. The chemical composition ratio of La:Al:Co was measured by inductively coupled plasma (ICP) mass spectrometry and estimated to be 1:2:1,000. The schematic structures of the co-doped CoCO_3 and Co_3O_4 and the D-LCO are shown in Fig. 1a. In a

typical doping method, the dopants usually diffuse into the LiCoO_2 layer structure and substitute the Co atoms via a solid-state reaction at high temperature^{17,18,25}. However, this dopant diffusion in the solid-state is very limited and a large amount of the dopants are diverted to coating dots on a submicrometre or micrometre scale.

Transmission electron microscopy (TEM) images of both D-LCO (Fig. 1b) and pristine LCO (P-LCO) (Supplementary Fig. 1) show pure, continuous lattice fringes with a d -spacing of 4.70 nm. In high-angle annular dark-field (HAADF) images of the D-LCO (Supplementary Fig. 2), the location of the La can be clearly seen. In Supplementary Fig. 2a, the dots show different contrast in the transition metal layers with the La looking brighter due to the Z-contrast in the HAADF images, showing that the substitution doping is working well. However, some La dopants can also be seen in Li layers in Supplementary Fig. 2a,b due to cation mixing. To distinguish the subtle difference in crystal structure between the P-LCO and D-LCO, high-resolution X-ray diffraction (HRXRD) measurements were carried out at the Advanced Photon Source (APS), clearly showing that the c lattice parameter increases by

