Surface Structural Transition Induced by Gradient Polyanion-Doping in Li-Rich Layered Oxides: Implications for Enhanced Electrochemical Performance

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Lithium-rich layered oxides (LLOs) exhibit great potential as high-capacity cathode materials for lithium-ion batteries, but usually suffer from capacity/voltage fade during electrochemical cycling. Herein, a gradient polyanion-doping strategy is developed to initiate surface structural transition to form a spinel-like surface nanolayer and a polyanion-doped layered core material in LLOs simultaneously. This strategy integrates the advantages of both bulk doping and surface modification as the oxygen close-packed structure of LLOs is stabilized by polyanion doping, and the LLO cathodes are protected from steady corrosion induced by electrolytes. A LLO material modified with 5 at% phosphate (5%P@LLO) shows a high reversible discharge capacity of ≈300 mAh g⁻¹ at 0.1 C, excellent cycling stability with a capacity retention of 95% after 100 cycles, and enhanced electrode kinetics. This gradient doping strategy can be further extended to other polyanion-doped LLO materials, such as borate and silicate polyanions.

1. Introduction

Currently, the rechargeable lithium ion battery (LIB) is one of the most important chemical energy storage technologies. Layered transition metal oxides, with the general formula LiTMO₂ (TM = Ni, Co, Ni/Mn/Co), are the most widely used positive electrode materials in commercialized LIBs due to their high operating voltage and high specific capacity of 140–180 mAh g⁻¹.[1–3] The cationic doping with other metallic cations (such as Mg,[21] Al,[22] Ti,[23] Sn,[24] Ru,[25] Y,[26] Zn,[27] etc.) and polyanion doping (such as borate and silicate polyanions, with the general formula xLi₂MnO₃·(1-x)LiTMO₂ (TM = Mn, Ni, Co, etc.), are promising candidates as they possess higher reversible capacity (>250 mAh g⁻¹), improved safety and much reduced cost.[4–9] Recent microscopic evidence reveals the intergrowth of rhombohedral LiTMO₂ (R-3m) and the monoclinic Li₂MnO₃-like layered structure (C2/m) at the atomic scale in the oxide grains.[10] The Li₂MnO₃ component serves as an electrochemically active phase for Li storage when cycled above 4.5 V versus Li/Li⁺.[8,11–14]

Nevertheless, these LLO materials undergo steady voltage/capacity decay when cycled above 4.5 V, resulting in a substantial decrease of the cathode energy density.[15–18] The origin of voltage/capacity decay upon cycling stems from cation migration between TM layers and Li layers and subsequent phase transformation.[19,20] The cationic doping with other metallic cations (such as Mg,[21] Al,[22] Ti,[23] Sn,[24] Ru,[25] Y,[26] Zn,[27] etc.) and polyanion doping based on nonmetal elements, such as BO₄⁻,[28] PO₄³⁻,[29] SiO₄⁴⁻,[30] etc., have been employed to improve the cyclic durability by weakening the TM–O covalency in the oxygen close-packed structure. In addition, surface coatings using metal oxides,[31–34] fluorides and phosphates,[35–37] LiNiPO₄ and Li₃VO₄,[38–40] have been applied to protect the surface structure from side reactions with the electrolyte under high voltage and to restrain the layered-to-spinel transformation which occurs preferentially on the crystal surface and leads to capacity fading of LLO materials. However, the ionic dopants and coating materials are mostly electrochemically inactive, so the improved cycling stability is achieved at the expense of reduced specific capacity/energy density of the cathode. Moreover, a conformal and continuous coating on the surface of oxide particles is rather difficult to obtain practically. Hence, advancing the structural and cycling stability in both the bulk material and the surface structure through a simple way is highly desired for potential applications of LLO materials.

