**Synthesis and electrochemical performance of micro-sized Li-rich layered
cathode material for Lithium-ion batteries**

Lingchao Pan^a, Yonggao Xia^{a,*}, Bao Qiu^a, Hu Zhao^a, Haocheng Guo^a, Kai Jia^a,
Qingwen Gu^a, Zhaoping Liu^{a,*}

^a *Ningbo Institute of Materials Technology & Engineering (NIMTE), Chinese
Academy of Sciences, Zhejiang 315201, PR China*

---

*Corresponding authors. Tel./Fax: +86-574-8668-5096.

E-mail: xiayg@nimte.ac.cn (Y. Xia), liuzp@nimte.ac.cn (Z. Liu).

ABSTRACT

Li-rich layered oxides with micro-sized primary particles usually exhibit higher pellet density and better cycling performance. However, it is often at the expense of high reversible capacity. Here, we reported a simple strategy through a new chemical lithiation with micro-sized spinel-precursors and $\text{Na}_2\text{S}_2\text{O}_8$ surface treatment to obtain micro-sized particles in the Li-rich $\text{Li}_{1.172}\text{Ni}_{0.135}\text{Co}_{0.135}\text{Mn}_{0.539}\text{O}_2$ oxide without compromising its discharge capacity (260 mAh/g at 0.1 C). Benefited from its larger particles and lower specific surface area, the obtained micron Li-rich layered material manifests its higher pellet density (3.18 g/cm^3) and better cycling performance in comparison with the nano-sized Li-rich layered material. After 100 cycles at 0.1 C, it can still deliver a capacity of 192 mAh/g with retention of 74 %, much higher than 167 mAh/g with retention of 67 % of the nano-sized sample. Moreover, the micron Li-rich layered material also exhibits good rate performance with a capacity of 174 mAh/g at 2 C benefited from the 3D Li^+ insertion/extraction channel of its surface spinel content. These results may provide a new insight on improving pellet density of high-performance Li-rich layered cathode materials.

Keywords:

Li-ion batteries; Micron Li-rich layered oxides; Two-step chemical lithiation method

1. Introduction

Lithium ion batteries (LIBs), since they were firstly commercialized by SONY Corporation, have been widely used in portable devices and will continue to play a major role in electric vehicles in the future [1-3]. However, for the realization of the later, developing higher-energy-density cathode materials are urgently needed. Among the reported cathode materials so far, Li-rich layered cathode materials, with a general formula of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M}=\text{Mn}, \text{Co}, \text{Ni}, \text{etc}$), have been regarded as one of the most promising candidates for next-generation cathode materials recently due to their low cost as well as high reversible capacity ($\sim 250 \text{ mAh g}^{-1}$) [4-10].

However, the Li-rich layered materials faced some drawbacks, namely, poor cycling performance, inferior rate performance, voltage decay and low pellet density. In order to overcome these defects, considerable efforts have been devoted, such as doping, coating, surface treatment and nano-crystallization [11-16]. Among all the modified methods, nano-crystallization is the most widely used strategy to enhance their discharge capacities and rate capabilities owing to short diffusion length and large active surface areas [11, 17, 18]. However, nano-materials easily cause side reactions with electrolyte and result in poor cycling performance [19-22]. For example, Manthiram and his group have synthesized nano-sized $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ with particle size of about 150 nm through Pechini method. After 50 cycles at 0.1 C, the capacity retention was only about 75% [12]. Furthermore, nano-crystallization also leads to low pellet density to decrease their volumetric energy density. Thus, it is necessary to develop a new strategy for Li-rich layered cathode materials towards

high pellet density and excellent cycling performance.

To the best of our knowledge, larger primary particles can do favor to the higher pellet density and better cycling performance in Li-ion cathode materials [23, 24]. Recently, Guo *et al.* prepared micro-sized conducting polymer coated LiFePO₄ with a high tap density of 2.02 g/cm³ and a high capacity retention of 87 % at 20 °C after 1000 cycles [23]. Meanwhile, Yue *et al.* synthesized submicron LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ with a capacity retention of 93.7 % at 1 °C after 40 cycles [24]. Some researchers have also attempted to prepare Li-rich layered oxides with large particle size by increasing calcination temperature or calcination time. Unfortunately, the particle size of Li-rich layered materials can hardly exceed 500 nm even at a high sintering temperature of 1000 °C and a long sintering time of 24 h [12]. What's worse, the sub-micron particles usually expense the discharge capacity of the Li-rich layered materials. Therefore, new synthesized route is designed to obtain larger Li-rich layered materials. Furthermore, surface treatment is also indispensable to enhance their discharge capacities.

In this paper, high-pellet-density Li-rich layered materials without compromising their electrochemical performance can be simply achieved by our newly developed two-step chemical lithiation method with which a micro-sized spinel-precursor was employed as the template. Moreover, based on our previous works [13], surface treatment by Na₂S₂O₈ aqueous solution further promote the reversible discharge capacity and rate capability. The structure, particle morphology, pellet density, BET specific surface area, valence of the transitional metal ions, electrochemical behaviors,

Cyclic Voltammetry and resistance of the Li-rich layered materials with micro-sized particles and nano-sized particles were investigated and compared. The results may provide a new insight on improving pellet density of high-performance Li-rich layered cathode materials, which is also suggestive to other cathode materials.