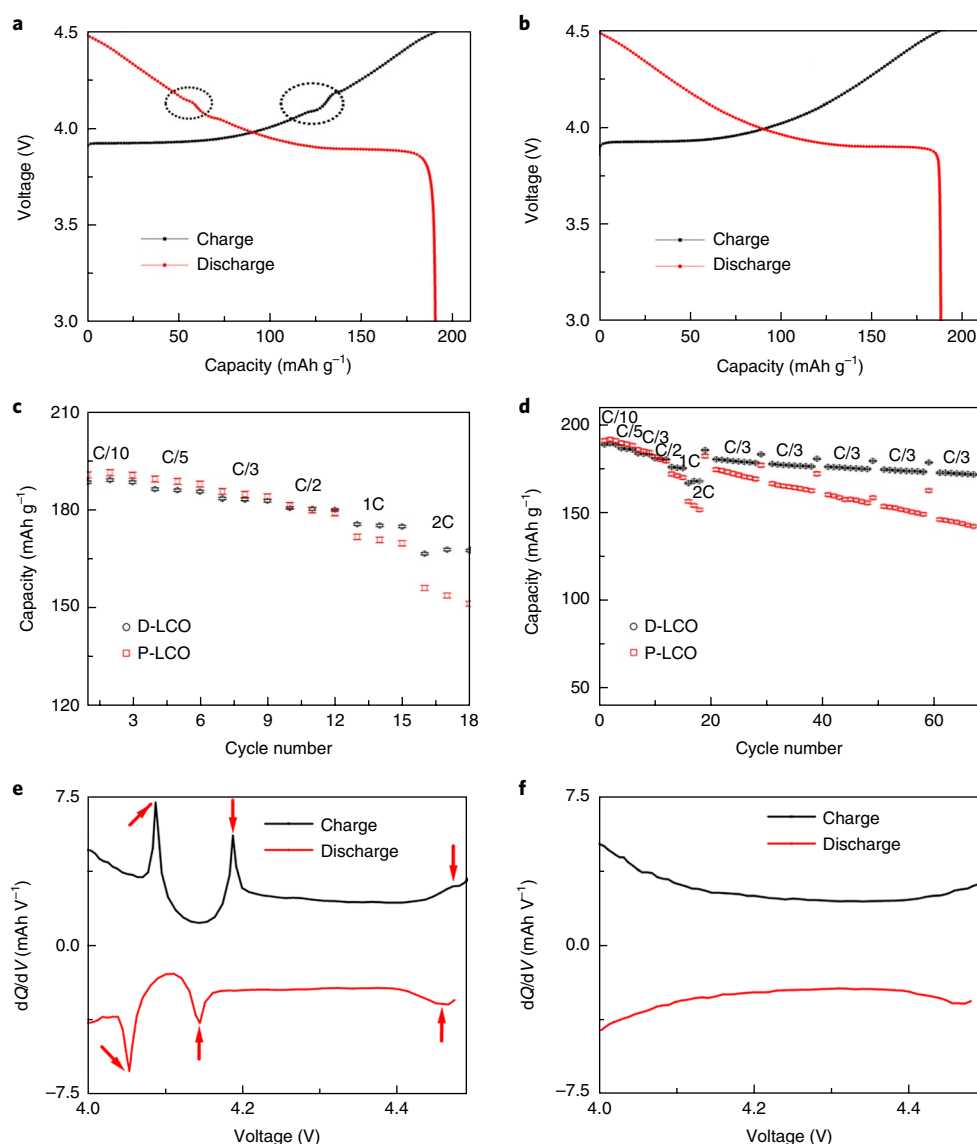


Fig. 2 | Electrochemical characterization of P-LCO and D-LCO. **a**, Charge-discharge voltage profile of P-LCO at C/10 (the order-disorder transition is highlighted in the black dashed circle) **b**, Charge-discharge voltage profile of D-LCO at C/10. **c**, Rate performance comparison of P-LCO and D-LCO. **d**, Cycling performance comparison of P-LCO and D-LCO. **e**, The dQ/dV curve of P-LCO during the formation test (the arrows in the profile indicate three distinct phase transitions respectively). **f**, The dQ/dV curve of D-LCO during the formation test.

0.03% from 14.0545 Å in P-LCO to 14.0588 Å in D-LCO, while the *a* lattice parameter decreases by 0.01% from 2.8159 Å to 2.8156 Å. The increased *c* lattice parameter and decreased *a* lattice parameter in D-LCO are further verified by the (003) peak shifting to a lower angle compared with that of P-LCO (Fig. 1e) and by the merging of the (31-1) and (01,20) peaks (Fig. 1f). Further inspection of the HRXRD patterns indicates that the co-element doping also improves the LiCoO₂ crystallinity, as evidenced by the sharper peaks in D-LCO compared with P-LCO.

At the same time, our HRXRD results clearly show that there is a small decrease of intensity ratio between (003) and (104), indicating that a small amount of La is located in the Li site due to cation mixing, consistent with our HAADF images (Supplemental Fig. 2). Our scanning electron microscopy (SEM) images show that both P-LCO and D-LCO are made up of ~15–25 μm particles (Fig. 1g, Supplementary Fig. 3). In addition, the effect of Co dissolution was investigated according to a previously reported approach²⁸, showing that the content of Co ions in solution after storing the half cells with Li metal as the anode at 60 °C for 14 days was 4.2 ppm for D-LCO

and 91.1 ppm for P-LCO. The loss of Co for these two electrodes was 0.07% and 1.51%, respectively (Supplementary Table 1). Obviously, the doping mitigates the Co ion dissolution at the increased cut-off voltage, which can be ascribed to the improved structural stability. Though Co dissolution does occur in the system, it is negligible in the dry solutions without invasion of water²⁹.

Electrochemical performance and phase transition

The electrochemical results clearly show that the introduction of a small amount of La and Al can have a profound effect on the performance. As shown in Fig. 2a, a specific capacity of 190 mAh g⁻¹ has been achieved at 0.1 C for the D-LCO with a cut-off voltage of 4.5 V, which amounts to 70% of the theoretical capacity of LiCoO₂. In comparison, though P-LCO can also deliver a high specific capacity of 190 mAh g⁻¹ at 0.1 C (Fig. 2b), the rate and cycle performance is quite different. When working at a higher rate such as 2 C, the D-LCO can deliver 167 mAh g⁻¹, 14 mAh g⁻¹ higher than that of P-LCO (Fig. 2c). Importantly, at 25 °C the capacity retention of D-LCO is 96% over 50 cycles with a cut-off voltage of 4.5 V,

