Mitigating voltage and capacity fading of lithium-rich layered cathodes by lanthanum doping

Ruizhi Yu, Gang Wang, Meihong Liu, Xiaohui Zhang, Xianyou Wang,* Hongbo Shu,

Xiukang Yang, Weihua Huang

(National Base for International Science & Technology Cooperation, Key Laboratory of

Environmentally Friendly Chemistry and Applications of Ministry of Education, Hunan Province

Key Laboratory of Electrochemical Energy Storage and Conversion, School of Chemistry,

Xiangtan University, Xiangtan 411105, China)

Abstract: La-doped lithium-rich layered oxide material $\text{Li}_{1.2}\text{Mn}_{0.54-x}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_x\text{O}_2$ ($x = 0.01, 0.02, 0.03$) is firstly synthesized via a solvothermal method and subsequent high-temperature calcination technique. The effects of La substitution for partial Mn on the structure and electrochemical performance of materials are systematically studied by inductively coupled plasma optical emission spectroscopy (ICP-OES), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and electrochemical measurement. The results reveal that La is effectively and homogeneously doped into the materials, which can expand pathway for intercalation/deintercalation of Li^+ ions. In addition, owing to La doping, the $\text{Li}_{1.2}\text{Mn}_{0.52}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.02}\text{O}_2$ sample exhibits 93.2% capacity retention after 100 cycles at 1 C. More importantly, this doping can effectively restrain the decrease of

* **Corresponding author:** Xianyou Wang, Tel: +86 731 58293377; Fax: +86 731 58292695.

E-mail address: wxianyou@yahoo.com

average discharge voltage upon cycling, which is one of the longstanding fatal drawbacks for lithium-rich layered oxide material. Moreover, La doping can stabilize the layered framework upon long term cycling and suppress voltage fading, and thus resulting in the better cycling performance. Additionally, the rate capability is also improved by La doping due to the higher diffusion velocity of Li^+ ions.

Keywords: Lithium-rich layered oxide material; Lanthanum doping; Solvothermal method; Lithium ion batteries; Suppressing voltage and capacity decay

1. Introduction

In the past decades, humans have enjoyed dazzling economic booming and great creature comforts due to the rapid development of electric automation, electronics and internet technologies [1-4]. More recently, electric vehicles (EVs) and hybrid electric vehicles (HEVs) powered by LIBs are going through growth spurts around the world. In addition, modern smart grid is springing up in many countries. All those improvements can not realize without the advanced energy supply system, energy storage and conversion equipment [5-7]. Lithium-ion batteries (LIBs), as clean and green power source, have experienced the development of more than twenty years since 1990s, and now have been widely used as the major energy sources for portable electronic devices, EVs and HEVs [8,9]. Moreover, significant research attention is now being paid to further expand the use of LIBs in the EVs and for possible deployment in grid storage applications. The new demands have requested the

researchers to enhance the properties of LIBs, such as energy density, power density, cycle life, safety and environmental compatibility [10,11].

The investigation of cathodes is an important approach to promote the improvement of LIBs. In the ongoing search for new positive electrode materials, lithium-rich or Li-excess layered oxide (LLO) has been emerged as one of the most promising candidate, which is described with two different chemical notations: $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$) and $\text{Li}_{1+(x/(2+x))}\text{M}'_{1-(x/(2+x))}\text{O}_2$ ($M' = \text{Mn}+\text{M}$) in different literatures [12-16]. It can provide much higher reversible capacity (250-300 mAh g⁻¹) and operating voltage (>4.6 V vs. Li⁺/Li) than the traditional cathode materials such as LiCoO₂, spinel LiMn₂O₄ and olivine LiFePO₄, because of its particular crystal structure. In the recent years, the studies on the relationship between structure and electrochemical performance of LLO material have been widely reported [17-25]. However, the studies for the structure of LLO materials and effect of the structure on their electrochemical performance still remain controversial. Recently, Yu et al [13,26-27]. studied the surface and interior structure of LLO material by synchrotron X-ray diffraction (SXRD), scanning transmission electron microscopy (STEM), selected area electron diffraction (SAED) and argon ion slicer technique. The results demonstrated that it was consisted of two different local structures of rhombohedral LiMO₂ (space group $\bar{R}3m$) and monoclinic Li₂MnO₃ (space group C2/m) at an atomic scale. Armstrong et al [28]. found that the Li₂MnO₃ structure is significant, and it is the origin of the high capacity by in situ differential electrochemical mass spectrometry (DEMS). During the initial charge process, the Li⁺

can be extracted from the Li_2MnO_3 lattice at ~ 4.5 V voltage plateau accompanied by the oxygen loss and structural rearrangement, which results in a new layered MnO_2 phase. The formed MnO_2 can act as a host structure for the following Li^+ intercalation/deintercalation process and then enhance the capacity of LLO material [16,22,28,29].

