A Li-rich layered-spinel cathode material for high capacity and high rate lithium-ion batteries fabricated via a gas-solid reaction

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ABSTRACT Lithium-rich layered oxide (LLO) cathode materials have drawn extensive attention due to their ultrahigh specific capacity and energy density. However, their commercialization is still restricted by their low initial coulombic efficiency, slow intrinsic kinetics and structural instability. Herein, a facile surface treatment strategy *via* gaseous phosphine was designed to improve the rate performance and capacity stability of LLOs. During the solid-gas reaction, phosphine reacted with active oxygen at the surface of LLOs due to its reductivity, forming oxygen vacancies and spinel phase at the surface region. As a result, Li ion conductivity and structural stability were greatly enhanced. The phosphine-treated LLOs (LLO@P) showed a layered-spinel hybrid structure and delivered an outstanding rate performance of 156.7 mA h g⁻¹ at 10 C and a high capacity retention of 74% after 300 cycles at 5 C.

Keywords: cathode materials, Li-rich, layered-spinel structure, high rate performance, phosphine

INTRODUCTION

Lithium-ion batteries (LIBs) are considered to be one of the most promising energy storage devices for electric vehicles due to their high energy density and long life span [1,2]. However, further improvement in energy density is necessary for their applications in electric vehicles and storage systems [3–5]. The practical capacity of cathode materials is the key factor influencing the energy density of LIBs [6]. Li-rich layered oxide (LLO) cathode materials have been brought into focus due to their ultrahigh specific capacity and energy density (Fig. S1) [6–9].

However, there are still some challenges which restrict the industrialization and commercial applications of LLOs [10,11], including poor kinetics, inferior structural stability and low initial coulombic efficiency [12–14]. LLOs consist of rhombohedral LiMO₂ (M = Mn, Ni or Co) phase and monoclinic Li₂MnO₃ phase [15,16]. The special oxygen anion redox process provides LLOs with a high specific capacity of over 300 mA h g⁻¹ [1]. However, oxygen is easily and irreversibly extracted from the crystal structure during the active processes of Li₂MnO₃, which simultaneously destroys the crystal structure of LLOs and leads to large irreversible specific capacity as well as low initial coulombic efficiency [17–19]. Furthermore, the released oxygen can react with electrolyte and generate various byproducts, which accelerates the accumulation of inert components and increases the internal impedance [1,20,21]. Besides, LLOs show poor kinetics due to the introduction of Li₂MnO₃ component with inferior ion and electron conductivities [13]. As a result, the rate performance and cycle stability of LLOs need to be further improved for their commercialization.

Since oxygen release is closely related to the surface structure of LLOs, surface engineering strategies have been widely used to enhance the electrochemical performance of LLOs [3]. It has been reported that NH₃ and CO₂ can react with LLOs to reduce the oxygen partial pressure and inhibit oxygen release [20,22]. Moreover, the increase of oxygen vacancies can induce the formation of spinel structure at the surface region to enhance the Li ion conductivity. Our group also developed a facile gaseous sulfur treatment strategy to modify the surface

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structure of LLOs and the modified LLOs show excellent rate and cycle performances [1].

Inspired by the above considerations, a spinel-coexisting structure was designed based on the facile gas-solid reaction between phosphine and LLOs. Solid sodium hypophosphite was used as the phosphine source, which was low-cost and readily available. Phosphine reacted with oxygen at the surface of LLOs, which induced the increase of oxygen vacancies and the formation of spinel phase. As a result, the oxygen release was inhibited and Li ion conductivity was enhanced effectively after PH_3 treatment. The modified LLOs (LLO@P) delivered an outstanding rate performance of $156.7 \text{ mA h g}^{-1}$ at a current density of 10 C ($1 \text{ C} = 200 \text{ mA g}^{-1}$), much higher than that of pristine LLOs ($128.0 \text{ mA h g}^{-1}$). Moreover, LLO@P also exhibited an excellent cycle performance with a capacity retention of 74.0% after 300 cycles at 5 C , whereas the capacity retention of LLOs was only 54.4% under the same condition. The enhanced electrochemical performance can be attributed to the modified surface structure by phosphine.

EXPERIMENTAL SECTION

Synthesis of pristine LLOs

In a typical process [1], LLOs ($\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$, which could also be written as $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333}\text{O}_2$) were synthesized by oxalic acid coprecipitation, followed by hydrothermal as well as calcination processes. Stoichiometric amounts of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and an excess amount of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ (10% molar ratio) were all dissolved in ethanol. The resulting solution (named solution A) was stirred at room temperature for 0.5 h. Solution B was prepared by dropwise adding oxalic acid to solution A. Then, solution B was transferred to a Teflon-lined stainless steel autoclave and heated at 180°C for 12 h. After that, the precipitate was collected by vacuum filtration and dried at 120°C for 3 h. Then, it was pressed into plates and first annealed in air at 450°C for 5 h and then sintered in air at 850°C for 15 h. Finally, the LLOs were obtained after gridding carefully.