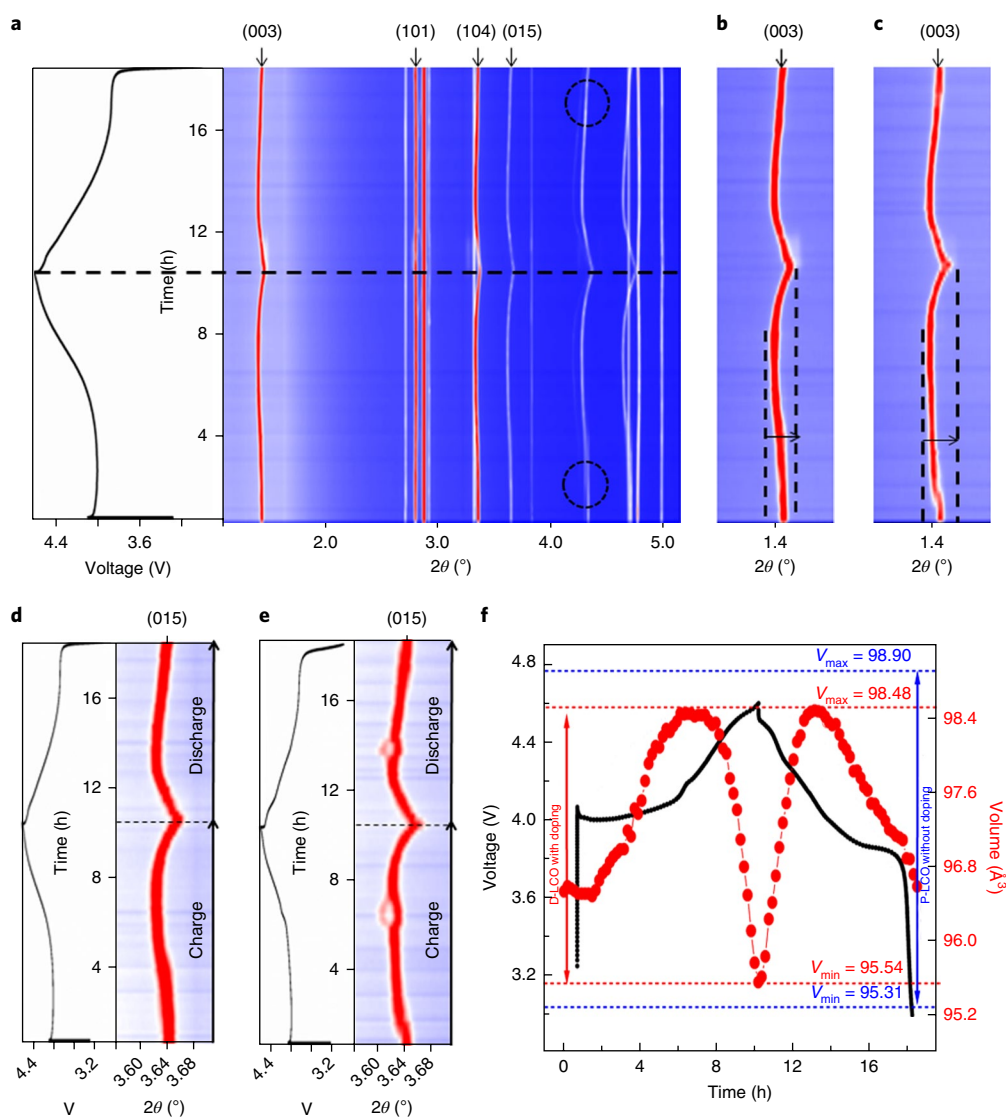


Fig. 3 | In situ synchrotron HEXRD characterization for D-LCO during the first charge-discharge process. **a**, The voltage profile and corresponding contour plot of the XRD pattern evolution of D-LCO (the insulator-metal transition is highlighted in the black dashed circle). **b**, Contour plot of the (003) peaks evolution of D-LCO. **c**, Contour plot of the (003) peaks evolution of P-LCO (the amplitudes of the peak shifts is marked by the arrows). **d**, The voltage profile and corresponding contour plot of the (015) peaks evolution of D-LCO. **e**, The voltage profile and corresponding contour plot of the (015) peaks evolution of P-LCO; phase transition between hexagonal to monoclinic appeared around 6 and 14 hr, which shows split features (indicated with light red). **f**, The voltage profile (black) and the cell volume evolution process (red) of D-LCO. $V_{\max}$ and $V_{\min}$ are the maximum and minimum cell volume, respectively. The volume data are also shown (in blue) for P-LCO.

compared with 84% for P-LCO (Fig. 2d). Even at an elevated temperature of $\sim 45^\circ\text{C}$ or in a full-cell configuration using graphite as the anode and the D-LCO and P-LCO as the cathode, the doping effect is obvious and the cycling performance is much better in D-LCO than P-LCO (Supplementary Figs. 4 and 5). Moreover, a.c. impedance spectra clearly show that D-LCO exhibits a smaller resistance than P-LCO and partially explains the reason for the improved performance (Supplementary Fig. 6). Considering that Co dissolution is not significant in the D-LCO system, the major reason could be ascribed to the structural aspects as described in detail below. Such an improvement suggests that not only has the crystal structural stability of D-LCO been improved, but the Li diffusivity has also been increased.

Results for dQ/dV during the formation cycle can be used to investigate the phase transition behaviour. Notably, our dQ/dV curve for P-LCO shows that three distinct phase transitions occur at 4.1 V, 4.2 V and 4.46 V versus Li/Li^+ when charging to 4.5 V (Fig. 2e).