2. Experimental

2.1. Preparation of samples

Firstly, micro-sized $\text{Li}_{1.172}\text{Ni}_{0.135}\text{Co}_{0.135}\text{Mn}_{0.539}\text{O}_2$ was synthesized by a newly developed two-step chemical lithiation method, which was derived from the common sol-gel method [12]. $\text{C}_2\text{H}_3\text{O}_2\text{Li}\cdot 2\text{H}_2\text{O}$ (Aladdin, 99 % pure), $\text{C}_4\text{H}_6\text{O}_4\text{Mn}\cdot 4\text{H}_2\text{O}$ (Aladdin, 99.5 % pure), $\text{C}_4\text{H}_6\text{O}_4\text{Ni}\cdot 4\text{H}_2\text{O}$ (Aladdin, 99 % pure), and $\text{C}_4\text{H}_6\text{O}_4\text{Co}\cdot 4\text{H}_2\text{O}$ (Aladdin, 99 % pure) with mole ratio of 3 : 4 : 1 : 1 were firstly dissolved in deionized water. EDTA (Sinophar, 99.5 % pure) and $\text{C}_6\text{H}_8\text{O}_7\cdot \text{H}_2\text{O}$ (Sinophar, 99.5 % pure), acting as chelating agents, were added to NH_4OH (Sinophar, 25-28 % in water) aqueous solution. The metal acetate solution was then added to EDTA/citric acid solution. The PH of the mixture solution was adjusted to 8 by ammonium hydroxide. Then the purple mixture solution was heated in oil bath at 90 °C until a wet gel was formed. The wet gel was dried at 120 °C in the blast furnace. Then, a black fluffy aerogel was obtained, which was then fired at 450 °C for 5 h to remove the organic residues. Afterwards, the obtained precursor was calcined at 850 °C for 12 h to gain the micron spinel-precursor. Finally, required amounts of LiCO_3 (exceed 2 %) were mixed with the spinel-precursor. After sintered at 900 °C for 20 h, the desired micron

Li-rich layered oxide was obtained.

Secondly, the micro-sized Li-rich layered oxide was treated with $\text{Na}_2\text{S}_2\text{O}_8$ aqueous solution at a concentration of 40 g L^{-1} under continuous stirring for 24 h to further promote its electrochemical performance by chemical pre-delithiation. Afterwards, the powders were washed with deionized water. Finally, the samples were dried and fired at 300°C for 10 h with a heating rate of 5°C min^{-1} in air.

To understand the difference between the micron and nano-sized Li-rich layered oxide, the nano-sized Li-rich layered oxide was prepared by the conventional sol-gel method which includes the same procedures as the aforementioned two-step chemical lithiation method except for experiencing the spinel-precursor. The total sintering time and the sintering temperature are as same as the two-step method.

Herein, the $\text{Li}_{1.172}\text{Ni}_{0.135}\text{Co}_{0.135}\text{Mn}_{0.539}\text{O}_2$ prepared *via* a conventional method and a new two-step chemical lithiation method was designated as C-LR-NCM and N-LR-NCM, respectively. Meanwhile, the micron N-LR-NCM after treatment with $\text{Na}_2\text{S}_2\text{O}_8$ aqueous solution was named as T-LR-NCM.

2.2. Characterization

The crystal structure of the samples was characterized by X-ray diffraction (XRD, Bruker D8 Advance) with $\text{Cu K}\alpha$ radiation at a scan rate of 1° min^{-1} between 10 and $90^\circ 2\theta$. The XRD data with Rietveld refinement were carried out using GSAS software. The morphology was observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S4800). Raman spectra were recorded on a Raman

spectrometer (Renishaw inVia Reflex) coupled with microscope in a reflectance mode with a 532 nm laser source. Infrared spectra were collected on a Fourier transform infrared spectrometer (FT-IR, Thermo Fisher Scientific NICOLET6700). XPS measurements were carried out with an X-ray photoelectron spectrometer (Kratos AXIS Ultra DLD), using a focused monochromatized Mg K α radiation (1253.6 eV). All binding energies were referenced with respect to aliphatic carbon signal (C_{1s}) to 248.8 eV. The specific surface area was measured by specific surface area analyzer (Micromeritics ASAP 2020M). The metal contents of the materials were carried out by an inductively coupled plasma-atomic emission spectrometry (ICP, Optima 2100). The Pellet density (PD) was obtained by making 15 mm diameter pellets with about 0.3 g of powder under the pressure of 20 MPa. The thickness and diameter of the pellet were measured and the PD was calculated. *Electrochemical measurement*