Synthesis of LLO@P

First, LLOs and sodium hypophosphite were separately placed in a tailor-made glass reactor, as shown in Fig. S2. Then the reactor was sealed by an alcohol blast burner with the assistance of a vacuum pump to avoid interference of air and loss of phosphine. Finally, the glass reactor was heated for the desired time at a specific

temperature to conduct the gas-solid reaction and LLO@P were obtained without further treatment.

Material characterizations

Powder X-ray diffraction (XRD) patterns of the cathode materials were obtained with a Rigaku D/max-2500 diffractometer using $\text{Cu K}\alpha$ radiation. Rietveld refinements were executed by General Structure Analysis System (GSAS) software package. The microstructure and element mapping of the material were analyzed by using a transmission electron microscope (JEM-2800). The electronic states of the sample were analyzed by X-ray photoelectron spectroscopy (XPS) on Escalab 250Xi spectrometer (Thermo Scientific). Raman spectra were collected using a Renishaw InVia Raman spectrometer with a wavelength of 514.5 nm.

Electrochemical measurements

CR2430 coin-type cells were assembled for electrochemical measurement and characterization. Specifically, the as-prepared cathode materials, Super P carbon black and polyvinylidene fluoride (PVDF) in 8:1:1 mass ratio were mixed in *N*-methyl-2-pyrrolidone to form a homogeneous slurry, which was then coated onto aluminum foil. The electrode sheet was dried at 60°C for 3 h and 150°C for 1 h under vacuum. Then, it was pressed and cut into discs with a radius of 6 mm. The mass loading of active material was about 2.5 mg cm^{-2} . Then, CR 2430 coin-type cells were assembled in an Ar-filled glove box. The cells consisted of the as-prepared cathodes, Li metal anodes, Celgard 2325 separators and electrolyte ($1 \text{ mol L}^{-1} \text{ LiPF}_6$ in a 1:1 vol% ethylene carbonate (EC)-dimethyl carbonate (DMC) mixture). Galvanostatic charge/discharge tests were conducted at specific rates on a battery test system (LAND CT2001A model, Wuhan LAND Electronics, Ltd.). Cycle voltammetry measurements were performed with a scanning rate of 0.05 mV s^{-1} on Autolab system (Metrohm). Electrochemical impedance spectroscopy (EIS) was conducted on the same electrochemical workstation and the test frequency ranged from 100 kHz to 0.01 Hz.

RESULTS AND DISCUSSION

After optimizing the conditions (reaction time, reaction temperature and PH_3 content, the details are given in the Supplementary Information) for the gas-solid reaction, it was found that LLO@P obtained with a PH_3 content of 0.3 mmol at 250°C for 10 h exhibited the best electrochemical performance (Figs S3 and S4). As shown in Fig. 1a, LLO@P delivered a high reversible capacity of

Figure 1 (a) Initial charge-discharge curves at 0.05 C, (b) high rate performance of LLOs and LLO@P. Cycling performance at (c) 0.5 C and (d) 5 C, (e) EIS plots, (f) lithium ion diffusion coefficient of LLOs and LLO@P before cycling and after 60 cycles at 0.5 C, (g) CV profiles of LLOs and LLO@P.

267.4 mA h g⁻¹ and a superior initial coulombic efficiency of 89.1% at 0.05 C, higher than that of pristine LLOs (260.8 mA h g⁻¹, 84.5%). Moreover, LLO@P also exhibited excellent rate performance. At 0.1, 0.2, 0.5, 1, 2, 5 and 10 C, the discharge capacities of LLO@P were 257.8, 246.5, 226.9, 216.0, 199.3, 175.6 and 156.7 mA h g⁻¹ (Fig. 1b), respectively. In contrast, pristine LLOs showed lower discharge capacities of 253.1, 246.0, 226.5, 206.1, 180.9, 151.9 and 128.0 mA h g⁻¹ at the same rates. When the test current density reduced back to 0.5 C, LLO@P recovered its capacity, which indicated that the structure of LLO@P was stable after treatment. After 100 cycles at 0.5 C, LLO@P retained a remarkable discharge capacity of 199.2 mA h g⁻¹ with a capacity retention of 90.0%, whereas LLOs only retained 188.9 mA h g⁻¹ with a capacity retention of 84.4% under the same conditions (Fig. 1c). Even at higher current density (5 C), LLO@P retained a discharge capacity of 131.1 mA h g⁻¹ after 300 cycles with a capacity retention of 74.0% (Fig. 1d), which was much higher than those of pristine LLOs (96.1 mA h g⁻¹ and 54.4%).