Herein, we develop a novel LLO material with a nanoscaled spinel-like surface layer through gradient doping of polyanions.
such as PO$_4^{3-}$, as shown in Scheme 1. The concentration gradient driven diffusion of PO$_4^{3-}$ polyanions triggers surface structural transition to form a nanoscaled spinel-like surface layer and a polyanion-doped layered core material in a single process. The off-stoichiometric, spinel-like surface structure, characteristic of enrichment of Ni and P (depletion of Mn), can serve to protect the LLO material from steady corrosion induced by organic electrolytes and facilitate Li$^{+}$ and electron transport. In addition, a moderate amount of polyanions is doped into the LLO bulk material, which can effectively stabilize the oxygen close-packed structure and enhance the electrochemical stability of the LLO cathode materials. Similar surface structural changes are found in other polyanion-doped LLO materials, such as BO$_4^{5-}$, SiO$_4^{4-}$, etc. Detailed microscopic and spectroscopic analyses are performed to get a better understanding of the structural properties behind the enhanced battery performance.

2. Results and Discussion

The average structural information for the materials with and without PO$_4^{3-}$ doping was characterized using powder X-ray diffraction (XRD) (Figure 1). All the XRD patterns, normalized on the basis of the intensity of (003) reflection, can be indexed to a layered α-NaFeO$_2$-type structure (space group of R$m$3$m$) and a Li$_2$MnO$_3$-like structure (space group of C2/m). The enlarged graphs of the (003) and (104) reflections (Figure 1b) suggest that the PO$_4^{3-}$ doping leads to a substantial increase in (003) and (104) d-spacings relative to pristine material. To obtain quantitative crystallographic information, Rietveld refinement of the XRD data was conducted and the results are shown in Figure S1 and Tables S1 and S2 of the Supporting Information. The calculated lattice parameters are tabulated in Table 1. It is apparent, in the PO$_4^{3-}$-doped materials, that both lattice parameters $a$ and $c$ increase steadily as the doping level is raised.$^{[30]}$ As shown in Figure 1c, additional XRD peaks in the 2-theta range of 20–22° are considered as superlattice reflections of the Li$_2$MnO$_3$-like phase. As the PO$_4^{3-}$ doping level reaches 5 at% or higher, sharper and stronger (020) peaks are observed when compared with the pristine material (Figure 1c). This phenomenon indicates that the magnitude of Li and TM cation ordering within the TM layers becomes prominent as more PO$_4^{3-}$ polyanions are incorporated. This can be ascribed to the PO$_4^{3-}$ polyanions, with higher electronegativity, that alter the

![Scheme 1. Schematic illustration of surface structural transition induced by gradient polyanion-doping in LLO materials.](image)

![Figure 1. Structural information for as-prepared LLOs with and without PO$_4^{3-}$ doping. a) Powder XRD patterns of pristine and PO$_4^{3-}$-doped samples. b) Enlarged regions for the (003) and (104) reflections taken from the corresponding powder XRD patterns in (a). c) Enlarged region of XRD patterns showing details of the superlattice reflection peaks.](image)
local electronic structure of the layered oxides. Moreover, at a concentration of 7 at% $\text{PO}_4^{3-}$, an impurity phase of $\text{Li}_3\text{PO}_4$ appears (Figure 1a), which is consistent with observations in a previous report.

The electrochemical behavior of the materials with and without $\text{PO}_4^{3-}$ doping was evaluated using galvanostatic charge-discharge testing. Figure 2a compares the initial charge-discharge curves of the pristine and $\text{PO}_4^{3-}$-doped LLO materials at a current density of 0.1 C (25 mA g$^{-1}$) from 2.0 to 4.8 V at room temperature. With $\text{PO}_4^{3-}$ content increasing from 1 to 5 at%, the charge plateaus below 4.4 V shift to lower voltages, whereas the discharge plateaus shift to higher voltages (arrows 1 and 3 in Figure 2a). The pristine material delivers an initial charge capacity of 382 mAh g$^{-1}$ and the charge capacities gradually decrease to 328 mAh g$^{-1}$ for the 7% P@LLO material (arrow 2 in Figure 2a), while the pristine material delivers an initial discharge capacity of 276 mAh g$^{-1}$. Hence, the initial Coulombic efficiency of the pristine material is only 72%, whereas the 5% P@LLO material exhibits a discharge capacity of $\approx$300 mAh g$^{-1}$ and a Coulombic efficiency of 86% for the first cycle; both values are much higher than those for pristine (Table S3, Supporting Information). A further increase $\text{PO}_4^{3-}$ polyanion concentration, however, leads to lower specific

![Graph](image_url)

**Figure 2.** Electrochemical performance of as-prepared LLOs with and without $\text{PO}_4^{3-}$ doping tested between 2.0 and 4.8 V (vs $\text{Li}^+$/Li). a) Initial charge-discharge profiles tested at a rate of 0.1 C. b) Cycling performance of as-prepared LLOs with and without $\text{PO}_4^{3-}$ doping. c,d) Galvanic discharge profiles (3rd, 25th, 50th, and 100th cycles) of the pristine and 5% P@LLO materials at a rate of 1 C. e,f) Charge-discharge profiles of the pristine and 5% P@LLO materials at various C rates.