As reported in a previous study, when LiCoO_2 is delithiated, the material experiences a series of phase transitions³⁰. Initially, there is an insulator-metal transition in the low voltage region associated with a first-order phase transition with a coexistence region. As the material continues to be delithiated and when half of the Li^+ is removed from LiCoO_2 , the cathode experiences an order-disorder transition, which drives the phase transition from the hexagonal structure (O3) to the monoclinic structure. Further delithiated LCO tends to experience the O3-(H1-3)-O1 phase transition^{11,31}. As seen in Fig. 2e, two minor peaks appear at 4.1 V and 4.2 V, which are associated with order-disorder transitions near $\text{Li}_{0.5}\text{CoO}_2$. The peak at 4.46 V is likely due to the appearance of the H1-3 phase. However, no such phase transition peaks are seen for D-LCO (Fig. 2f), indicating that the order-disorder transition has been eliminated and the H1-3 phase transition has been suppressed. In our designed D-LCO, the Al is smaller than Co but has a charge of 3+, so it could serve as a fixed-charge centre to block the rearrangement

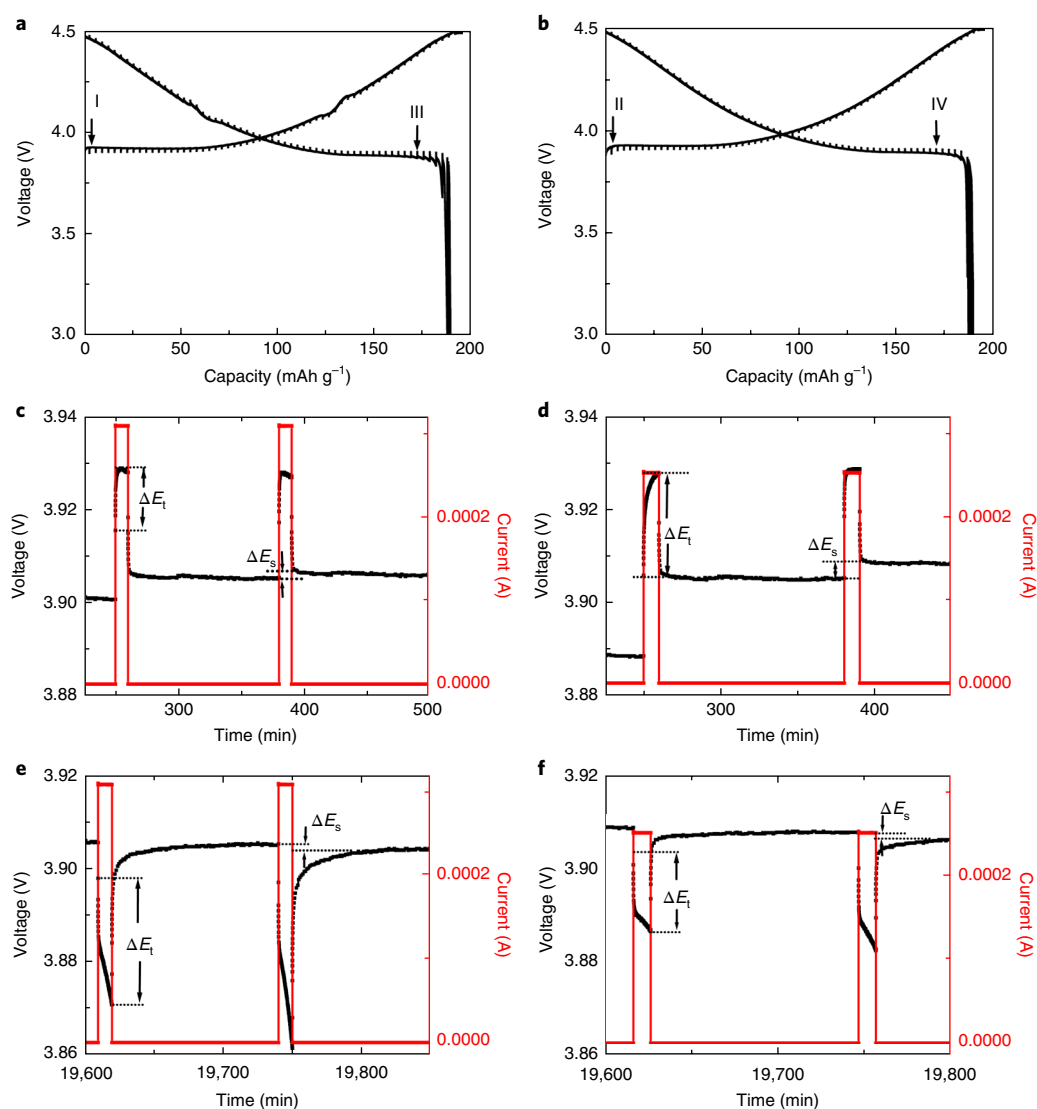


Fig. 4 | Li ion diffusion coefficient determination of P-LCO and D-LCO via GITT. **a**, The GITT curve of P-LCO as a function of capacity. **b**, The GITT curve of D-LCO as a function of capacity. **c**, The GITT curve of P-LCO at the initial charging time marked as 'I' in **a**. The red and the black curves correspond to the applied pulse current and responding voltage change, respectively. **d**, The GITT curve of D-LCO at the initial charging time marked as 'II' in **b**. **e**, The GITT curve of P-LCO at the final discharging time marked as 'III' in **a**. **f**, The GITT curve of D-LCO at the final discharging time marked as 'IV' in **b**. ΔE_s is the change of the steady-state voltage of the cell for the related step, and ΔE_t is the total transient voltage change of the cell for the related step.

of lithium vacancies³². The absence of a phase transition further confirms that Al is successfully introduced into the D-LCO lattice, suppressing the phase transitions with a cut-off voltage of 4.5 V. Because all performance changes should be rooted in the material structure and the lithium insertion–deinsertion processes, in situ synchrotron high-energy X-ray diffraction (HEXRD) and galvanostatic intermittent titration technique (GITT) characterizations were conducted to further understand the structure evolution and lithium insertion/deinsertion mechanism.