Fig. 1e and f show the EIS results of LLO@P and LLOs before cycling and after 60 cycles. Both curves in Fig. 1e consist of a semicircle and a sloped straight line. The semicircle in intermediate frequency region is related to the charge transfer process and its diameter is proportional to the charge transfer resistance (R_{ct}). The other part in the low frequency region represents the solid-state diffusion of Li ions (Warburg impedance, Z_w) in the ac-

tive materials [23,24]. As shown in Table S1, R_{ct} values of LLO@P were much smaller than those of LLOs before and after cycling. Specifically, LLOs exhibited an R_{ct} value of 80.53 Ω before cycling and 150.87 Ω after 60 cycles, while the corresponding values for LLO@P were only 47.80 and 102.40 Ω (Fig. S5). The Li ion diffusion coefficient (D_{Li}) was calculated based on the previous work [24]. It was found that D_{Li} increased from 2.68×10^{-16} to 5.8×10^{-16} cm² s⁻¹ after PH₃ treatment. Moreover, the D_{Li} of LLO@P remained almost unchanged before cycling and after 60 cycles, whereas that of LLOs decreased from 2.68×10^{-16} to 1.64×10^{-16} cm² s⁻¹ under the same conditions (Fig. 1f). These results illustrated higher Li ion conductivity and structural stability for LLO@P, accounting for its excellent rate performance (Fig. 1b).

Cyclic voltammetry (CV) measurements of LLO@P and LLOs are shown in Fig. 1g. The CV curves of both LLO@P and LLOs showed two oxidation peaks at around 4.0 and 4.5 V, which were related to the transition metal redox and Li₂MnO₃ activation processes, respectively. An extra redox peak appeared at ~2.86 V in the CV curve of LLO@P, indicating the formation of spinel phase [20,25].

To further explore the effect of PH₃ treatment, XRD, TEM, Raman and XPS analyses were conducted for both LLO@P and LLOs. The main crystal structure of LLO@P remained the same as that of pristine LLOs, which exhibited the same patterns as the previous work [26] (Fig. 2a, b and Fig. S6). The refinement results of LLO@P

Figure 2 (a) XRD patterns of LLOs and LLO@P, (b) the refinement results of LLO@P. (c) TEM image of LLO@P and the EDS mapping of (d) Co, (e) Mn, (f) Ni, (g) O and (h) P.

and the control sample LLOs exhibited similar unit cell parameters but a slight reduction of oxygen occupation (from 0.981 to 0.964) (Table S2), consistent with the fact that the gas-solid reaction occurred mainly at the surface of the materials rather than the bulk.

TEM-EDX analysis was performed to observe the effect of PH_3 treatment on the morphologies of cathode materials (Fig. 2c–h and Fig. S7b–f). It can be seen that Co, Mn, Ni and O elements were uniformly distributed in the LLOs and LLO@P cathode materials. Phosphorus was distributed homogeneously at the surface of the LLO@P cathode material, indicating the successful gas-solid reaction between PH_3 and LLOs.

Fig. 3 and Fig. S7a present the high resolution TEM (HRTEM) images of LLO@P and LLOs, respectively. A set of lattice fringes with an interplanar spacing of about 0.4807 nm was observed in the TEM images of both LLO@P and LLOs, corresponding to the (003) layer of $R\bar{3}m$ in layered materials. It demonstrated that the bulk structure remained unchanged after PH_3 treatment,

which was in accordance with the results of XRD. Apart from the above (003) planes, there was another interplanar spacing of 0.2020 nm at the surface of LLO@P, which can be indexed to the (400) planes of spinel phase, indicating the formation of spinel layer [27–29].

Raman spectroscopy was carried out to further understand the structural difference between LLOs and LLO@P. As shown in Fig. 3c, the spectrum of LLOs consisted of two distinct peaks at around 475 and 593 cm^{-1} , belonging to E_g bending vibration and A_{1g} stretching vibration in layered structure, respectively [3,30,31]. There was an extra peak ($\sim 629 \text{ cm}^{-1}$) in the Raman spectrum of LLO@P (Fig. 3d), related to Mn–O vibration in the spinel structure [6,32]. This also demonstrated that a new spinel layer emerged at the surface region of LLO@P after PH_3 treatment, which was consistent with the results of CV and HRTEM.

