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Abstract

Lithium-rich layered cathodes are known famously for its superior capacity over traditional layered oxides but trapped for lower initial coulombic efficiency, poorer rate capability and worse cyclic stability in spite of diverse attempts. Herein, a new K-stabilized Li-rich layered cathode synthesized through a simple oxalate co-precipitation is reported for its super electrochemical performances. Compared with pristine Li-rich layered cathode, K-stabilized one reaches a higher initial coulombic efficiency of 87% from 76% and outruns for 94% of capacity retention and 244 mAh g⁻¹ of discharge capacity at 0.5C after 100 cycles. Moreover, 133 mAh g⁻¹ of discharge capacity can be delivered even charged at 10C showing a highly-improved rate capability. X-ray diffraction and electrochemical impedance spectroscopy tests show that enlarged Li slab layer caused by K⁺ accommodation can provide facile Li⁺ diffusion paths and facilitate Li⁺ migration from the crystal lattice. As a consequence, the introduction of K⁺ in the host layered structure can inhibit the detrimental spinel structure growth during cycling. Therefore, the K-stabilized Li-rich layered materials can be considered to be an attractive alternative to meet with the higher power and energy density demands of advanced lithium-ion battery.

Keywords

structural, stabilization, $\text{Li}_{1.232}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$, k, host, doping, performances, attempt, toward, superior, electrochemical, $\text{Li}_{1.232}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$

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Host Structural Stabilization of $\text{Li}_{1.232}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$ through K-Doping Attempt: toward Superior Electrochemical Performances

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Abstract: Lithium-rich layered cathodes are known famously for its superior capacity over traditional layered oxides but trapped for lower initial coulombic efficiency, poorer rate capability and worse cyclic stability in spite of diverse attempts. Herein, a new K-stabilized Li-rich layered cathode synthesized through a simple oxalate co-precipitation is reported for its super electrochemical performances. Compared with pristine Li-rich layered cathode, K-stabilized one reaches a higher initial coulombic efficiency of 87% from 76% and outruns for 94% of capacity retention and 244 mAh g⁻¹ of discharge capacity at 0.5 C after 100 cycles. Moreover, 133 mAh g⁻¹ of discharge capacity can be delivered even charged at 10 C showing a highly-improved rate capability. X-ray diffraction and electrochemical impedance

spectroscopy tests show that enlarged Li slab layer caused by K^+ accommodation can provide facile Li^+ diffusion paths and facilitate Li^+ migration from the crystal lattice. As a consequence, the introduction of K^+ in the host layered structure can inhibit the detrimental spinel structure growth during cycling. Therefore, the K-stabilized Li-rich layered materials can be considered to be an attractive alternative to meet with the higher power and energy density demands of advanced lithium-ion battery.

Keywords: Lithium-rich cathode; K-doped; Li^+ diffusion paths; Electrochemical performance

1. Introduction

Nowadays, high energy and high power rechargeable lithium-ion batteries (LIBs) continue to dominate the power sources market for electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1-4]. It is believed that the key factor which limits the performance of rechargeable LIBs is the cathode materials. Among the cathode materials used at present, lithium-rich Mn-based oxide materials $\text{Li}[\text{M}_{1-x}\text{Li}_x]\text{O}_2$ ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}$), which can be written either as a solid solution $\text{Li}[\text{Li}_{x/3}\text{Ni}_{\alpha(1-x)}\text{Co}_{\beta(1-x)}\text{Mn}_{2x/3+\gamma(1-x)}]\text{O}_2$ or a composite material $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}$) [5-8], have been considered as the most promising cathode material for practical application since their environmental benignancy, low cost and encouraging high capacity (*ca.* 250 mAh g⁻¹) when charged above 4.5 V [9, 10]. In spite of these merits, however, some serious drawbacks are needed to be resolved, including their intrinsically large initial irreversible capacity loss (ICL), inferior rate capability and cycle performance, and fast voltage decay during cycling [11-13].