In situ synchrotron HEXRD characterization

To further elucidate the doping effects, in situ HEXRD measurements on the P-LCO and D-LCO cells were performed at the APS. As seen in Fig. 3a, the evolution of the HEXRD patterns correlates well with the electrochemical process. The symmetric structure evolution behaviour indicates that the insertion–deinsertion processes for the D-LCO are completely reversible when cycled at the cut-off voltage of 4.5 V. The highly reversible structure change is consistent with the observed electrochemical process (Fig. 2b,d), explaining

why the D-LCO exhibits highly reversible capacity and nearly 100% Coulombic efficiency. The P-LCO has quite different structural evolution compared with that of D-LCO during the charging–discharging processes (Fig. 3a and Supplementary Fig. 7).

First, the D-LCO exhibits a single-phase solid-solution insertion–deinsertion behaviour after the initial insulator–metal transition highlighted by the black dashed circle in Fig. 3a, while a series of phase transitions can be clearly identified for the P-LCO as fully revealed in Supplementary Fig. 7a. As shown in Fig. 3d, the intensity and position of the (015) peaks for the D-LCO evolve smoothly and no new peaks emerge during the charge–discharge process between 3.0 V and 4.5 V, indicating that the order–disorder phase transition between hexagonal and monoclinic phases has been successfully suppressed, consistent with our dQ/dV results (Fig. 2f). By contrast, during the charge process from 3.0 V to 4.5 V, the (015) peaks of the P-LCO electrode split into two components indicated by the appearance of light-red peaks when the charging reaches ~4.1 V, which can be ascribed to the phase transition from hexagonal Li_xCoO_2 to monoclinic Li_xCoO_2 . Then the two peaks merge together, indicated

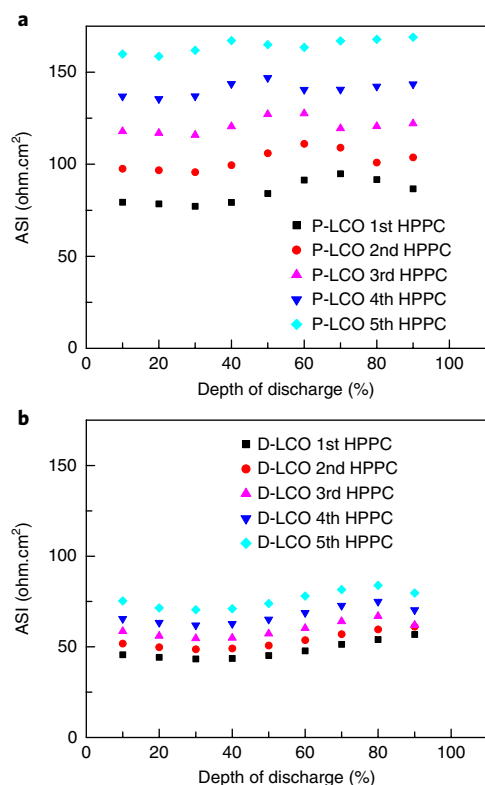


Fig. 5 | ASI data of P-LCO and D-LCO determined via HPPC. a, The ASI pattern of P-LCO in the first five cycles. **b,** The ASI pattern of D-LCO in the first five cycles.