Despite the high capacity, the LLO material suffers from several drawbacks that impede its commercial applications in advanced LIBs. The structure of this material exhibits instability and its capacity usually decreases rapidly upon long-term cycling. Furthermore, it is confronted with low rate capability and average discharge voltage decay during cyclic process. Presently, considerable literatures [26-33] reported that the LLO material would suffer from layered-to-spinel phase transformation and lattice distortion/amorphization when charged to a high potential ($>4.5\text{V}$) because of the Li vacancies, Mn migration and oxygen loss in the Li_2MnO_3 framework. In addition, the electrode can be etched (at least by part) by acidic species in the electrolyte at the high potential [29,34]. The spinel clusters with different orientations yield in the distorted/amorphized lattice, and the detrimental interfacial reaction between the active material and electrolyte could induce instable and fragmental structure in material and then deteriorate the properties of the material. Additionally, layered-to-spinel phase transformation leads to the shift of the potential towards lower value, due to the redox activity of spinel phase around 3 V ($\text{Mn}^{4+}/\text{Mn}^{3+}$) [29,35]. In this case, the layered-to-spinel transformation is an important factor to account for the poor rate capability, continuous capacity fading and voltage decay of the LLO

materials. Since the structural degradation is one of the major defect of the LLO material for being applied in advanced LIBs, numerous approaches have been carried out to overcome it.

Surface modification is an effective approach for suppressing capacity fading of LLO material. For instance, coating the lithiated oxide particles with nanoscale metal compounds is a usual method, it can prevent the surfaces of particles from being in direct contact with the electrolyte, and then weaken harmful surface interactions with acidic species [36]. Qiu et al [37]. synthesized the ZnO coated lithium-rich layered $0.3\text{Li}_2\text{MnO}_3\text{-}0.7\text{LiNi}_{5/21}\text{Co}_{5/21}\text{Mn}_{11/21}\text{O}_2$ cathode material via a reactive magnetron sputtering (RMS) process, the initial discharge capacity and rate capability have been improved. Wu et al [38]. reported a AlPO_4 coated $\text{Li}[\text{Li}_{0.2}\text{Fe}_{0.1}\text{Ni}_{0.15}\text{Mn}_{0.55}]\text{O}_2$ and obtained high discharge capacity, remarkable cycling performance and rate capability. Besides, decorating the surface of LLO material with polymer is another efficient technique to enhance its electrochemical properties. For example, our group [39,40] has reported that the capacity retention increases from 88% to 92.4% (at 0.5C after 200 cycles) and the discharge capacity increases from 122.8 to 146.2 mAh g⁻¹ through surface modification of lithium-rich layered-spinel composite cathode materials with polyaniline. However, the surface coating layer is so heterogeneous and thin that it may wear off during extensive cyclic process, thus leading to capacity fading. Furthermore, the surface coating cannot satisfactorily obstruct the layered-to-spinel phase transformation upon cycling, which causes voltage degradation [41,42].

Recently, it has been reported that doping LLO material with metal ions such as

Mo⁶⁺ [43], Al³⁺ [29,44], Mg²⁺ [45-48], K⁺ [49] and Y³⁺ [50] could availablely stabilize the structure of the material. Remarkably, Tang et al [44]. reported an Al³⁺-doped Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O₂ material with a capacity retention of 98% (at 0.5C after 30 cycles), and considered that a suitable amount of Al³⁺ ions substituted for partial Co³⁺ can play an important role in supporting structure and improving electrochemical properties. Li et al [49]. synthesized a novel in situ K⁺-doped Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂, this material can deliver an outstanding cycling performance with 85% of initial discharge capacity after 110 cycles. Moreover, the K⁺ can effectively suppress the formation of spinel structure and refrain from voltage decay upon cycling. In our previous work [48], Mg²⁺ ions can be introduced into Li⁺ sites of LLO material via the co-precipitation method and the subsequent high-temperature solid state process, and the capacity fading and discharge voltage degradation of the material can effectively be alleviated. Though many works have been done to improve the property of LLO material by metal ions doping, the research on the effect of metal element substitution for the redox active Mn alone was rarely reported, in which redox activity around 3.0 V results in a decrease in the discharge voltage plateau upon cycling.