Many endeavors have been devoted to addressing these obstacles. Reduction of the particle size to nano-scale level, for instance, can shorten the Li^+ diffusion pathway and enhance the rate capability significantly. However, nano-materials also have some shortages, including low thermodynamics stability, low packing density and large side reactions between electrode and electrolyte [14]. Surface coating has also been performed to strengthen the cyclic stability and rate capability of layered lithium-rich materials, such as coating with metal oxides (Al_2O_3) [15], metal phosphates (LiNiPO_4) [16], and metal fluoride (AlF_3) [17]. The coating layer can

effectively prevent attack of the electrode surface by HF in the electrolyte, thus restraining the electrode erosion and improving the stability of battery system. Furthermore, some coating layers, such as V_2O_5 [18], Co_3O_4 [19] and $LiNi_xMn_{2-x}O_4$ [20], can enhance the initial coulombic efficiency dramatically for serving as an insertion host to accommodate the irreversible lithium ions in the first electrochemical cycle. Another effective way to stabilize the thermal and structural stability is to use the cation doping in the bulk structure. The alien elements such as Fe [21], Mo [22], Al [23] and Ru [24] doping into the lattice structure of lithium-rich materials to substitute a small amount of Ni or Mn in the transition metal layer can boost the inherent conductivity and thermal stability, and then perfect the electrochemical performance. Currently, it is recognized that enlarging the Li layer spacing can accelerate the intercalation/extraction of Li^+ in the bulk lattice, thus significantly improving the rate capability. He *et al.* [25] used Na dope into the Li site of the lithium-rich material to synthesize a Na-containing oxide which possesses a larger space in the Li layer and delivers a superior rate performance (139 mA h g^{-1} at 8 C).

Based on the above successful case of substitution Li with Na to obtain a superior electrochemical performance oxide, it would be a reasonable and convenient design to prepare a high-rate capability and stable cyclic performance lithium-rich oxide simply by introducing the appropriate alkali ions into the Li layer. Because K ($[Ar]4s^1$) has an identical outer shell with Na ($[Ne]3s^1$), and also has a larger ionic radius and lower electronegativity than Na. Hence, it can be realized that doping K into the layered oxides to achieve more excellent electrochemical properties. Up to

now, there have been few reports about doping K into the lithium-rich Mn-based oxide to render a material superior in kinetics and stability [26].

Herein, in situ K-doped $\text{Li}_{1.232}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$ material is successfully prepared and the effect of K-doping on the superior rate performance and cycling stability are systematically investigated. Our results indicate that the excellent electrochemical performance of K-doped oxide is related to the K doping into the Li slab layer which can expand the Li^+ diffusion channels and meanwhile stabilize the host layered structure by prohibiting the undesired spinel structure formation upon cycling.

2. Experimental section

2.1 Sample preparation

The $\text{Li}_{1.232}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$ (labeled as LMN) sample was prepared *via* a co-precipitation method. Proper amounts of nickel acetate tetrahydrate ($\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, AR) and manganese acetate tetrahydrate ($\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, AR) were dissolved in distilled water in term of the stoichiometric ratio, and then pumped into a continuous stirred tank reactor (CSTR). Simultaneously, the oxalic acid and citric acid, as the precipitant and chelating agent respectively, were separately fed into the CSTR at 65 °C. The pH value was carefully controlled at 4.0 ± 0.2 and the stirring speed was monitored at around 500 rpm. Co-precipitated precursor was filtered and washed by distilled water for multiple times, and then dried at 100 °C for overnight. Afterwards, the calculated lithium carbonate (Li_2CO_3 , AR, excess 5%) was mixed with the obtained precursor powders thoroughly, and first preheated at 450 °C for 6 h and then calcined at 900 °C for 10 h in air. The K-doped sample (K-LMN) was synthesized by

the method alike above, but the mixture of Li_2CO_3 and KMnO_4 (in a molar ratio of design) were substituted for Li_2CO_3 .