by the disappearance of the light-red peaks at around ~ 4.2 V, indicating that further delithiation drives the phase transition from the monoclinic phase back to the hexagonal phase (order–disorder transition). A similar evolution is observed for other characteristic peaks such as (104), (107) and (018) (Supplementary Fig. 7), which is also consistent with our dQ/dV results on the P-LCO (Fig. 2e). Since the single-element La-doped LCO also experiences a series of phase transitions (Supplementary Fig. 8a), we can expect that it is the introduction of Al that suppresses the phase transition. Whereas the order–disorder transition lowers Li^+ diffusivity and the H1-3 phase transition leads to structural distortion³³, the single-phase transition process in D-LCO offers a significant advantage—the transformation path is much more facile and homogeneous than that of P-LCO with multiple phase transitions³⁴. Thus, the stresses and mechanical degradation of the material are significantly reduced during cycling.

Second, the unit cell volume change of D-LCO is smaller than that of P-LCO. As seen in Fig. 3b,c, the position of the (003) peak first shifts to a lower 2θ angle, then shifts back to the higher 2θ angle, indicating an initial steady increase of the c -lattice parameter with a subsequent decrease. The initial increase can be attributed to the increased electrostatic repulsion between adjacent CoO_2 layers due to the removal of Li^+ , while the subsequent decrease results from the CoO_2 layers shifting due to deep delithiation³⁵. The evolution of the position of the (003) peak for P-LCO shows the same trend but the amplitude of the shift is greater than that of D-LCO, as marked by arrows in Fig. 3b,c. With the changes in the (003) peaks, the unit cell volume also changes (Fig. 3f). For P-LCO, the unit cell volume increases from $96.50 \text{ \AA}^3$ to $98.90 \text{ \AA}^3$, after which it decreases to $95.31 \text{ \AA}^3$. The maximum volume change is 3.63% (Supplementary Fig. 7). On the other hand, the unit cell volume of D-LCO first increases from $96.54 \text{ \AA}^3$ to $98.48 \text{ \AA}^3$, and then decreases to $95.56 \text{ \AA}^3$ in the fully charged state. The maximum volume change for D-LCO is 2.97%,

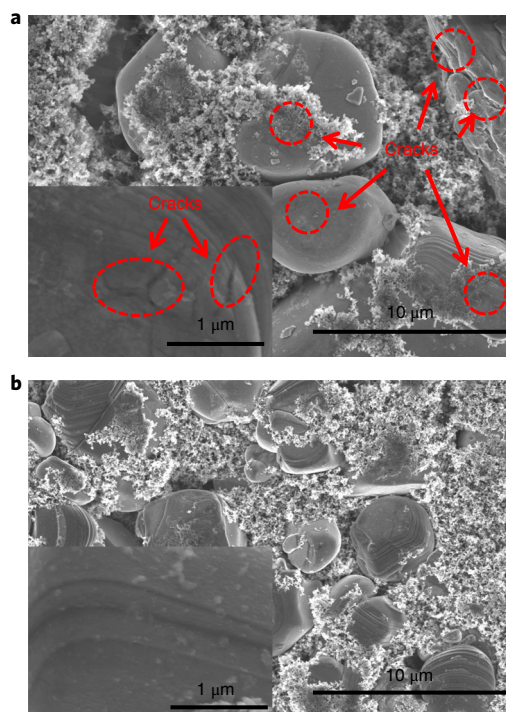


Fig. 6 | SEM characterization of P-LCO and D-LCO particles after the cycling test. a, The SEM images of P-LCO. The inset shows an image with high resolution. **b,** The SEM images of D-LCO.

which is smaller than that for P-LCO. As a result, the improved performance of the D-LCO can be explained by the absence of phase transitions (including the order–disorder transition) and the smaller volume change results in lower structural distortion and reduced mechanical degradation of the material.

Lithium ion diffusion coefficient determination

The lithium ion diffusion coefficients for P-LCO and D-LCO were determined via GITT (Supplementary Table 2). As seen in Fig. 4a,c,e, the lithium ion diffusion coefficient for the P-LCO was determined to be $6.5 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at the initial charging stage and $4.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at the final discharging stage. In comparison, the lithium ion diffusion coefficient of D-LCO is $1.2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at the initial charging stage and $4.7 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at the final discharging stage according to Fig. 4b,d,f. Note that the values for D-LCO are twice those for P-LCO at the initial charging stage and ten times greater at the final discharging stage. In addition, the GITT result shows that the lithium ion diffusion coefficient for single-element La-doped LCO is much higher than that of P-LCO, reaching almost the same value as that of D-LCO (Supplementary Fig. 8). These results clearly verify that the co-doping can provide a beneficial increase of Li^+ diffusivity for D-LCO, which is partially associated with the introduction of La. The activation barrier for the diffusion depends on the spacing of the lithium layer, and the increase of the layer distance along the c axis significantly increases the Li^+ diffusivity. As evidenced by the HRXRD and HAADF (Supplementary Fig. 2), the larger La ions in the structure effectively enlarge the c -axis spacing and facilitate the Li^+ diffusion. In addition, because the introduction of Al suppresses the order–disorder transition, the Al doping also partially contributes to the increase of the Li^+ diffusivity of D-LCO, since the phase transition suppression and structural stabilization are always coupled with the increase of Li^+ diffusivity³³. Further work is in progress to investigate the dependence of Li^+ diffusivity on the doping amounts of Al and La.