Lanthanum (La) has been used as a substitution element in many cathode materials such as LiCoO₂ [51], LiMn₂O₄ [52] and LiFePO₄ [53]. The effect of La in these materials is to improve the structural stability and the electronic conductivity. However, to the best of our knowledge, it is rarely reported on the La-doped LLO composite so far. Moreover, La³⁺ with 0.115 nm ionic radius is bigger than Mn⁴⁺ (0.053 nm) [50,51] and other doping element, such as Mg²⁺ (0.072 nm) [48], Al³⁺

(0.0535 nm) [29,44], Mo^{6+} (0.059 nm) [43] and Y^{3+} (0.09 nm) [50], and it cannot be oxidized during the charge/discharge process. Thus, La substitution for partial redox active Mn in the LLO material may expand and stabilize the pathway for intercalation/deintercalation of Li^+ , which could enhance the rate capability and suppress the voltage and capacity fading during cycling. Herein, we synthesized the La-doped LLO composite via a solvothermal method and subsequent high-temperature solid state technique. The effects of La substitution for partial Mn on the structure and electrochemical properties of the LLO material are systematically studied.

2. Experimental section

2.1 Materials preparation

La-doped lithium-rich layered cathode materials $\text{Li}_{1.2}\text{Mn}_{0.54-x}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_x\text{O}_2$ ($x = 0, 0.01, 0.02, 0.03$) was synthesized by a solvothermal method and subsequent high-temperature calcination technique. All the chemicals (analytically pure) were purchased from Guang Dong Guanhua Sci-Tech Co., Ltd., and used without further purification. For example, to prepare $\text{Li}_{1.2}\text{Mn}_{0.53}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.01}\text{O}_2$, 5.3 mmol $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 1.3 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1.3 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.1 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were firstly dissolved in 30 ml ethanediol under stirring, named solution A. Then 8 mmol NH_4HCO_3 was dissolved into another 30 mL ethanediol at room temperature under stirring, named solution B. Then the solution B was added slowly to the solution A under strong magnetic stirring. Thereafter, the resulting

mixed solution was transferred immediately into a 100 mL Teflon-lined stainless steel autoclave, sealed and heated in an oven at 180 °C for 24 h. After reaction, the precipitate was collected by filtration and washed with deionized water and ethanol for several times. Then the sample was dried at 80 °C for 12 h. Subsequently, the dried sample was preheated at 500 °C for 6 h to convert into an oxide powder in a muffle furnace. To form the final cathode material, the oxide powder was mixed with an appropriate amount of Li_2CO_3 and calcined at 850 °C for 12 h in air before it is naturally cooled down to room temperature. In addition, $\text{Li}_{1.2}\text{Mn}_{0.54-x}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_x\text{O}_2$ ($x = 0, 0.02, 0.03$) were prepared in the similar way. And these four samples ($\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, $\text{Li}_{1.2}\text{Mn}_{0.53}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.01}\text{O}_2$, $\text{Li}_{1.2}\text{Mn}_{0.52}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.02}\text{O}_2$ and $\text{Li}_{1.2}\text{Mn}_{0.51}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.03}\text{O}_2$) are denoted as L0-LLO, L1-LLO, L2-LLO and L3-LLO according to the variation of x .

2.2 Materials characterizations

The chemical compositions of the prepared materials were analyzed by using an inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300 DV, Perkin Elmer Co.). The morphologies of the cathode materials were investigated by a field-emission scanning electron microscopy (FESEM, Quanta FEG 250). Further structural characterization and elemental distribution of these materials were carried out by a transmission electron microscopy (TEM, JEOL JEM-2100F) equipped with an energy dispersive X-ray spectroscopy (EDS) detector and a focused-ion-beam scanning electron microscope (FIB-SEM, FEI Helios Nanolab 600) equipped with a EDS unit. The crystal structures of the samples were observed by

X-ray diffraction (XRD) patterns recorded on an X-ray diffractometer (Bruker AXS D8, Bruker AXS GmbH), equipped with Cu K α radiation ($\lambda = 0.154178$ nm). The XRD data were collected in the scattering angle (2θ) range of 10° - 110° at a step size of 0.02° and a counting time of 2 s per step, and the structural analysis was carried out using the General Structure Analysis System (GSAS) program. The value state of chemical composition was detected via X-ray photoelectron spectroscopy (XPS) with a K-Alpha 1063 using mono Al K α (Thermo Fisher Scientific). Raman spectroscopic studies were carried out on a confocal Raman system (Xplora, Horiba) using a 532 nm excitation line with a laser power of 0.1 mW on the sample surface.