Electrochemical performances were evaluated with 2032-type coin cells between 2.0 and 4.8 V. The coin cells were composed of the as-prepared Li-rich layered oxides cathode, lithium metal anode, 1 M LiPF₆ in ethylene carbonate / diethyl carbonate (v / v=3 : 7) electrolyte, and Celgard polypropylene separator. The cathode was prepared by casting slurries onto an aluminum foil. The slurry consists of 80 wt.% active material, 10 wt.% super P carbon, and 10 wt.% polyvinylidene (PVdF) binder with *N*-methyl-2-pyrrolidone (NMP) as the solvent. Then, the casted mixture was dried at 80°C to evaporate the solvent in the air. Afterwards, the cathode disks were punched out to prepare the coin cells. Each disk was loaded 4 ~ 5 mg active materials. The coin cells were assembled in a glovebox filled with highly pure argon gas. The

galvanostatic charge-discharge measurements were carried out on LAND battery test systems (Wuhan, China) between 2.0 and 4.8 V with various charge-discharge rates from 0.1 to 2 C at room temperature and 55 °C, respectively. 1 C equals to a current density of 250 mA/g. The Cyclic Voltammetry was measured by the Autolab modular electrochemical workstation (Autolab PGSTAT302N) with a scan rate of 0.1 mV s⁻¹ in the voltage range of 2.0 to 4.8 V. Electrochemical impedance spectroscopy (EIS) was measured on an Autolab modular electrochemical system (Autolab PGSTAT302N) over a frequency range of 100 kHz to 0.1 Hz **after 2 cycles at 0.2 C in a voltage of 2.0-4.8 V.**

3. Results and discussion

3.1. Structure and morphology

Fig. 1 (a) shows the morphology of the Li-rich layered material prepared by the conventional sol-gel method (C-LR-NCM) with particle size of ~400 nm. In contrast, the micron sample (Fig. 1 (c)) prepared thorough the new two-step method (N-LR-NCM) was obtained successfully by maintaining the polyhedral structure with particle size of ~2 μm of the spinel-precursor (Fig. 1 (b)). The surface of the particles of the micro-sized sample after Na₂S₂O₈ treatment (T-LR-NCM) is more rough (Fig. 1 (d)), which is well consistent with the reported literature [25]. The specific surface areas and pellet density of all the samples are shown in Table 1. The specific surface area of the micro-sized N-LR-NCM after treatment (3.84 m²/g) is obviously lower than that of the C-LR-NCM (5.49 m²/g), which may do favor to its cycle performance.

Moreover, the pellet density of the T-LR-NCM (3.18 g/cm^3) is much higher than 2.92 g/cm^3 of the C-LR-NCM resulted from its micron particles. The high pellet density is known to be favorable to the achievable volumetric energy density.

In order to estimate the accurate delithiated amount, Li, Mn, Co and Ni contents of N-LR-NCM and T-LR-NCM were determined by ICP (from the ratios of the amounts of Li, Mn, Co and Ni and fixing the total amount of transition metal ions to 0.809), as shown in Table 2. The Ni, Co, Mn contents of the prepared N-LR-NCM are same as the designed $\text{Li}_{1.172}\text{Ni}_{0.135}\text{Co}_{0.135}\text{Mn}_{0.539}\text{O}_2$ chemical stoichiometry, although the Li content is slightly lower than the designed amount. It is also founded that 0.053 Li^+ has extracted from the N-LR-NCM after treatment with $\text{Na}_2\text{S}_2\text{O}_8$ solution as designed. As we know, Li-deficit surface content tends to facilitate the formation of surface spinel after heat treatment.

Fig. 2 shows that all the samples have a well-defined hexagonal $\alpha\text{-NaFeO}_2$ crystal structure with a space group of $R\text{-}3m$. The weak reflections between 20° and 25° can be indexed to the monoclinic $C2/m$ space group, which are relevant to the LiMn_6 cation ordering in the transition metal layers of Li_2MnO_3 [4, 9, 26]. Besides, the experimental XRD patterns were analyzed by *Rietveld* method with an assumption of $R\text{-}3m$ structure to investigate the detail structural information. The Rietveld refinement results are shown in Table 3. The c/a of all the samples is greater than 4.899 implying an explicit layer structure. The remarkable splits in $(006)_{\text{hex}}/(102)_{\text{hex}}$ and $(108)_{\text{hex}}/(110)_{\text{hex}}$ further verify the layered structure of all the samples and the good structural compatibility between Li_2MnO_3 and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ [27].

However, it should be noted that there are 0.0334 (total 0.133) Ni in the 3a site in the C-LR-NCM, significantly more than 0.0109 and 0.0114 in the micron N-LR-NCM and T-LR-NCM. This result indicates that nano-sized C-LR-NCM suffers from more severe cation disordering, which is harmful to the electrochemical performance.

Infrared spectra of the as-prepared materials are shown in Fig. 3. The bands at 614 cm^{-1} and 550 cm^{-1} appear for the N-LR-NCM, which are assigned to the O–M–O bending modes and the asymmetric stretching modes of M–O bonds in MO_6 octahedral in the layered phase [27-29]. However, after treatment with $\text{Na}_2\text{S}_2\text{O}_8$ aqueous solution, the peak at 614 cm^{-1} disappeared for the micro-sized LR-NCM, which is attributed to a change in M-O covalence causing by the formation of some oxygen vacancies [13].