2.2 Sample characterization

The elemental molar ratios of the as-synthesized samples were detected by a Spectro ARCOS FHS12 inductively coupled plasma-atomic emission spectrometer (ICP-AES). The structures of the as-prepared compounds were characterized by X-ray diffraction (XRD, PW1730, Cu K_α , $\lambda=1.5418 \text{ \AA}$). Structural refinement was performed using TOPAS software. Particle size and morphology of the prepared samples were measured by scanning electron microscopy (SEM, S4800). The chemical valence state of the Ni, Mn, K were determined by X-ray photoelectron spectroscopy (XPS, PHI QUANTUM 2000) with monochromatic Al- K_α anode source, and the binding energy (BE) of XPS calibrated with reference to C 1s spectrum of carbon (284.8 eV). The microstructures of these composites were observed by transmission electron micrograph (TEM, JEM-2100).

2.3. Electrochemical tests

Electrochemical properties of the LMN and K-LMN samples were evaluated in CR-2032 type coin cells which consist of the as-prepared oxide cathode, Li metal anode and a porous polypropylene separator (Celgard 2400) with 1 M LiPF_6 solution in EC-DMC (1 : 1 in volume rate) as the electrolyte. The electrodes were fabricated by coating a slurry containing 80 wt % as-prepared active material, 13 wt % carbon black, and 7 wt % polyvinylidene difluoride (PVDF) on an aluminum foil. Subsequently, the electrodes were dried at 100 °C for 12 h in the vacuum oven. The

dried cathode sheet was cut into discs with diameter of 14 mm, and then pressed under a pressure of 20 MPa. The loading of the active material in the electrode was 3 - 4 mg cm⁻². All coin cells were assembled and sealed in an argon-filled glove box. The cells were charged and discharged galvanostatically at room temperature with different current densities (1 C = 200 mA g⁻¹) in the voltage range of 2.0 to 4.8 V (vs. Li/Li⁺). Electrochemical impedance spectroscopy (EIS) was recorded on an electrochemical workstation (Zenium, IM6) over a frequency range of 100 kHz to 10 mHz with an alternating-current amplitude of 5 mV.

3. Results and discussion

ICP-AES results of the chemical compositions of LMN and K-LMN samples are summarized in Table 1. It is illustrated that the experimental ratios of Li : K : Mn : Ni in the two samples are approximately consistent with the designed stoichiometry within experimental errors.

XRD refinements for LMN and K-LMN samples are employed to probe the effect of K-doping on the lattice structure (Fig. 1). All the strong peaks in both of the samples can be indexed by α -NaFeO₂ rock structure with space group $R\bar{3}m$ which is normally taken as the layered characteristic of LiMO₂ (M = Ni, Mn) phase [5, 6, 27], and some weak reflections peaks between 20 ° and 25 ° (2 θ value) are consistent with the hexagonal LiMn₆ super-ordering in Li₂MnO₃ monoclinic phase with C2/m symmetry [5, 6, 27]. Additionally, the reflections corresponding to K are not observed in the XRD patterns for K-LMN sample (Fig. 1b) due to its low mass doping. The refined lattice parameters of LMN and K-LMN samples are listed in Table 2.