2.3 Electrochemical measurements

Positive electrodes were fabricated by mixing the active material, polyvinylidene fluoride (PVDF), graphite and acetylene black with a weight ratio of 80:10:5:5 in N-methyl pyrrolidinone (NMP) solution, which were then pasted on an aluminum foil current collector, followed by drying under vacuum at 110°C for 12 h. The dried electrodes were pressed, then punched into circular films with diameter of 10 mm. Generally, the loading mass of the active material is $4\text{-}5\text{ mg cm}^{-2}$. CR2025 coin cells were assembled using lithium foil as the anode, 1 mol L^{-1} LiPF $_6$ in solvent of solvent of ethylene carbonate (EC): dimethyl carbonate (DMC) = 1:1 as the electrolyte, and porous polypropylene based membrane (Celgard) as the separator in an argon-filled glove box, where the water and oxygen concentration were kept lower than 5 ppm. The charge-discharge and galvanostatic intermittent titration technique (GITT) tests were performed on a Neware battery tester (CT-3008, Neware Co., Ltd.). For the

charge-discharge measurement, the batteries were charged and discharged at different current densities between 2.0 and 4.6 V (vs. Li^+/Li). The current density of 1C was based on a capacity of 200 mA g^{-1} . For the GITT test, the batteries were charged/discharged at 0.05 C for activation in the voltage range of 2.0-4.6 V, and then charged/discharged at 0.1 C for an interval τ of 10 min. Subsequently, the batteries were kept in an open-circuit voltage (OCV) for 60 min to allow the voltage to relax to the steady-state value E_s .

3. Results and discussion

The ICP-OES results of the as-obtained materials are tabulated in Table 1. According to the results of elemental analysis, it can be found that the compositions of the samples are very close to the targeted compositions. Especially, the concentration of La in each sample is in good agreement with the nominal stoichiometry and the Mn content decreases with the increase of La, as expected.

Table 1. The designed and experimental results of the average chemical compositions of the obtained samples.

Sample	Designed molar content of	Experimental molar content of
	Li:Mn:Ni:Co:La	Li:Mn:Ni:Co:La
$\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$	1.2:0.54:0.13:0.13:0	1.198:0.541:0.130:0.129:0
$\text{Li}_{1.2}\text{Mn}_{0.53}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.01}\text{O}_2$	1.2:0.53:0.13:0.13:0.01	1.200:0.528:0.129:0.131:0.012
$\text{Li}_{1.2}\text{Mn}_{0.52}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.02}\text{O}_2$	1.2:0.52:0.13:0.13:0.02	1.201:0.521:0.128:0.130:0.021
$\text{Li}_{1.2}\text{Mn}_{0.51}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.03}\text{O}_2$	1.2:0.51:0.13:0.13:0.03	1.201:0.508:0.132:0.128:0.031

The SEM was used to observe the difference between the pristine (L0-LLO) and La-doped (L1-LLO, L2-LLO and L3-LLO) samples. As being seen from Fig. 1, these samples reveal a similar spherical-like morphology with an average size of approximately 1 μm , and a few holes can be clearly observed on the surfaces of the samples, which may be caused by the emission of CO_2 gas during the calcination process. According to the literature, this porous structure will facilitate to electrolyte percolation [47,54]. Furthermore, all the spherical-like particles are comprised of densely aggregated primary grains with diameter in the range of 80-200 nm, and the primary grains size increases with the increasing of La content, signifying that the addition of La may affect the growth of primary grains.

Fig. 1. SEM images of (a, e) L0-LLO, (b, f) L1-LLO, (c, g) L2-LLO and (d, h) L3-LLO samples.

To evaluate the structure and distribution of Mn, Ni, Co and La elements in the La-doped samples, the FIB-SEM, TEM and EDS were examined. Fig. 2a shows TEM image of a randomly selected L2-LLO particle, Fig. 2c-f display the elemental mapping performed over the particle with respect to Mn, Ni, Co and La, and Fig. S1

exhibits the cross-sectional SEM image and the corresponding EDS elemental mapping for the L2-LLO material. The elemental mapping demonstrates that all the elements are uniformly distributed throughout the particles. Fig. 2b exhibits the HRTEM image and Fig. 2g is the Fast Fourier transform (FFT) pattern taken from Fig. 2b. The FFT image confirms that the appeared reflections of the L2-LLO material are uniquely indexed on the basis of the monoclinic structure of Li_2MnO_3 (space group: C2/m). The lattice fringes corresponding to the monoclinic structure, (111), (131) and (020), are seen in the high resolution transmission electron microscopy (HRTEM) image (as shown in Fig. 2b).