To explore the origin of spinel phase, XPS was carried out for LLOs and LLO@P. As seen from the XPS spectra of Ni 2p and Co 2p of the cathode materials (Fig. 4a and

Figure 3 (a, b) The HR-TEM images of LLO@P. Raman spectra of (c) LLOs and (d) LLO@P.

Figure 4 XPS spectra of (a) Ni, (b) Co, (c) Mn, and (d) P for LLOs and LLO@P. XPS spectra of O for (e) LLOs and (f) LLO@P.

b), there were two pronounced peaks at 854.85 and 780.17 eV, respectively, which coincided with those of Ni^{2+} and Co^{3+} . The Mn 2p peak of pristine LLOs was located at 642.57 eV, which was assigned to Mn^{4+} [33] (Fig. 4c). After PH_3 treatment, the Mn 2p peaks shifted to a lower binding energy region, meaning the reduction of Mn. A pronounced peak emerged at around 133.0 eV in the P 2p spectrum of LLO@P, indicating the gas-solid reaction between PH_3 and LLOs. The phosphorus content in optimized LLO@P was estimated to be ~0.75 at.% based on the inductively coupled plasma optical emission spectrometry (ICP-OES) results. O 1s spectra of LLOs and LLO@P are shown in Fig. 4e and f. There were two pronounced peaks at 529.7 and 531.5 eV in Fig. 4e and f, corresponding to the lattice oxygen atoms (O–M–O) and oxygen vacancies, respectively. In the O 1s spectrum of LLO@P (Fig. 4f), the peak located at 531.3 eV increased greatly, which indicated the increase of oxygen vacancies after PH_3 treatment. This agreed well with the refinement results of XRD.

Combining the above results, the PH_3 treatment process could be concluded in Fig. 5. First, sodium hypophosphite decomposed and released PH_3 at specific temperature. Then, gaseous PH_3 showed high reductivity

and reacted with LLOs. This gas-solid reaction consumed reactive oxygen atoms at the surface region of LLOs, resulting in the formation of oxygen vacancies and the slight reduction of Mn. As a result, a new spinel layer emerged at the surface region of LLOs, which significantly enhanced the rate performance of LLOs. Besides, the increase of oxygen vacancies also inhibited the oxygen release during cycling, suppressing the related side reactions and promoting the cycle performance of LLOs. Thus, the obtained LLO@P showed excellent electrochemical performance (Fig. 1).

CONCLUSIONS

In summary, a layered-spinel hybrid structure was prepared by a facile gas-solid PH_3 treatment. It was found that PH_3 reacted with the active oxygen atoms and lowered the oxygen partial pressure at the surface of LLOs. Thus, the oxygen release during cycling was effectively inhibited followed by reduced side reactions. Moreover, after PH_3 treatment, the generated oxygen vacancies induced the phase transformation from layered structure to spinel structure at surface region, which enhanced the Li ion conductivity of LLO@P. As a result, the obtained LLO@P showed excellent cycle and rate performances

Figure 5 Schematic diagram of the PH_3 treatment and structural components of the LLO@P.

simultaneously. At a high current density of 10 C, LLO@P showed a discharge specific capacity of $156.7 \text{ mA h g}^{-1}$. After 300 cycles at 5 C, the capacity retention was as high as 74%, much higher than that of pristine LLOs (54.4%). Thus, the proposed method would be of importance to develop the cathode materials with high rate and long cycle performance.

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Author contributions Chen Y conceived and designed the research; Xu L fabricated the cathode materials and assembled the cells; Sun Z conducted partial characterization and analyses; Zhu Y, Han Y, Wu M, Ma Y and Huang Y were involved in some experiments; Xu L and Zhang H wrote the paper, with support from Chen Y; Chen Y and Zhang H coordinated the study. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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通过气固反应制备高容量和高倍率性能的层状-尖晶石复合正极材料

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摘要 富锂材料具有较高的比容量和能量密度, 因而受到了广泛关注. 但是富锂材料仍然面临着库伦效率低、动力学性能差以及结构稳定性差等缺点, 限制了其进一步的商业化应用. 本文中通过气相的磷化氢对富锂材料进行热处理, 来提高其倍率性能和循环稳定性. 在热处理过程中, 具有较高还原活性的磷化氢会与富锂材料的表面活性氧原子进行反应, 进而在材料表面生成氧空穴和尖晶石相结构. 改性后, 富锂材料的锂离子电导率和结构稳定性显著提升, 当以 10 C 的大电流进行充放电时, 放电比容量可达 156.7 mA h g⁻¹, 在 5 C 下循环 300 圈后容量保持率仍然可达 74%.