Compared to the LMN sample, the lattice constant a is largely unchanged for K-LMN sample. However, the lattice constant c is increased from 14.2442 Å (LMN) to 14.2748 Å (K-LMN). This observation is in agreement with previous reports for Na-doped Li-rich materials [25]. Theoretically, about 1.65% (molar ratio) K^+ ions (1.38 Å) introduced into the Li layer in the lattice, the effective ionic radius can be calculated as 0.77 Å for the ions at 3b sites, slightly larger than that of 0.76 Å for Li^+ , thus the lattice parameter c should be enlarged after doping. Moreover, the increased c -lattice parameter in the K-LMN sample provides a direct evidence for the enlargement of Li layer spacing, which would cause a substantially higher Li^+ diffusivity [28]. The c/a and $I_{(003)}/I_{(104)}$ values of K-LMN are also higher than LMN sample, implying a more well-defined layered structure and a lower level of cation disordering after K doping into the pristine material [29-31]. Table 2 also presents the variation of transition metal (Ni) content in the Li layer for those two samples. The Ni content in the Li layer (2.02%) of the K-LMN is lower than that of the LMN (2.79%), which is corresponding to the analysis of $I_{(003)}/I_{(104)}$ ratio. The change in interslab spacing between oxygen layers is calculated, which generates the tetrahedral sites that facilitate the Li^+ diffusion. The interslab spacing distance of LiO_2 (I_{LiO_2}) is calculated to be enlarged for K-LMN. Previous investigations reveal that the activation barrier of Li hopping from original octahedral sites to interslab tetrahedral sites is strongly dependent on the distance between oxygen layers (I_{LiO_2}), the larger the I_{LiO_2} , the faster the Li^+ diffusion [24, 26, 32]. Hence, it is expected that the electrochemical performances, especially rate capability, would be improved by K doping.

X-ray photoelectron spectroscopy (XPS) measurements are carried out to investigate the variation in chemical states of the as-prepared LMN and K-LMN samples (Fig. S1 in the Supplementary Information). The XPS spectra of Mn 2p_{3/2} and Ni 2p_{3/2} at binding energies of 642.2 eV and 854.5 eV are consistent with the previous reports for Mn⁴⁺ and Ni²⁺ in similar oxide cathode materials, respectively [33-35]. The observed XPS peak sites of transition metals for the two samples are similar with each other, indicating the effects of K-doping on the oxidation states of Mn and Ni elements can be negligible. However, two additional small peaks (> 290 eV) are observed in the binding energy region from 280 eV to 297 eV for K-LMN sample. These two peaks can be well assigned to K 2p_{1/2} and K 2p_{3/2} as previous reports [36, 37]. This observation of K 2p peaks provides a direct evidence for the existence of potassium in the K-LMN sample.

Fig. 2 shows the SEM and TEM images of LMN and K-LMN samples. As can be seen, the LMN sample consists of sphere-like particles with a homogeneous distribution and an average particle size of about 300 nm (Fig. 2a), whereas the K-LMN sample exhibits a cubic-like shape with distinct edges and corners and a slightly larger size of about 400 nm (Fig. 2b). The morphological difference in the two samples is also observed in previous reports for Na-doped Li-rich oxides, and the explanation is that the alkali ions into the Li slab can reinforce the stability of the host layered structure so that the growth of the crystal tends to follow the direction of the layer [25]. The selected area electron diffraction (SAED) patterns of these samples (inset of Fig. 2c and d) show typical layered lattice structures, which are collected

from a crystal analyzed along the $[8\bar{8}01]_{\text{Hex}}$ zone axis and $[\bar{2}021]_{\text{Hex}}$ zone axis, respectively. The two lattice fringes of the samples are measured to be 0.47 nm (Fig. 2e and f), which is well indexed to the $(003)_{\text{Hex}}$ plane of LiMO_2 ($M = \text{transition metals}$) and/or $(001)_{\text{Mon}}$ plane of Li_2MnO_3 [38].