Fig. 2. (a) TEM image of a random selected particle of L2-LLO material, (b) HRTEM image taken from (a), EDS elemental mapping with respect to (c) Mn, (d) Ni, (e) Co and (f) La in (a), and (g) FFT patterns of the selected area in (f).

The phase composition and crystal structure of the as-prepared cathode materials were

identified by XRD, as illustrated in Fig. 3a. All the samples exhibit a typical hexagonal α -NaFeO₂ type structure (space group: $R\bar{3}m$) with a few weak diffraction peaks between 20° and 25°, which could be caused by the short-range superlattice ordering of the Li and Mn atoms in the transition metal layers of monoclinic Li₂MnO₃ (space group: C2/m). The related crystal structures of these two phases are shown in Fig. 3b and c. Meanwhile, two pairs of the (006)/(102) and (018)/(110) peaks of these samples are well split, suggesting a well-defined layered structure formed in the lattice [55,56]. To further gain quantitative crystallographic information, Rietveld refinements of the XRD data for all samples were conducted. The XRD patterns were analyzed based on the mixture of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ ($R\bar{3}m$) and Li₂MnO₃ (C2/m) for all samples. For the L3-LLO material, LaMnO₃ was taken into account as an additional component. For all samples, cation mixing of Ni in Li (3a) site of the $R\bar{3}m$ phase was adopted. For the La-doped samples, La in the M (3b) sites (M = Mn, Ni, Co) of the $R\bar{3}m$ phase and Mn (4g) sites of the C2/m phase were also constrained for the Rietveld Refinement. The refinement results are shown in Fig. 3d-g and Table 2. The reliability factor R_{wp} and χ^2 of the refinement showed in Table 2 are around 7% and 2.5, demonstrating that the results are reliable. It is apparently observed that the La prefer to occupy Mn (4g) site in the Li₂MnO₃ phase. Moreover, with the increasing of doping amount, more La in the Mn (4g) site can be noted. The lattice parameters (a, b and c) increase with the increasing content of La. However, the ratios of $R\bar{3}m$ phase to C2/m phase for all samples are almost constant. Thus, the expansion of the crystal structure is mainly attributed to the substitution of smaller Mn⁴⁺ ion (0.053 nm)

by larger La^{3+} ion (0.115 nm) [50,51], suggesting that the pathway for intercalation/deintercalation of Li^+ could be expanded. Furthermore, some low intensity peaks appear in the L3-LLO sample while the amount of La further increases to a high level, which could be attributed to the formation of La-related impurity phase and may degrade the electrochemical properties of the composite.

Fig. 3. Structural information for as-prepared LLOs with and without La doping. (a) XRD patterns of L0-LLO, L1-LLO, L2-LLO and L3-LLO samples; crystal structure of the (b) rhombohedral LiMO_2 structure ($M = \text{Mn, Ni, Co}$) and (c) monoclinic Li_2MnO_3 structure; Rietveld refined XRD profiles of the (d) L0-LLO, (e) L1-LLO, (f) L2-LLO and (g) L3-LLO samples.

Table 2. The lattice parameters and brief Rietveld parameters for L0-LLO, L1-LLO, L2-LLO and L3-LLO samples ($M = \text{Mn, Ni, Co}$).

		L0-LLO	L1-LLO	L2-LLO	L3-LLO
$R\bar{3}m$ phase	a value (nm)	0.2848525(11)	0.2849267(21)	0.2850228(16)	0.2851529(15)
	b value (nm)	0.2848525(11)	0.2849267(21)	0.2850228(16)	0.2851529(15)
	c value (nm)	1.4229799(14)	1.4232315(19)	1.4258619(24)	1.4259569(22)
	Ni in Li (3a)	7.8%	7.3%	7.0%	8.0%
	La in M (3b)	—	0.02%	0.06%	0.12%
C2/m phase	a value (nm)	0.4940935(22)	0.4947139(16)	0.4953944(21)	0.4956859(19)
	b value (nm)	0.8540158(11)	0.8543026(20)	0.8549588(17)	0.8552536(14)
	c value (nm)	0.5024927(24)	0.5028536(13)	0.5032395(23)	0.5041937(19)
	La in Mn (4g)	—	1.79%	3.58%	5.32%