<table>
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<tr>
<th>Materials</th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
<th>$c/a$ ratio</th>
<th>Refinement parameters</th>
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<td>14.13188</td>
<td>4.9622</td>
<td>Rwp: 5.92</td>
</tr>
</tbody>
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**Table 1.** Refined crystallographic parameters for as-prepared LLOs with and without $\text{PO}_4^{3-}$ doping.
capacity, probably due to the formation of the Li₃PO₄ impurity phase. The results indicate that incorporation of a reasonably high amount of PO₄³⁻ polyanions may facilitate Li⁺ diffusion and markedly reduce the irreversible removal of Li₂O from the Li₂MnO₃ component during the charge process.

The cycling performance of the materials with and without PO₄³⁻ doping is shown in Figure 2b. The specific capacity of the pristine material degrades substantially when cycled at 1 C (Figure 2b) and the corresponding discharge profiles experience noticeable voltage decay with increased cycling (Figure 2c). In contrast, the PO₄³⁻-doped materials exhibit excellent cycling performance after 100 cycles at 1 C (Figure 2b) and voltage decay is effectively suppressed (Figure 2d). In particular, the 5% P@LLO material demonstrates excellent cycling stability with a capacity retention rate of 95% after 100 cycles at 1 C and maintains a stable capacity of 270 mAh g⁻¹ as the rate is changed back to 0.1 C rate (Figure 2b and Table S4, Supporting Information). Furthermore, the rate performance of PO₄³⁻-doped materials is notably enhanced in contrast with the pristine material (Figure S2, Supporting Information). The 5% P@LLO material shows high rate performance with 252 mAh g⁻¹ at 0.2 C, 194 mAh g⁻¹ at 1 C, 165 mA h g⁻¹ at 2 C, 135 mA h g⁻¹ at 4 C, and 121 mA h g⁻¹ at 6 C. The pristine material, on the other hand, delivers a discharge capacity of 197 mAh g⁻¹ at 0.2 C, 83 mAh g⁻¹ at 1 C, 57 mA h g⁻¹ at 2 C, 31 mA h g⁻¹ at 4 C, and 17 mA h g⁻¹ at 6 C (Figure 2e,f).

To elucidate the origin of the comprehensive improvements in the electrode kinetics, the first cycle irreversible capacity and long-term cycling stability observed in the PO₄³⁻-doped materials, structural changes to both the bulk and electrode surface need to be characterized. The XRD analysis above does not provide direct evidence of local structure and coordinate chemical information, so the surface structures were examined using electron microscopies (scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and aberration-corrected scanning transmission electron microscopy (STEM)) and X-ray photoelectron spectroscopy (XPS). The SEM images of the materials with and without PO₄³⁻-doping, as shown in Figure 3a,c and Figure S3 of the Supporting Information, reveal that all materials consist of well-crystallized particles with very similar dimensions and morphologies. Figure 3b shows a typical HRTEM image and FFT (fast Fourier transformed) diffraction patterns taken from the core (region 1) and the surface part (region 2) of pristine material. Well-defined lattice fringes with an average spacing of 0.475 nm and similar FFT patterns along the [010] hexagonal zone axis confirm that the whole pristine particle shows a high degree of crystallinity and well faceted surfaces. For the PO₄³⁻-doped materials, in addition to a well-defined layered structure in the core part, there exists a surface layer (~2 nm thick) along certain crystallographic facets (Figure 3d). For the FFT patterns along [010] hexagonal zone axis of the core parts, another set of diffuse streak patterns is evident in the FFT images taken from the surface regions in the doped materials, shown as red circles in the FFT pattern (Figure 3d). These diffuse streak patterns arise from the surface layer and are indexed to a spinel-like phase (Fd₃m) along the [01-1] zone axis.