The 1st and 6th charge/discharge curves of the LMN and K-LMN samples at 0.1 C (20 mA g⁻¹) between 2.0 and 4.8 V are presented in Fig. 3a. Apparently, the initial charge profiles of the two samples show a smooth sloping region below 4.5 V and a high voltage plateau at around 4.5 V. The sloping region below 4.5 V can be ascribed to the Li⁺ deintercalation from layered structure by oxidation of Ni²⁺ to Ni⁴⁺ [39, 40]. The plateau at around 4.5 V can be attributed to the irreversible removal of Li₂O from Li₂MnO₃ component which leads to a large initial irreversible capacity loss [39, 40]. The LMN and K-LMN electrodes deliver charge/discharge capacities of 352/266, 344/299 mAh g⁻¹, with coulombic efficiencies of 76% and 87%, respectively. The enhanced coulombic efficiency is possibly due to the effect of K⁺ ion, with a larger unchangeable ionic radius, doping into the Li slab layer can suppress the collapse of lattice structure. After deintercalation of Li ions, the maintained structure could better facilitate subsequent intercalation of Li ions than a collapsed structure. Moreover, the 6th charge/discharge curves of these samples are also displayed. Obviously, there are distinct differences between the 1st and 6th charge/discharge curves, due to the activation process of Li₂MnO₃ around 4.5 V on the first cycle. To intuitively investigate the impact of K doping on the electrochemical reactions, the corresponding differential capacity vs. voltage curves (dQ/dV) are presented in Fig. 3b

(1st cycle) and Fig. 3c (6th cycle). As can be seen, the samples exhibit the same dQ/dV plots at the first cycle, however, an additional anodic peak is observed around 3.2 V (marked by green circle) at 6th cycle for K-LMN. This peak can be reasonably attributed to the redox reactions of the Mn component in the different structural environment. This phenomenon also suggests that the K doping may make more Mn participation in the MnO₂ layers to contribute additional reversible capacity.

Fig. 4a shows a continuous cycling result at incremental rates from 0.1 C to 10 C then recovering back to 0.1 C. As can be seen, the discharge capacities of K-LMN are improved dramatically at all rates when compared to the pristine LMN. This phenomenon is supposed to be related to the doping of K that effectively mitigated the migration of Mn⁴⁺ ions (MnO₂-like structure after Li₂MnO₃ activation at first cycle) from octahedral sites (layered structure) to adjacent tetrahedral sites (spinel variant), resulting more Mn retained in the MnO₂-like structure and this produces an expected LiMnO₂ (layered O3 structure) after intercalation to supply more reversible capacity (as shown in Fig. 3c). The K-LMN electrode delivers the discharge capacities of 299, 278, 258, 235, 198, 165 and 133 mAh g⁻¹, whereas the LMN electrode exhibits the discharge capacities of 266, 246, 222, 195, 162, 121 and 90 mAh g⁻¹ at 0.1 C, 0.2 C, 0.5 C, 1 C, 3 C, 5 C and 10 C, respectively. The relevant charge/discharge curves of the samples at different rates are shown in Fig. S2. The capacity retentions of the samples at different rates relative to 0.1 C are shown in Fig. S3. The rate capability of K-LMN is superior to LMN, and the capacity retentions for K-LMN are 93%, 86%, 79%, 66%, 55% and 44% at 0.2 C, 0.5 C, 1 C, 3 C, 5 C and 10 C, respectively. Such

significant enhancement in rate capability for K-LMN sample is reasonably attributed to two reasons: one of which is the enlarged Li layer spacing that caused by K doping can accelerate the diffusion of Li^+ ions in the bulk structure; the other one is the preferred orientation growth of the K-doped lattice follow the direction of the layer (as seen in Fig. 2d), which facilitates the fast insertion and extraction of Li^+ ions. In order to more visually understand the impact of structure on the electrochemical performance, the schematic illustration of the unit cells of trigonal LiMO_2 ($R\bar{3}m$) and Li/KMO_2 ($R\bar{3}m$) in LMN and K-LMN samples are represented in Fig. 4b and Fig. 4c, respectively. In the structural models, the Mn and Ni atoms partially occupy octahedral 3a sites with no specific ordering while K and Li occupy octahedral 3b sites [41, 42]. In addition, a few 3b sites are occupied disorderedly by the Li/Ni/K due to their similar radius. After K doping into the Li layers, the c -parameter becomes larger as shown in Fig. 4c, and this kind of expansion can provide broader channels for the fast Li^+ migration and meanwhile alleviate the mechanical strain induced by volume change during the repeated Li^+ insertion/extraction processes. As reported [43], furthermore, the Na-ion batteries have more robust structure than Li-ion batteries, therefore, the K-LMN sample may have a higher structural stability than LMN sample, which can tolerate the impact of high current density and guarantee the high discharge capacity.