Percentage	$R_{\bar{3}m}$ phase	53.4%	53.1%	53.0%	53.5%
compositions	C2/m phase	46.6%	46.9%	47.0%	46.5%
Reliability	R_{wp}	5.32%	6.46%	5.98%	5.24%
factors	R_p	4.04%	4.83%	4.44%	3.98%
	χ^2	2.539	1.985	2.484	2.463

In order to confirm the oxidation states of the metal elements (Mn, Ni, Co and La) in the undoped and La-doped samples, L0-LLO and L2-LLO samples were characterized by XPS, and the corresponding spectra are presented in Fig. 4. All of the binding energies (BEs) in the XPS analysis are corrected for specimen charging by referencing them to the C 1s peak (set at 284.6 eV). As shown in Fig. 4a-d, the observed binding energies of Mn 2p_{3/2} and Co 2p_{3/2} for L0-LLO and L2-LLO samples coincide well with the data reported in references [49,57], indicating the presence of Mn⁴⁺ and Co³⁺ in two samples. Furthermore, it can be seen from the Fig. 4f that a peak appears at the binding energy of about 834.08 eV which can well be assigned to La 3d_{5/2}, demonstrating the La element doped exists as La³⁺ in the L2-LLO sample [58]. Additionally, as illustrated in Fig. 4e and f, the Ni 2p_{3/2} binding energies for these two samples are in accordance with the standard Ni²⁺ and Ni³⁺, which are theoretically located at 854.6 eV and 855.7 eV, respectively [59]. However, the L2-LLO sample is compensated by the presence of higher concentration of Ni³⁺ to maintain the charge neutrality, resulting from the substitution of La³⁺ for Mn⁴⁺ [29]. And the higher concentration of Ni³⁺ may enhance Li⁺ diffusion and mitigate the layered-to-spinel transformation which can lead to voltage decay [60].

Fig. 4. XPS spectra of (a) Mn 2p, (c) Co 2p and (e) Ni 2p for L0-LLO; (b) Mn 2p, (d) Co 2p and (f) Ni 2p and La 3d for L2-LLO.

To investigate the electrochemical characteristics of L0-LLO, L1-LLO, L2-LLO and L3-LLO materials, Fig. 5a and c-f display the cycling performance of L0-LLO, L1-LLO, L2-LLO and L3-LLO electrodes at 1 C, after activating by initial cycling at 0.1 C in the voltage range of 2.0-4.6 V. During the initial cycling, all the electrodes

display same electrochemical characteristic as LLO material. The initial charge process can be divided into two regions: a gradual increase in voltage before 4.5 V and a long plateau at about 4.5 V. During the charge process, Ni^{2+} and Co^{3+} are oxidized to Ni^{4+} and Co^{4+} , and Li^+ extracts from LiMO_2 component below 4.5 V. Then Li^+ removes from the Li_2MnO_3 component associated with oxygen loss at the 4.5 V plateau. During the first discharge process, sloping discharge voltage profiles are observed in the voltage range applied (4.6-2.0 V), which are correlated with the intercalation of Li^+ into the generated layered Li_xMO_2 frameworks. However, the extracted oxygen is difficult to reintroduce into the lattice in the discharge processes, and this directly results in the irreversible capacity loss in the initial cycle [61,62]. Moreover, all the electrodes display an extremely high initial discharge capacity ($>280 \text{ mAh g}^{-1}$) and coulombic efficiency ($>87\%$), except for the L3-LLO electrode (245.3 mAh g^{-1} , 82%). These results indicate that appropriate amount of La does not influence the initial specific capacity and the initial activation process of the monoclinic Li_2MnO_3 phase.

After initial cycling, the specific capacity of the L0-LLO electrode degrades substantially and the corresponding discharge profiles experience noticeable voltage decay with increased cycling. On the contrary, the La-doped electrodes exhibit better cycling performance, and voltage decay is effectively suppressed. In particular, the L2-LLO electrode delivers the excellent cycling stability with a capacity retention of 93.2%. Generally, voltage decay during cycling is a fatal weakness of LLO material, which will lead to rapid degradation of energy reserve ability. Fig. 5b compares the