The Raman scattering, a sensitive probe for the local symmetry, is also introduced for better understanding their structures (Fig. 4). According to earlier works, there are only two Raman-active peaks (E_g and A_{1g}) in the ideal LiMO_2 ($M = \text{Co}$ and/or Ni) layered oxides with $R\bar{3}m$ space group. In the case of Li_2MnO_3 with $C2/m$ space group, six Raman-active vibrational modes ($4A_{1g}+2B_g$) exist [30-32]. It should be noted that additional bands, wavenumber shifts and broadenings may occur for a non-ideal material characterized by non-stoichiometry, substitutions or exchanges. In present study, four major Raman active modes have been observed at about 630 cm^{-1} , 595 cm^{-1} , 550 cm^{-1} , 485 cm^{-1} for the T-LR-NCM with some weak peaks at 667 cm^{-1} , 426 cm^{-1} , 402 cm^{-1} , 370 cm^{-1} . The peaks at 595 cm^{-1} and 485 cm^{-1} are assigned to A_{1g} and E_g of the LiMO_2 ($M = \text{Mn}, \text{Co}$ and Ni), respectively [32]. The weak bands below 440

cm⁻¹ originate from the Li₂MnO₃-like structure of the Li-rich layered oxides [31]. The additional shoulder peaks at about 667 cm⁻¹ is attributed to the presence of a shorter Mn–O and/or Co–O bond resulted from local structure distortion [32]. The Raman-active band at about 630 cm⁻¹ originates from the spinel-like structure in the composite materials [31]. For such a band in all the samples, the reason may be that the lithium amount is not sufficient to form the ideal Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ with layered-layered structure during the preparation process. Compared to that of the T-LR-NCM, the Raman spectra of the C-LR-NCM and N-LR-NCM possess similar bands with a little change of position and intensity of the peaks. To estimate the amount of spinel-like content, the peaks area ratios between the peaks area at 630 cm⁻¹ and the total peaks area were calculated (Table 4). Among the three samples, the T-LR-NCM contains the most spinel-like content (18.4 %) due to the formation of surface spinel **facilitated by Li-deficit surface content** as our previous works reported [13]. The N-LR-NCM contains a little less spinel-like content (14.8 %) than the C-LR-NCM (15.4 %).

Additionally, the X-ray photoelectron spectroscopy (XPS) was carried out to analyze the valence of the transition-metal ions. Fig. 5 (a) shows the Mn 2p spectra, which mainly reflect the existence of the Li_{1.172}Ni_{0.135}Co_{0.135}Mn_{0.539}O₂ oxide particles. Two peaks are observed in all the three samples, which can be assigned to the manganese 2p_{3/2} at 642.4 eV and 2p_{1/2} at 654.1 eV. These binding energies are in good agreement with the data on MnO₂, which means the chemical state in Mn⁴⁺ [33]. **The 2p_{3/2} and 2p_{1/2} binding energies of Co in the three samples are 779.9 eV and 795.6 eV**

corresponding to Co_2O_3 , representing chemical state of Co^{3+} [34, 35]. Additionally, two shakeup satellite peaks (denoted as “sat”) (789.9 and 805.7 eV) confirmed the chemical state of Co^{3+} . Due to the difference of sign-noise ratio, the intensity of satellite peaks may change among the three samples, such as Co $2p_{3/2}$ satellite peak at 789.9 eV. In comparison with the nano-sized sample, sign-noise ratio of XPS spectra for the micron Li-rich oxides is lower because of their poorer electronic conductivity which leads to lower intensity of satellite peaks in return. The $2p_{3/2}$ and $2p_{1/2}$ binding energies of Ni in the three samples are 854.8 eV and 872.8 eV corresponding to NiO, representing chemical state of Ni^{2+} [34, 35]. For Mn, Co and Ni, there is no obvious peak shift between the N-LR-NCM and T-LR-NCM, indicating that valence of Mn, Co and Ni didn’t change after surface treatment even though the surface spinel phase formed during the surface treatment process. This is ascribed to that the O_2 release, which mainly occurred in the Li_2MO_3 (M = Ni, Co, Mn), can hardly introduce the further oxidation of the tetravalent transition metal ions [13].

3.2. Electrochemical measurements

Fig. 6 (a) shows the first charge/discharge curves of the C-LR-NCM, N-LR-NCM and T-LR-NCM at 0.1 C. All samples possess similar first charge capacities of 120 mAh/g before 4.5 V. This capacity of slope is corresponding to the oxidation of Ni^{2+} and Co^{3+} to Ni^{4+} and Co^{4+} . It means similar chemical states of Ni and Co in the three samples, which well complies with the XPS studies. The initial charge capacity at 4.5 V plateau of the N-LR-NCM is lower than that of the C-LR-NCM because Li_2MnO_3