The long-term cycling tests of LMN and K-LMN materials are shown in Fig. 5. After 100 cycles, the LMN sample barely releases a discharge capacity of 189 mAh g^{-1} at 0.5 C with poor capacity retention of 84%. However, the K-LMN sample

exhibits excellent cycling stability with good capacity retention. The discharge capacity at 0.5 C approaches as high as 261 mAh g⁻¹ at first cycle and maintains up to 244 mAh g⁻¹ after 100 cycles. Additionally, high coulombic efficiency for the two samples is nearly 100% during cycles, which reveals a good reversibility for these electrodes.

It is generally known that the voltage decay during long-term cycling which originates from phase transformation from layered to spinel/layered intergrowth structure is a huge challenge for lithium-rich oxides [11, 13]. Therefore, in order to compare the voltage fading upon cycling more intuitively, the 5th, 15th, 25th, 50th, 80th and 100th discharge profiles at 0.5 C after normalization of capacity are shown in Fig. 6. Clearly, the K-LMN sample exhibits the lower voltage decay compared with LMN sample, and the voltage difference at the half capacity between the 5th and 100th discharge curves is merely $\Delta V_{(5^{th}-100^{th})} = 0.65$ V, indicating the fast voltage fading upon cycling can be alleviated through K⁺ ion doping. In addition, the dQ/dV curves of different cycles shown in Figure. 7 are employed to investigate the voltage decline. dQ/dV plots of both samples show three individual reduction processes during discharging, *i.e.*, R_{e1} is related to the Li occupation within tetrahedral sites according to the NMR studies; R_{e2} is related to Li occupation within octahedral sites accompany with Ni/Co redox; R_{e3} is associated with Mn redox related to Li occupation within octahedral sites [44]. Here, the R_{e3} is selected to reveal the transformation of bulk layered structure. Obviously, the R_{e3} peak shifts continuously toward lower potential upon cycling, and the difference of R_{e3} between LMN and K-LMN samples is

increasingly expanded, which indicates a more unstable structure for potassium-free sample. At 50th cycle, the sharp peak at 2.62 V for LMN sample is linked to the spinel structure [41, 45]. This layered-spinel intergrowth is considered as an important factor which is responsible for the fast capacity loss and voltage decline upon cycling. Comparatively, for K-LMN sample, the R_{e3} peak is observed at 3.18 V, indicating the absence of spinel phase during these cycling processes. The reason can be attributed to the large K^+ ion (1.38 Å), which is much bigger than Li^+ ion (0.76 Å), that is difficult to migrate out from the lattice during the charge and discharge processes. Therefore, the K^+ ions would act as fixed pillars in the Li layers to ensure the structural stability [25]. Furthermore, some K^+ ions exist in the Li slab can inhibit the migration of transition metal ions from octahedral coordination to adjacent tetrahedral sites, which is crucial for the structure transformation from layered structure to the spinel variant [46]. It has already been confirmed that large cations are hard to form spinel structure within a fixed oxygen framework, and vice versa [41, 46]. K^+ ionic radius is much larger than Li^+ , hence, the spinel phase would be suppressed in the larger K^+ ions doped Li-rich oxides due to the steric hindrance in the K-containing domains. This could be better understood by the $Na_{0.5}MO_2$ that has more steady structure than $Li_{0.5}MO_2$ and transition from layered to spinel structure cannot occur in the Na compound by first principles calculations [43].