average discharge voltage profiles of the four samples. It can be found that the undoped L0-LLO electrode exhibits a rapid voltage degradation with average discharge voltage decreasing from 3.20V (2nd) to 2.72 V (101st) after 100 cycles at 1 C, while the voltage fading of La-doped electrode is mitigated and the average discharge voltage of L2-LLO electrode only decreases to 3.13 V in the same condition. To further investigate the electrochemical reactions that occurred during cycling, the 2nd and 101st differential capacity curves (dC/dE vs. E) at 1 C for the four samples are provided, as illustrated in Fig. 5g-j. The broad cathodic peak appearing in the voltage range of 2.5-3.2 V derives from the Mn⁴⁺/Mn³⁺ redox activity, which are related to the layered-to-spinel phase transformation and deterioration of the generated spinel-like phase [29,63]. In this regard, it is important to compare between the cathodic peak potentials of the 2nd and 101st cycles. For the L2-LLO electrode, the decrease of cathodic peak potential after 100 cycles is 0.15 V, while the decreases for the undoped L0-LLO or slightly doped L1-LLO samples are higher than 0.36 V. These results indicate that incorporation of suitable amount of La may stabilize the discharge voltage upon long term cycling. Thus, although the La doping cannot solve the problem of lithium-rich cathode material once for all, it can indeed mitigate the structural degradation during cyclic process.

Fig. 5. (a) Cycling performance of L0-LLO, L1-LLO, L2-LLO and L3-LLO electrodes at 1 C rate after activating by initial cycling at 0.1 C in the voltage range of 2.0-4.6 V; (b) the corresponding average discharge voltage vs. cycle number plots of L0-LLO, L1-LLO, L2-LLO and L3-LLO electrodes; the 1st, 2nd and 101st voltage profiles of (c) L0-LLO, (d) L1-LLO, (e) L2-LLO and (f) L3-LLO electrodes and the differential capacity dC/dE vs. E plots for the 2nd and 101st cycles of (g) L0-LLO, (h) L1-LLO, (i) L2-LLO and (j) L3-LLO electrodes.

To account for the comprehensive improvements in the cycling performance of La-doped LLO material, the pristine and cycled positive electrodes were characterized by Raman spectroscopy, as shown in Fig. 6. The weak band which appears at $\sim 430 \text{ cm}^{-1}$ in the spectrum of the pristine L0-LLO and L2-LLO positive electrodes is ascribed to the vibration of Li_2MnO_3 phase, and this weak band disappears after cycling due to the activation of Li_2MnO_3 [64,65]. The other two broad bands appear around 485 and 595 cm^{-1} in the spectra of pristine positive electrodes, which derive from E_g and A_{1g} vibrations of the Raman-active LiMO_2 phase, respectively [64-66]. These two Raman bands are shifted to high values (498 and 622 cm^{-1}) in the spectra of cycled L0-LLO positive electrode, which reveals that the L0-LLO sample suffers

from serious layered-to-spinel phase transformation during cyclic process [29]. However, there is no Raman band at 625 cm^{-1} can be observed in the spectra of cycled positive L2-LLO electrode. Therefore, it can be concluded that the La doping indeed mitigates the layered-to-spinel phase transformation and hence enhances significantly the electrochemical properties.

Fig. 6. Raman spectra of pristine and cycled positive electrodes of L0-LLO and L2-LLO samples.

In addition to the cycling performance, the La-doped LLO material also displays eminent rate capability compared with the undoped LLO material. Fig. 7a displays the discharge capacities of the L0-LLO and L2-LLO electrodes at different rates ranging from 0.1 C to 10 C. With increasing C-rate, the L2-LLO electrode outperforms the L0-LLO electrode and maintains a good reversible discharge capacity of 127.1 mA h g^{-1} at a high rate of 10 C, showing that it has much better rate capability than L0-LLO electrode (65.7 mA h g^{-1}). Additionally, there is a slight fading on the capacity of the

L0-LLO electrode when the current density decreases from 10 C to 0.1 C, but the capacity of the L2-LLO electrode can be recovered quickly. To further study the cycling performance of L0-LLO and L2-LLO electrodes at high rate, the samples were cycled at 5 C in the voltage range of 2.0-4.6 V, as presented in Fig. 7b. When cycled at a high rate of 5 C, the discharge capacity decreases more sharply due to the large polarization and structural instability [67,68]. All the electrodes exhibit faster capacity fading compared with those cycled at 1 C. However, La-substituted electrode still shows higher cycling capacity retention compared with the La-free electrode. It can be found that an expected capacity of $\sim 150 \text{ mA h g}^{-1}$ can be remained after 100 cycles for the L2-LLO electrode and the capacity retention is 88.8%. On the contrary, the L0-LLO electrode suffers a fast capacity fading and it only delivers 75.9 mA h g^{-1} with a capacity retention of 54.2% after 100 cycles. Such outstanding electrochemical performance of L2-LLO electrodes is a manifesto of the advantage of La doping. The reason is probably that the large increase in lattice parameters for the L2-LLO material can enhance the diffusion coefficient of Li^+ and lower the activation barrier for Li^+ diffusion with the increasing current, and the rate capability of the cathode materials is relevant to the electrochemical insertion/extraction of Li^+ [69,70]. In addition, the La substitution for partial Mn can stabilize the framework of the La-doped material during cyclic process, which presents a stable pathway for intercalation/deintercalation of Li^+ .