Structural stability during cycling

Long-term cyclability at a high cut-off voltage such as 4.5 V is always challenging for LiCoO_2 . As discussed above, our designed D-LCO with the absence of an order–disorder transition, less stress variation and increased Li^+ diffusivity makes it possible to achieve 96% capacity retention over 50 cycles when cycling at 4.5 V. A hybrid pulse power characterization (HPPC) was carried out to study the area specific impedance (ASI) change during cycling. As seen in Fig. 5a,b, the impedance of D-LCO increases more slowly than that of P-LCO during cycling, which can be attributed to the reduced stress and suppression of phase transitions (including the order–disorder transition). By contrast, the phase transition at high voltages associated with larger mechanical stress must undoubtedly cause mechanical failure of the P-LCO and thus fracture the solid–electrolyte interface (SEI). So, the broken and rebuilt SEI on P-LCO would tend to increase the ASI during cycling. The phase transition is believed to severely stress the structure. Therefore, mitigating the phase transition, especially the H1-3 transition, can significantly reduce the crystal volume and stress expansion when cycling to high voltage. Consequently, we can find various tiny cracks on the surface of the P-LCO particles but find none for the D-LCO particles after long-term cycling at 4.5 V (Fig. 6a,b). This distinctly different behaviour further confirms that the stress evolution of LiCoO_2 associated with phase transitions during cycling is effectively mitigated by the La and Al co-doping. In summary, the La and Al co-doped into the LiCoO_2 layers not only stabilize the crystal structure and enhance the d -spacing along the c axis, but also serve as positively charged centres, facilitating Li^+ diffusion and suppressing the phase transition.

Conclusions

At the present time, doping is considered to be an effective way to improve the electrochemical performance of LiCoO_2 . However, most approaches have only partially improved the structural stability of the material and have met with a limited degree of success. Though the upper cut-off voltage of LiCoO_2 can be increased from 4.2 V to 4.35 V, working at a higher voltage such as 4.5 V typically inflicts a heavy penalty on the cycling performance³⁶. In this work, we have demonstrated that the La-and-Al-doping strategy on a Co-containing precursor can improve the structure stability and Li^+ diffusivity of LiCoO_2 . Such a doped LiCoO_2 can achieve 96% capacity retention over 50 cycles at a cut-off voltage of 4.5 V. Importantly, commercial LiCoO_2 -based batteries never work properly at 4.5 V. Our approach, with the potential to be easily scaled up, may make these D-LCO batteries commercially feasible. Finally, considering that the other commercial cathode materials such as $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ($x+y+z=1$) possess a similar layered structure, our method could suggest an approach to create a wide variety of high-voltage and high-energy-density layered cathode materials for LIBs.

Methods

Material synthesis. In this synthesis, reagent-grade CoSO_4 , Na_2CO_3 and compounds of Al (a metal that has a radius similar to $\text{Co}^{3+}/\text{Co}^{4+}$) and La (a transition-metal that has a larger radius than $\text{Co}^{3+}/\text{Co}^{4+}$) were used as starting materials to prepare Al and La co-doped CoCO_3 powder via a controlled crystallization method at a specific pH value. Then, the mixture of the Al and La co-doped CoCO_3 and the compound of Al were calcined at 800 °C for 6 h to form Al and La co-doped Co_3O_4 precursor. The P-LCO and D-LCO powders were synthesized by heat treatment of a stoichiometric mixture of Li_2CO_3 and Co_3O_4 at 1,050 °C for 12 h. The chemical composition ratio of La:Al:Co was measured via ICP (ICP-MS, Agilent 5100 ICP-OES) and is estimated to be 1:2:1,000.