Fig. S4 shows XRD patterns of the LMN and K-LMN electrodes after 100 cycles at 0.5 C between 2.0 and 4.8 V. A strong peak at about 65.4° (2θ value) for the two electrodes is corresponding to the Al current collector. In comparison with K-LMN, it

can be clearly observed that the XRD patterns of LMN cathode become broader and un conspicuous, suggesting that the K doping electrode has a strong structural stability during long-term cycling. Furthermore, ICP-AES measurement is used to detect whether the K^+ ions migrate out from the crystal lattice during electrochemical process or not. The chemical formula of K-LMN electrode after 100 cycles at 0.5 C is $Li_{1.043}K_{0.021}Mn_{0.592}Ni_{0.169}O_2$. The Li content is lower than the fresh electrode ($Li_{1.212}K_{0.020}Mn_{0.615}Ni_{0.154}O_2$) probably due to the irreversible loss of Li_2O for Li_2MnO_3 component in the first cycle, but the K content is almost the same as the fresh one. The results demonstrate that the K^+ ions are not moved out from the parent structure.

Electrochemical impedance spectroscopy (EIS) has been performed to get insights into the difference in electrochemical performance of LMN and K-LMN samples. The measurements are carried out after 5th, 15th, 25th and 50th cycle examination (Fig. 5). All Nyquist plots are shown in Fig. 8, and the corresponding equivalent circuits are presented in the inset. In this equivalent circuit, R_s represents the resistance of the electrolyte and cell components, R_{ct} corresponds to charge transfer resistance in the electrode-electrolyte interfaces, and W1 is the Warburg impedance for depicting Li^+ ion diffusion process in the electrode materials [47, 48]. Each impedance spectrum is fitted well with suggested equivalent circuit model, and the corresponding resistance parameters are summarized in Table 3. By monitoring both samples, a similar variation trend is found that the R_s remains almost unchanged, whereas R_{ct} has a clear growth upon cycling possibly due to a continuous structural

evolution. In all the observed cycles, the R_{ct} for LMN is higher than K-LMN, and its R_{ct} increased rapidly with the extent of cycling, compared to the K-LMN sample. In general, the lower R_{ct} value indicates an improvement in the kinetics of Li^+ diffusion and charge-transfer reactions and a consequent increase in electrochemical performance. The lower R_{ct} for K-LMN can be reasonably attributed to the influence of K^+ ions on the expansion of c -parameter and inhibition of spinel variant formation in the bulk structure.

4. Conclusion

K substituted layered $\text{Li}_{1.212}\text{K}_{0.02}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$ cathode material for lithium ion battery is successfully synthesized *via* the oxalate co-precipitation method. Its morphology, structure and electrochemical properties are investigated in this work. Compared to the undoped sample, the K-doped material shows a more ordered $\alpha\text{-NaFeO}_2$ structure with regular cubic-like morphology and enlarged Li layer spacing. The electrochemical measurements confirm that the substitution of K for Li results in a higher specific discharge capacity (299 mAh g^{-1} at 0.1 C), higher initial coulombic efficiency (87%), greatly enhanced rate capability (133 mAh g^{-1} at 10 C) and excellent cycling stability (94% capacity retention after 100 cycles at 0.5 C). Moreover, the significant EIS results indicate that, compared to the potassium-free LMN sample, the K-LMN has a smaller charge transfer resistance (R_{ct}) because K^+ ion can restrain the spinel variant formation in the layered structure upon cycling. Such superior electrochemical performances are reasonably ascribed to the K doping into the Li slab layer causing the enlargement of Li slab space, which facilitates the

fast Li^+ insertion/extraction from the crystal lattice and meanwhile stabilizes the host layered structure by inhibiting the undesired spinel structure formation during cycling. More importantly, this work provides a simple and convenient method to address the huge challenge of layered-spinel intergrowth in the lithium-rich materials that could significantly lower the energy density of the whole battery.

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Figure captions

Fig. 1 Rietveld refinement of the X-ray diffraction patterns for (a) LMN and (b) K-LMN samples.

Fig. 2 SEM and TEM images of the (a, c, e) LMN sample; (b, d, f) K-LMN sample.

Fig. 3 (a) 1st and 6th charge/discharge curves; (b), (c) the corresponding charge/discharge dQ/dV plots of the LMN and K-LMN samples at 0.1 C (20 mA g⁻¹) between 2.0 and 4.8 V.