in the N-LR-NCM with micro-sized particles is more difficult to be electrochemically activated. After treatment with $\text{Na}_2\text{S}_2\text{O}_8$ solution, the N-LR-NCM holds a similar first charge capacity at 4.5 V plateau. Furthermore, the first discharge capacity of the micron N-LR-NCM was greatly enhanced from 217 mAh/g to 260 mAh/g after $\text{Na}_2\text{S}_2\text{O}_8$ treatment. Meanwhile, $\text{Na}_2\text{S}_2\text{O}_8$ treatment leads to a higher discharge potential during the initial 30 mAh/g and lower discharge potential for the rest of the discharge curve. The features are characteristics of a spinel-like component which is consistent with the Raman results. The obvious improvement of specific discharge capacity of the micron N-LR-NCM is benefited from its generated surface spinel with 3D Li^+ migration channel, which has been systematically proved by our previous works [13]. This may provide a potential strategy to prepare Li-rich layered oxides with high energy density for practical application. The rate capabilities of three samples were compared by testing at incremental discharge rates of 0.1, 0.2, 0.5, 1 and 2 C after charged at 0.1 C (Fig. 6 (b)). Benefited from the 3D Li^+ insertion/extraction channel of its surface spinel, the micro-sized T-LR-NCM manifests its best rate performance among the three samples. Even at 2 C discharge rate, it can deliver a capacity of 174 mAh/g (about 65.1% of its capacity at 0.1 C). Fig. 6 (c) and (d) show the discharge profiles of the C-LR-NCM and T-LR-NCM at different discharge rate. With the increase of the discharge rate, the discharge voltage of all the samples decreases because of higher polarization at larger discharge current.

The cycling performance of the cathodes was also tested at room temperature and 55°C. Fig. 7 (a) shows the cycling performance of the cathodes at a charge/discharge

rate of 0.1 C. After 100 cycles at 0.1 C, the micron N-LR-NCM manifests its best cycling performance with capacity retention of 80 % among the three samples. On the contrary, the nano-sized C-LR-NCM suffers from rapid deterioration of specific capacity with the lowest retention of 67 % after 100 cycles. It is generally believed that side reactions are harmful to the cycle stability. Therefore, the lower specific surface area of the micro-sized N-LR-NCM is beneficial to excellent cycling-ability due to less side reactions with the electrolyte. The micron T-LR-NCM delivers a capacity of 192 mAh/g with retention of 74 % after 100 cycles. The decrease of capacity retention of the T-LR-NCM is attributed to a slight increase of the specific surface area of the T-LR-NCM compared to that of the N-LR-NCM. Fig. 7 (b) shows the cycling performance at 0.5 C after 3 cycles at a charge/discharge rate of 0.2 C at 55 °C . All the samples exhibit better electrochemical performance at high temperature than that at room temperature, consistent with works reported before [10]. Furthermore, the micro-sized samples before and after treatment both exhibit higher capacity retention at 55 °C than that of the nano-sized sample, which are consistent with the results at room temperature. The micron T-LR-NCM exhibits a capacity of 218 mAh/g with retention of 90.7 % after 70 cycles at 55 °C. In contrast, the C-LR-NCM only delivers a capacity of 180 mAh/g with retention of 84.2 % after 70 cycles in the same tested condition.

To investigate different redox processes occurring during the electrochemical reaction, cyclic voltammograms (CVs) of three samples were tested in the voltage range of 2.0-4.8 V at a scan rate of 0.1 mV/s. Fig. 8 shows that the shapes of the CVs

and electrochemical reactions of the three samples are in good agreement with previous studies [17, 25, 36]. In the initial anodic processes of the N-LR-NCM and C-LR-NCM, there are two oxidation peaks at about 4.1 V and 4.6 V. The 4.1 V peak is due to the oxidation process of $\text{Ni}^{2+}/\text{Co}^{3+}$ to higher oxidation states. While, the 4.6 V peak originates from the removal of superfluous lithium from the transition-metal layer along with simultaneous oxygen evolution [37, 38]. Besides the two oxidation peaks like the samples before treatment in the initial anodic process, one additional small oxidation peak appears at about 2.95 V for the T-LR-NCM, which is attributed to a surface spinel contribution [25, 39]. The CV result complies with the ICP and Raman spectrum results and further confirms the existence of surface spinel in the T-LR-NCM. It should be noted that the peak at about 4.6 V in the first charge process of the T-LR-NCM becomes as strong as that of the C-LR-NCM, indicating that the micro-sized sample is activated effectively after $\text{Na}_2\text{S}_2\text{O}_8$ treatment. During the following cathodic processes of the three samples, one weak reduction peak at voltage range between 4.35 and 4.5 V and other main peak at about 3.8 V are observed, which are related to the reduction of the $\text{Ni}^{4+}/\text{Co}^{4+}$ to lower oxidation states. Moreover, a reduction peak at about 3.3 V related to the structural transformation of layer to spinel-like phase becomes more and more obvious as cycle increases. Interestingly, a small reduction peak at about 2.6 V appears in the initial cathodic reaction of the C-LR-NCM and T-LR-NCM and vanishes in the following cycles. This irreversible peak is ascribed to the reduction of oxygen or its species considering that if the peak originates from the redox of $\text{Mn}^{3+}/\text{Mn}^{4+}$, it would be reversible [40].