Fig. 7. (a) Rate capabilities of L0-LLO and L2-LLO electrodes; (b) the discharge capacity vs. cycle number for L0-LLO and L2-LLO electrodes at 5 C in the voltage range of 2.0-4.6 V.

To gain further insight into the difference in electrochemical performance between La-doped and un-doped LLO material, a GITT method is applied to evaluate the Li⁺ chemical diffusion coefficient (D_{Li^+} , cm² s⁻¹). A computational formula for the D_{Li^+} can be determined by Fick's second law as shown below.

$$D_{\text{Li}^+} = \frac{4}{\pi} \left(I_0 \frac{V_m}{FS} \right)^2 \left(\frac{dE/dx}{dE/dt^{1/2}} \right)^2, \quad t \ll \frac{L^2}{D_{\text{Li}^+}} \quad (1)$$

I_0 (A) is the applied current, V_m (cm³ mol⁻¹) represents the molar volume of compound, which is deduced from the crystallographic data, F (C mol⁻¹) is the Faraday constant, S (cm²) refers to the surface area of the electrode, and L (cm) represents the diffusion length.

Fig. 8a and b show the GITT curves of L0-LLO and L2-LLO electrodes during the second charge-discharge process from 2.0 V to 4.6 V, respectively. The plots of dE/dx and $dE/dt^{1/2}$ as a function of stoichiometry x during the charge process are exhibited in Fig. 8c and d, and the D_{Li^+} has been calculated based on formula (4) and the plots of D_{Li^+} as a function of x are exhibited in Fig. 8e. Comparatively, in spite of the variation of D_{Li^+} along with the x , the L2-LLO electrode can display a higher value

of Li^+ chemical diffusion coefficient compared with L0-LLO electrode. For the L2-LLO electrode, the D_{Li^+} can retain at an almost constant value ($\sim 6.20 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$). However, the average D_{Li^+} value of L0-LLO electrode is about $2.42 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. The results of GITT indicate that more stable matrix and broader Li^+ diffusion channel result from La substitution for partial Mn.

Fig. 8. The GITT curves of (a) L0-LLO and (b) L2-LLO electrodes as a function of time between 2.0 V and 4.6 V; (c) dE/dx , (d) $dE/dt^{1/2}$, and (e) the calculated D_{Li^+} values for the L0-LLO and L2-LLO electrodes as a function of the stoichiometry x .

4. Conclusions

In summary, a facile La doping strategy for the preparation of lithium-rich layered oxide material has been successfully put forward. The La can be introduced into Mn site via the solvothermal method and subsequent high-temperature calcination technique, generating a structural stabilization effect on the material. It's worth noting

that the $\text{Li}_{1.2}\text{Mn}_{0.52}\text{Ni}_{0.13}\text{Co}_{0.13}\text{La}_{0.02}\text{O}_2$ material displays optimal electrochemical performance among all La-doped samples. It delivers a high specific capacity of 286.4 mAh g⁻¹ at 0.1 C with high coulombic efficiency of 90.4 % and excellent cycling performance with 93.2% capacity retention, as compared to 58.4% for un-doped LLO electrode after 100 cycles at 1 C. Interestingly, the layered-to-spinel transformation and voltage fading can be efficiently mitigated by La substitution for partial Mn. Moreover, the La-doped LLO material reveals higher Li⁺ diffusion velocity and better rate capability than undoped LLO material, and it shows a high specific capacity of 127.1 mAh g⁻¹ at 10 C and outstanding cycling stability with 88.8% capacity retention after 100 cycles even at a high rate of 5 C. Besides, although this is the first report about La-doped lithium-rich layered oxide material, which represents remarkable cycling performance, mitigated voltage fading and eminent rate capability, the La-doped LLO cathode material is a promising and beneficial exploration for the development of high performance cathode material of lithium-ion batteries.

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