Fig. 4 (a) Rate capability of LMN and K-LMN samples between 2.0 and 4.8 V; (b), (c) unit cells of trigonal LiMO₂ ($R\bar{3}m$) and Li/KMO₂ ($R\bar{3}m$), respectively.

Fig. 5 Cycling performance and coulombic efficiency of the LMN and K-LMN electrodes at 0.5 C between 2.0 and 4.8 V.

Fig. 6 Discharge curves of 5th, 15th, 25th, 50th, 80th and 100th cycles at 0.5 C after normalization of capacity for (a) LMN and (b) K-LMN samples.

Fig. 7 dQ/dV plots corresponding to 5th, 15th, 25th and 50th discharge profiles at 0.5 C for LMN and K-LMN samples.

Fig. 8 Nyquist plots and corresponding equivalent circuit (inset) of (a) LMN and (b) K-LMN after 5th, 15th, 25th and 50th cycles at 0.5 C between 2.0 and 4.8 V.

Table captions

Table 1 ICP-AES analysis results of Li : K : Mn : Ni ratio in the LMN and K-LMN samples.

Table 2 Refined lattice parameters of LMN and K-LMN samples.

Table 3 Fitting impedance parameters of equivalent circuit for the samples at different cycles.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Table 1

Sample	Atomic ratio				Deduced formula
	Li	K	Mn	Ni	
LMN	0.796	—	0.402	0.099	$\text{Li}_{1.224}\text{Mn}_{0.618}\text{Ni}_{0.152}\text{O}_2$
K-LMN	0.778	0.013	0.396	0.098	$\text{Li}_{1.210}\text{K}_{0.020}\text{Mn}_{0.616}\text{Ni}_{0.152}\text{O}_2$

Table 2

Sample	a (Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$	Ni in Li layer (%)	S_{MO_2} (Å) [@]	I_{LiO_2} (Å) [@]	R_p (%)	R_{wp} (%)
LMN	2.8547	14.2442	4.9897	1.56	2.79	2.1461	2.6020	2.38	2.84
K-LMN	2.8561	14.2748	4.9980	1.73	2.02	2.1336	2.6247	2.52	2.97

[@] Interslab thickness is calculated according to refs [24, 26, 32], $S_{\text{MO}_2} = (2/3 - 2z_{\text{ox}})c$, $I_{\text{LiO}_2} = c/3 - S_{\text{MO}_2}$, z_{ox} is the oxygen position at 6c sites.

Table 3

Cycle	LMN sample			K-LMN sample		
	$R_s(\Omega)$	$R_{ct}(\Omega)$	$R_{total}(\Omega)$	$R_s(\Omega)$	$R_{ct}(\Omega)$	$R_{total}(\Omega)$
5th	2.71	90.46	93.17	2.67	51.88	54.55
15th	2.71	182.80	185.51	2.66	100.90	103.56
25th	2.72	294.00	296.72	2.68	150.90	153.58
50th	2.70	452.62	455.32	2.69	227.70	230.39

Supplementary Information

Host Structural Stabilization of $\text{Li}_{1.232}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$ through K-Doping Attempt: toward Superior Electrochemical Performances

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Fig. S1 XPS spectra of Mn 2p, Ni 2p, C 1s and K 2p for LMN and K-LMN samples

Fig. S2 Charge/discharge curves of the samples at different rates between 2.0 and 4.8

V (a) LMN, (b) K-LMN

Fig. S3 Capacity retention at different rates of the samples (retention at 0.1 C is 100%[@])

Note @: the capacity retention at 0.1 C is defined to 100%, and the calculation equation can be written as $Q_{(\square C)}/Q_{(0.1 C)}$, Q represents the discharge capacity.

Fig. S4 XRD patterns of the LMN and K-LMN electrodes after 100 cycles at 0.5 C between 2.0 and 4.8 V