In order to investigate the dynamics of the three samples, we have introduced Electrochemical impedance spectra (EIS) after 2 cycles at 0.2 C for the three samples. Fig. 9(a) and (c) shows the Nyquist plots and Bode plots of the three samples, respectively. There are two semicircles in Nyquist plot of all the samples which correspond to two peaks in the Bode plots. The high-frequency semicircle is caused by SEI resistance (R_s). Compared to the micron samples, the nano-sized C-LR-NCM has a more flat high-frequency peak in the Bode plot. It can be explained that the C-LR-NCM has higher specific surface area than the N-LR-NCM material, leading to a higher surface activity and resulting in thicker SEI layer [41]. The intermediate-frequency semicircle originates from the charge-transfer resistance (R_{ct}). After $\text{Na}_2\text{S}_2\text{O}_8$ treatment, intermediate-frequency peak of the micron N-LR-NCM shifts to low frequency which implies the formation of some other surface content. In order to estimate resistance in detail, we have also fitted the experimental data by equivalent circuit (Fig. 9(b)). The impedance parameters of equivalent circuit are shown in the Table S1. All the fitting results are consistent with above analysis. Thinner SEI layer leads to lower R_s . Thus, the N-LR-NCM manifests lower R_s (17.4 Ω) than that of the C-LR-NCM (36.2 Ω) which is benefited from its poorer activity originating from lower specific surface area. After treatment with $\text{Na}_2\text{S}_2\text{O}_8$ solution, the R_s of N-LR-NCM slightly increased from 17.4 Ω to 24.6 Ω which is well consistent with the BET study. Due to its shorter Li^+ and electron migration distance, the R_{ct} of nano C-LR-NCM (590 Ω) is lower than that of micron N-LR-NCM (1386 Ω). Meanwhile, the R_{ct} of C-LR-NCM dramatically decreased to 298 Ω after $\text{Na}_2\text{S}_2\text{O}_8$

treatment which results from the 3D Li^+ diffusion channel of surface spinel.

4. Conclusions

In summary, a high-pellet-density Li-rich layered material without compromising its reversible capacity (260 mAh/g) was successfully obtained through a simple chemical lithiation with micro-sized spinel-precursors and $\text{Na}_2\text{S}_2\text{O}_8$ surface treatment. After a chemical lithiation process, the micro-sized spinel-precursor transformed to layered configuration along with good maintenance of the morphology. The micron particles result in much higher pellet density (3.21 g/cm^3) than that of the nano-sized Li-rich layered oxide (2.92 g/cm^3). Since the micro-sized Li-rich layered oxide often suffers from severe capacity compromising, surface treatment by $\text{Na}_2\text{S}_2\text{O}_8$ aqueous solution was employed to eliminate such drawback based on our previous work. In spite of different synthesis routes, all the obtained samples possess a well-defined layered structure with a space group of $R\bar{3}m$. However, the C-LR-NCM suffers from more severe cation mixing, which may deteriorate its electrochemical performance. Raman spectra and CVs verify the formation of surface spinel through chemical pre-delithiation and similar electrochemical reactivity with the nano-sized sample for the micron T-LR-NCM.

Compared to the nano-sized C-LR-NCM, the micron T-LR-NCM manifests its better cycling performance because of less side reaction with the electrolyte, which is significantly concerning to the specific surface area. After 100 cycles at room temperature, the capacity of the micron T-LR-NCM (192 mAh/g) is much higher than

167 mAh/g of the nano-sized C-LR-NCM at 0.1 C. The cycling performance at 55 °C follows the same law. Moreover, benefited from the 3D Li^+ insertion/extraction channel of its surface spinel, the T-LR-NCM exhibits good rate performance with a capacity of 174 mAh/g at 2 C. These results may provide a new insight on improving pellet density of high-performance Li-rich layered cathode materials, which is also suggestive to other cathode materials.

Acknowledgments

This work was financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA09010101), the Science and Technology Service Network Initiative of the Chinese Academy of Science (KFJ-EW-STS-110), the Ningbo Science and Technology Innovation Team (2012B82001), the Cooperation of the Chinese Academy of Science and the United states Department of Energy (174433KYSB20150047).