To analyze the surface structure at the atomic scale, high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were obtained. Figure 4a
shows a representative atomic resolution STEM image of a pristine particle along the [010] zone axis projection, where alternative stacking of Li slabs and TM slabs along the [003] direction is clearly observed. As the PO$_4^{3-}$-doped particles are viewed along the same [010] zone axis projection (Figure 4b), the presence of a spinel-like structure on selected surface facets of the particles is confirmed. The orientation relationship between the layered bulk and the spinel surface is described as: (003)$_L$/[1−11]$_S$ and [010]$_L$/[01−1]$_S$. Interestingly, Figure 4b shows that preferential exposure of {111} crystallographic planes exists on these surface layers, which are recognized as stable facets for the spinel structure.[41] It is worth noting that TM atoms (especially Ni) substitute for some of the lithium atom columns in the spinel lattice and the extra HAADF imaging contrast are due to the presence of antisite defects (line profile of Li slabs in Figure 4b). Atomic resolution X-ray energy-dispersive spectroscopy (XEDS) line scans across the surface confirm that there is segregation of Ni at the expense of Mn (Figure S4, Supporting Information). The structural and spectroscopic analyses confirm the idea that gradient polyanion-doping leads to a surface structural transition in the PO$_4^{3-}$-doped LLO materials. More fascinating, similar surface structural changes were also revealed in BO$_4^{5-}$- and SiO$_4^{4-}$-doped LLO materials (Figure 5).

XPS surface analysis and depth profiling were employed to provide further evidence for the presence of the off-stoichiometric, spinel-like surface layer induced by gradient polyanion-doping. Figure 6a–c compares typical XPS spectra for Ni 2p, Co 2p, and Mn 2p for the pristine and PO$_4^{3-}$-doped materials before etching. Incorporation of phosphate leads to slight shifts to higher binding energies for the Mn/Co cations, suggesting that the average valence of Mn/Co cations increases in order to balance the negatively charged PO$_4^{3-}$.[30] For the PO$_4^{3-}$-doped material, the P 2p peak is detected at 133.7 eV (Figure S5, Supporting Information), corresponding to the presence of phosphate polyanions.[42] To confirm that gradient polyanion-doping occurs in the material surface, XPS depth profiles were collected (Figure 6d–f).
Depletion of Mn is associated with the enrichment of Ni and P and is evidence of doping in the surface region (as marked by the dotted box) for the PO$_4^{3-}$-doped samples (Figure 6 d–f and Table S5, Supporting Information). The results suggest that $^{31}\text{P}$ cations tend to occupy the tetrahedral interstitial sites formed by three planes of MO$_6$ octahedra and one plane of a LiO$_6$ octahedron in the layered bulk material because of their small ionic radii of 0.34 Å (Figure S6a, Supporting Information). PO$_4^{3-}$-doping can effectively restrain the migration of TM cations and alleviate the first cycle irreversible capacity and capacity/voltage decay during electrochemical cycling. With the assistance of PO$_4^{3-}$ polyanions, a significant amount of Ni cations occupy the octahedral sites in the Li layer of the layered structure preferentially and induce the formation of nanoscaled spinel-like surface structure (Figure S6b,c, Supporting Information). Since this surface layer is associated with Mn depletion (Figure 6), attack by hydrofluoric acid (HF) and Mn dissolution can be effectively suppressed,[44,45] leading to more stable interfaces in contact with the electrolyte. Moreover, the nanoscale electrochemically active spinel-like surface layer, characterized by high electronic and Li$^+$ conductivity, facilitates Li$^+$ and electron transport on the electrode surface, which accounts for the reduced overall polarization and improved rate capability in the PO$_4^{3-}$-doped LLO materials.

To confirm the improvement of gradient PO$_4^{3-}$ polyanion-doping, XRD and HAADF-STEM analyses were carried out on the cycled materials with and without PO$_4^{3-}$ polyanion-doping (Figure 7). The XRD patterns show that the PO$_4^{3-}$-doped material possesses improved structural integrity compared with the pristine material during electrochemical cycling (Figure 7a). For the pristine oxide after 110 cycles (Figure 7b), the Z-contrast decreases significantly and local spinel/amorphous domains are formed in coexistence with the layered structure, indicating inferior structural stability. By contrast, the layered structure in the PO$_4^{3-}$-doped material is retained after the same amount of electrochemical cycling. Cation mixing or layered-spinel phase transformation occurs primarily on the surface regions (Figure 7c).