Material characterization. The particle size and size distribution of P-LCO and D-LCO powder were evaluated using a Cilas 1090 particle size analyser. The amount of Co dissolution was measured by ICP-MS (Agilent 5100 ICP-OES). The surface morphologies and compositions of P-LCO and D-LCO powder before and after the cycling test were characterized using a Hitachi S-4700 at 10 kV SEM. High-resolution TEM and HAADF images were conducted on a FEI Talos F200X scanning transmission electron microscope (STEM) with an accelerating voltage

of 200 kV at the Center for Nanoscale Materials, Argonne National Laboratory (ANL). The crystal structures of the samples were characterized via HRXRD at the beamline 11-BM ($\lambda=0.4593$ Å) of APS, ANL. The samples were loaded in 0.8 mm Kapton capillaries for the measurements.

Electrode preparation and electrochemical methods. The electrodes with P-LCO or D-LCO powder were prepared by spreading a slurry composed of 90% LCO, 5% poly(vinylidene difluoride) (PVDF) and 5% carbon black onto an alumina foil and then dried at 75 °C in a vacuum for 24 h. The coatings of the electrodes on Al foil were kept at $\sim 10\text{ mg cm}^{-2}$ with 30% porosity. 2032-type coin cells were made up of the as-prepared electrodes as the cathode, lithium metal or graphite as the anode, and the solution of 1.2 mol l^{-1} LiPF_6 in ethylene carbonate/ethyl methyl carbonate (3/7 by weight) as the electrolyte in all the cells.

Galvanostatic cycling tests of the home-made coin cells were conducted using a MACCOR battery cycler. The initial three formation cycles of the cells were carried out from 3.0 V to 4.5 V vs Li/Li^+ under a constant current of 0.1 C. After that, the cells were tested at rates of C/5, C/3, C/2, 1 C and 2 C from 3.0 V to 4.5 V. Finally, the cycling tests of the cells were carried out using a rate of C/3. The GITT measurements of the electrodes using P-LCO, D-LCO and single-element La-doped LCO powder were conducted using a MACCOR battery cycler at room temperature. The test procedure was as follows: a 10 min galvanostatic charge pulse (0.1 C) was applied to the cells, followed by 2 h of relaxation time without any current being passed through the cell. The cycle, consisting of a charge pulse and a relaxation period, was applied to the cell until its voltage increased to 4.5 V versus Li/Li^+ . Then a discharge pulse (0.1 C, 10 min) was applied to the cells, followed by a 2 h relaxation period without any current flowing through the cell. The cycle was applied to the cells until its voltage reached 3.0 V versus Li/Li^+ . Two charging–discharging cycles from 3.0 V to 4.5 V versus Li/Li^+ for GITT measurement were carried out on all electrodes. The HPPC was conducted during the cycling test, in which a 10 s 2 C discharge pulse and a 1.5 C regenerative charge pulse current were applied to the cells. There were 40 s rest periods between discharge and regenerative pulses. The pulse profiles were measured at every 10% depth of discharge. The ASI as a function of depth-of-discharge was established by calculating the voltage changes during pulses.

In situ HEXRD characterization. In situ HEXRD measurements were performed using beamline 11-ID-C at the APS, ANL. A monochromator with an Si (113) single crystal was used to provide an X-ray beam with an energy of 105.7 keV. A high-energy X-ray beam with a beam size of $0.2\text{ mm} \times 0.2\text{ mm}$ and a wavelength of 0.1173 Å was used to obtain two-dimensional diffraction patterns in the transmission geometry. XRD patterns were collected with a Perkin-Elmer large-area detector placed 1,800 mm away from the samples. In a typical in situ experiment, the home-made coin cells (LiCoO_2 on Al) were discharged–charged with a constant current of ~ 0.1 C. The diffraction data for each sample were collected every 360 s. The obtained 2D diffraction patterns were calibrated using a standard CeO_2 sample and converted to 1D patterns using FitD software. For our obtained XRD data, the general structure analysis software (GSAS) program was used to fit the observed diffraction patterns and obtain the lattice parameters.

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

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Author contributions

Y.L. and W.L. conceived the idea. Q.L., X.S. and D.L. designed and performed the experiments. X.S., Q.L. and Y.Q. performed the electrochemical characterization. Q.L., X.S., Y.R., F.G., R.K., X.X. and Y.Re. carried out the in situ and ex situ synchrotron measurements. Q.L., Y.R. and Y.Re. analysed and interpreted the synchrotron XRD data. D.L. and X.S. performed the SEM work. J.W., D.L. and Y.W. acquired the STEM and HAADF images. F.A. and J.B. contributed to discussions and interpretation of the electrochemical data. Q.L., D.L., X.S., Y.Re., W.L. and Y.L. wrote the paper. The project was supervised by Y.L., W.L. and Y.Re. All authors discussed the results and reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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