References

- [1] M. Armand, J.M. Tarascon, *Nature*, 451 (2008) 652-657.
- [2] Y.M. Chiang, *Science*, 330 (2010) 1485-1486.
- [3] J.M. Tarascon, M. Armand, *Nature*, 414 (2001) 359-367.
- [4] M.M. Thackeray, S.-H. Kang, C.S. Johnson, J.T. Vaughey, R. Benedek, S.A. Hackney, *Journal of Materials Chemistry*, 17 (2007) 3112-3125.
- [5] N. Yabuuchi, K. Yoshii, S.-T. Myung, I. Nakai, S. Komaba, *Journal of the American Chemical Society*, 133 (2011) 4404-4419.
- [6] F.F. Yang, Y.J. Liu, S.K. Martha, Z.Y. Wu, J.C. Andrews, G.E. Ice, P. Pianetta, J. Nanda, *Nano Letters*, 14 (2014) 4334-4341.
- [7] H. Yu, R. Ishikawa, Y.-G. So, N. Shibata, T. Kudo, H. Zhou, Y. Ikuhara, *Angewandte Chemie-International Edition*, 52 (2013) 5969-5973.
- [8] J. Bareno, C.H. Lei, J.G. Wen, S.H. Kang, I. Petrov, D.P. Abraham, *Advanced materials*, 22 (2010) 1122-1127.
- [9] Z.H. Lu, D.D. MacNeil, J.R. Dahn, *Electrochemical and Solid State Letters*, 4 (2001) A191-A194.
- [10] T. Ohzuku, M. Nagayama, K. Tsuji, K. Ariyoshi, *Journal of Materials Chemistry*, 21 (2011) 10179-10188.
- [11] Y. Zhang, P. Hou, E. Zhou, X. Shi, X. Wang, D. Song, J. Guo, L. Zhang, *Journal of Power Sources*, 292 (2015) 58-65.
- [12] C.-C. Wang, K.A. Jarvis, P.J. Ferreira, A. Manthiram, *Chemistry of Materials*, 25 (2013) 3267-3275.
- [13] S. Han, B. Qiu, Z. Wei, Y. Xia, Z. Liu, *Journal of Power Sources*, 268 (2014) 683-691.
- [14] G.-Z. Wei, X. Lu, F.-S. Ke, L. Huang, J.-T. Li, Z.-X. Wang, Z.-Y. Zhou, S.-G. Sun, *Advanced materials*, 22 (2010) 4364-+.
- [15] F. Wu, N. Li, Y. Su, H. Shou, L. Bao, W. Yang, L. Zhang, R. An, S. Chen, *Advanced materials*, 25 (2013) 3722-3726.
- [16] F. Zheng, C. Yang, X. Xiong, J. Xiong, R. Hu, Y. Chen, M. Liu, *Angewandte Chemie*, (2015).
- [17] P. Hou, L. Xu, J. Song, D. Song, X. Shi, X. Wang, L. Zhang, *Journal of Materials Chemistry A*, 3 (2015) 9427-9431.
- [18] H.-J. Kim, H.-G. Jung, B. Scrosati, Y.-K. Sun, *Journal of Power Sources*, 203 (2012) 115-120.
- [19] P. Oh, S. Myeong, W. Cho, M.-J. Lee, M. Ko, H.Y. Jeong, J. Cho, *Nano Letters*, 14 (2014) 5965-5972.
- [20] Y.-K. Sun, S.-M. Oh, H.-K. Park, B. Scrosati, *Advanced materials*, 23 (2011) 5050-5054.
- [21] Z. Han, H. Zhan, Y. Zhou, *Materials Letters*, 114 (2014) 48-51.
- [22] J. Shojan, C.V. Rao, L. Torres, G. Singh, R.S. Katiyar, *Materials Letters*, 104 (2013) 57-60.
- [23] L. Guo, Y. Zhang, J. Wang, L. Ma, S. Ma, Y. Zhang, E. Wang, Y. Bi, D. Wang, W.C. McKee, Y. Xu, J. Chen, Q. Zhang, C. Nan, L. Gu, P.G. Bruce, Z. Peng, *Nature Communications*, 6 (2015).
- [24] P. Yue, Z. Wang, W. Peng, L. Li, H. Guo, X. Li, Q. Hu, Y. Zhang, *Scripta Materialia*, 65 (2011) 1077-1080.
- [25] D.Y.W. Yu, K. Yanagida, H. Nakamura, *Journal of the Electrochemical Society*, 157 (2010) A1177-A1182.
- [26] A.R. Armstrong, M. Holzapfel, P. Novak, C.S. Johnson, S.-H. Kang, M.M. Thackeray, P.G. Bruce, *Journal of the American Chemical Society*, 128 (2006) 8694-8698.

- [27] T. Ohzuku, A. Ueda, M. Nagayama, *Journal of the Electrochemical Society*, 140 (1993) 1862-1870.
- [28] B. Ammundsen, G.R. Burns, M.S. Islam, H. Kanoh, J. Roziere, *Journal of Physical Chemistry B*, 103 (1999) 5175-5180.
- [29] C. Nithya, V.S.S. Kumari, S. Gopukumar, *Physical Chemistry Chemical Physics*, 13 (2011) 6125-6132.
- [30] L.Q. Zhang, K. Takada, N. Ohta, K. Fukuda, M. Osada, L.Z. Wang, T. Sasaki, M. Watanabe, *Journal of the Electrochemical Society*, 152 (2005) A171-A178.
- [31] C.M. Julien, M. Massot, *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, 100 (2003) 69-78.
- [32] C.V. Rao, J. Soler, R. Katiyar, J. Shojan, W.C. West, R.S. Katiyar, *Journal of Physical Chemistry C*, 118 (2014) 14133-14141.
- [33] N. Treuil, C. Labrugere, M. Menetrier, J. Portier, G. Campet, A. Deshayes, J.C. Frison, S.J. Hwang, S.W. Song, J.H. Choy, *Journal of Physical Chemistry B*, 103 (1999) 2100-2106.
- [34] L. Li, X. Zhang, R. Chen, T. Zhao, J. Lu, F. Wu, K. Amine, *Journal of Power Sources*, 249 (2014) 28-34.
- [35] K.M. Shaju, G.V.S. Rao, B.V.R. Chowdari, *Electrochimica Acta*, 48 (2002) 145-151.
- [36] J. Lin, D. Mu, Y. Jin, B. Wu, Y. Ma, F. Wu, *Journal of Power Sources*, 230 (2013) 76-80.
- [37] Z.H. Lu, L.Y. Beaulieu, R.A. Donaberger, C.L. Thomas, J.R. Dahn, *Journal of the Electrochemical Society*, 149 (2002) A778-A791.
- [38] L.F. Jiao, M. Zhang, H.T. Yuan, M. Zhao, H. Guo, W. Wang, X. Di Zhou, Y.M. Wang, *Journal of Power Sources*, 167 (2007) 178-184.
- [39] B. Song, H. Liu, Z. Liu, P. Xiao, M.O. Lai, L. Lu, *Scientific Reports*, 3 (2013).
- [40] Y. Chen, G. Xu, J. Li, Y. Zhang, Z. Chen, F. Kang, *Electrochimica Acta*, 87 (2013) 686-692.
- [41] C. Liang, L. Liu, Z. Jia, C. Dai, Y. Xiong, *Electrochimica Acta*, 186 (2015) 413-419.