3. Conclusion

In summary, a lithium-rich layered cathode with a nanoscale spinel-like surface layer was prepared through gradient doping of PO$_4^{3-}$ polyanions. The spinel-like surface nanolayer, characterized by Mn depletion, protects the cathode material from attack by hydrofluoric acid (HF) and Mn dissolution, and facilitates Li$^+$ and electron transport. In addition, a moderate amount of polyanions was doped into the bulk material, effectively stabilizing the oxygen close-packed structure and enhancing the electrochemical stability of the LLO cathode materials. Similar surface structural changes were found in other polyanion-doped LLO materials such as BO$_4^{5-}$, SiO$_4^{4-}$, etc. We anticipate that this gradient polyanion-doping strategy should shed light on the design and development of a wide range of other layered cathode materials.

4. Experimental Section

Materials Synthesis: Li$_{1.17}$Mn$_{0.5}$Ni$_{0.17}$Co$_{0.16}$(PO$_4$)$_x$O$_{2-4x}$ ($X = 0, 0.01, 0.03, 0.05, 0.07$) was prepared using a coprecipitation method, as described previously.[46] A 1 M mixed solution of MnSO$_4$·H$_2$O, NiSO$_4$·6H$_2$O, and CoSO$_4$·7H$_2$O (Mn:Ni:Co molar ratio of 3:1:1) and a 2 M NaOH aqueous solution with an appropriate amount of NH$_3$·H$_2$O were separately pumped into a continuously stirred reactor under N$_2$ atmosphere.
at 60 °C. During the coprecipitation process, the pH value was kept at 11. The coprecipitated product was filtered, washed with distilled water, and dried in a vacuum oven at 110 °C for 12 h. The obtained precursor was thoroughly mixed with a stoichiometric amount of NH₄H₂PO₄ and LiOH·H₂O (8% rich), calcined at 500 °C for 5 h and then heated to 850 °C for 15 h in air.

Materials Characterization: The chemical composition of the as-prepared Li₁.₁₇Mn₀.₅Ni₀.₁₇Co₀.₁₆(PO₄)ₓO₂₋₄ₓ materials was determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The crystallographic structure of the Li₁.₁₇Mn₀.₅Ni₀.₁₇Co₀.₁₆(PO₄)ₓO₂₋₄ₓ materials were characterized by powder XRD (Rigaku D/Max-2500 Diffractometer with Cu Ka radiation, λ = 1.54056 Å) and selected area electron diffraction (SAED) with a JEOL JEM-2100F field-emission transmission electron microscope (FE-TEM). The morphology was evaluated using a Nova Nano SEM230 field emission scanning electron microscope (FE-SEM). A FEI Titan3 G2 60–300 TEM equipped with a double aberration-corrector for both the probe-forming and imaging lenses was used to perform ABF/HAADF imaging. Chemical state and composition analysis were carried out by XPS using an ESCALAB 250Xi X-ray photoelectron spectrometer. Etching with Ar⁺ ions was used to obtain depth profiles of Mn, Ni, Co, and P. The etching rate was estimated as 5.4 nm min⁻¹. All XPS spectra were calibrated using the C 1s line at 284.8 eV. Curve fitting and background subtraction were accomplished using Thermo Advantage Version 5.52 software.

Electrochemical Characterization: The synthesized materials were mixed with acetylene black and polyvinylidene fluoride in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone to form a slurry. Subsequently, the slurry was coated onto Al foil and then dried at 110 °C for 12 h in a vacuum oven to obtain the as-prepared cathodes. The electrochemical testing was conducted with CR2025 coin-type half-cells assembled in an Ar-filled glove box. The half-cells consisted of an as-prepared cathode, a Li metal anode, a Celgard 2500 separator and 1 M LiPF₆ in EC-DMC (weight ratio 1:1) electrolyte solution. The cells were cycled on a battery testing system (LANHE CT2001A, Wuhan LAND Electronics Co., P. R. China) between 2.0 and 4.8 V.

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

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