Table and Figure captions

Table 1

BET specific surface area (BET) and Pellet density (PD) of all the samples.

Table 2

Chemical composition of N-LR-NCM and T-LR-NCM determined by ICP.

Table 3

Rietveld refinement results of XRD data of all the samples. The Rietveld refinement was carried out with the space group of *R-3m*.

Table 4

Estimated spinel-like content in percentage by the ratio between peak area at about 630 cm^{-1} and the total peaks area.

Fig. 1. FE-SEM images of the C-LR-NCM (a), spinel-precursor (b), N-LR-NCM (c), and T-LR-NCM (d) samples.

Fig. 2. XRD patterns of the C-LR-NCM (a), N-LR-NCM (b) and T-LR-NCM (c) samples and the Rietveld refinement results.

Fig. 3. IR spectra of the C-LR-NCM, N-LR-NCM and T-LR-NCM samples.

Fig. 4. Raman spectra of the C-LR-NCM, N-LR-NCM and T-LR-NCM samples. The spectra were fitted using pseudo-Voigt bands in order to allow their easier comparison. The x mark represents the experimental data, while the red solid lines are the fit results.

Fig. 5. XPS spectra of (a) Mn 2p, (b) Co 2p, (c) Ni 2p. A, B, C corresponding to the spectra collected from the C-LR-NCM, N-LR-NCM and T-LR-NCM samples, respectively. The 'sat' represents satellite peak.

Fig. 6. (a) Initial charge/discharge profiles at 0.1 C between 2.0 and 4.8 V, (b) Rate capability at different C rates after charging at 0.1 C in the voltage range of 2.0-4.8 V of the C-LR-NCM, N-LR-NCM and T-LR-NCM samples. The discharge curves of the C-LR-NCM sample (c) and the T-LR-NCM sample (d) at different C rates. 1 C equals to 250 mA/g.

Fig. 7. Cycling performance of the C-LR-NCM, N-LR-NCM and T-LR-NCM samples at (a) room temperature at 0.1 C, and (b) 55°C at 0.5 C after activation at 0.2 C between 2.0 and 4.8 V.

Fig. 8. Cyclic voltammograms measured between 2 and 4.8 V at the scan rate of 0.1 mV s⁻¹ of the C-LR-NCM, N-LR-NCM and T-LR-NCM samples.

Fig. 9. (a) Nyquist plots of the C-LR-NCM, N-LR-NCM and T-LR-NCM samples after 2 cycles at 0.2 C in the voltage range of 2.0-4.8 V. The inset picture is the corresponding amplified (a) at high frequency. (b) The equivalent circuits used to fit the experimental data. The open symbols represented the experimental data, while the solid line is the fit results. (c) Corresponding Bode representation of the phase angle.

Table 1

	C-LR-NCM	N-LR-NCM	T-LR-NCM
BET (m ² /g)	5.49	3.43	3.84
PD (g/cm ³)	2.92	3.21	3.18

Table 2

	Li	Ni	Co	Mn
N-LR-NCM	1.168	0.135	0.135	0.539
T-LR-NCM	1.115	0.135	0.135	0.539

Table 3

	$a_{\text{hex.}}/\text{\AA}$	$c_{\text{hex.}}/\text{\AA}$	c/a	Ni at 3a	Ni at 3b	$R_{\text{wp}}/\%$
C-LR-NCM	2.8508	14.2391	4.995	0.0334	0.0996	4.80
N-LR-NCM	2.8512	14.2385	4.994	0.0109	0.1221	5.16
T-LR-NCM	2.8508	14.2405	4.995	0.0114	0.1216	4.24

Table 4

	C-LR-NCM	N-LR-NCM	T-LR-NCM
Percentage spinel-like	15.4%	14.8%	18.4%

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.