**Eliminate the voltage decay of lithium-rich
 $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Ni}_{0.14}\text{Co}_{0.14}\text{O}_2$ cathodes by controlling the
electrochemical process**

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Broader Context

In order to resolve the global issues of fossil energy shortage and environmental pollution, intensive studies have been focused on the development of renewable energy sources and energy storage systems. Li-ion batteries have been regarded as a promising energy storage candidate for applications in electric/hybrid electric vehicles and smart grids. Among various cathode materials, Li-rich Mn-based layered solid-solution system has attracted much attention due to its high energy density and power density with significantly reduced cost and toxicity. And it has been considered as the next generation cathode material. However, it still confronts a severe problem of voltage decay while cycling, which makes it unable to monitor the voltage-capacity situation, and leads to the uniformity and safety problems of Li-ion batteries. Here we present a method to eliminate the voltage decay by tuning charge/discharge voltage range. The layered structure transforms to spinel phase at a high charge cut-off voltage, and remains steady at a low cut-off voltage with no apparent voltage decay occurring. The facile but effective method will greatly promote the practical use of Li-rich Mn-based material in the near future.

Li-rich cathode material $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Ni}_{0.14}\text{Co}_{0.14}\text{O}_2$ is prepared by a co-precipitation method. By tuning charge/discharge voltage range, the voltage decay during cycling is eliminated remarkably. The transmission electron microscope (TEM) images show that spinel phase occurs both in 2.0-4.6 V and 2.0-4.4 V condition, but not dominant in the latter. Interestingly, after 2.0-4.6 V cycling, spinel structure is uniform inside the grain, while at the grain surface lattice rotation structure is discovered with a spinel to layer phase occurs alternately, which has not been reported before. The Raman spectra reveal that spinel content significantly increases after 2.0-4.6 V cycling, but remains at a low level after 2.0-4.4 V cycling. The dQ/dV plots indicate voltage plateau of layered-spinel combined structure decreases from 3.2 V to 2.8 V after 200 cycles at 2.0-4.6 V, which confirms that the layered structure transforms to spinel phase at high charge cut-off voltage (4.6 V), while remains steady at low cut-off voltage (4.4 V). During 200 charge/discharge cycles, discharge voltage decay per cycle at 2.0-4.4 V is 0.2875 mV, while 1.7415 mV at 2.0-4.6 V, i.e. 6.06 times of the value of 2.0-4.4 V.

1. Introduction

Lithium ion batteries (LIBs) have been considered the most promising energy storage technologies for mobile electronics, electric vehicles and renewable energy systems^{1,2}. Comparing with conventional cathode materials such as LiCoO_2 , LiMn_2O_4 and LiFePO_4 , Li-rich Mn-based layered solid-solution system $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ($\text{M} = \text{Co, Ni, Mn}_{1/2}\text{Ni}_{1/2}, \text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}$) has emerged as potential next generation cathode materials for LIBs due to its high specific capacity, high energy density, low cost and low toxicity³⁻⁵. However, commercial application of Li-rich cathode materials is hindered by several drawbacks such as voltage decay and capacity decrease during cycling, poor rate performance and a large initial irreversible capacity (IRC) loss. Especially, voltage decay is a unique but critical problem that lithium-rich material confronts in comparison with other cathode materials. The main defect is making it impossible to monitor the voltage-capacity situation, and leading to the uniformity and safety problems of LIBs. Besides, according to electric energy $W=U \cdot I \cdot t$, the output energy density decreases with voltage decay.

Recent researches have focused on the voltage decay issue. Wang et al.⁶ studied the phase transformation process of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ while cycling, and raised the opinion about origin of voltage decay: formation of spinel phase. After AlF_3 coating, spinel formation can only be delayed but not be prevented. Sung et al.⁷ researched the electrochemical activation of $\text{Li}_{1.167}\text{Ni}_{0.233}\text{Co}_{0.100}\text{Mn}_{0.467}\text{Mo}_{0.033}\text{O}_2$ electrode at different operating voltage windows and achieved the conclusion that Li_2MnO_3 was

activated gradually at low voltage (4.55 V) but rapidly at high voltage (4.7 V, 4.8 V). Thackeray et al.⁸ prepared $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ material by using a Li_2MnO_3 template, and then acid treating to introduce transition metal ions. By this method transition metal ion content is tuned and voltage decay is countered.

Lithium-rich material owns a particularly high capacity owing to the activation of electrochemical inactive Li_2MnO_3 phase⁹⁻¹⁵. But at the same time, MnO_2 phase formed after Li_2MnO_3 activation confronts a severe problem of converting to spinel phase, and resulting in voltage decay. To our knowledge, this phenomenon is inherent property of layered manganese oxide materials and can hardly be overcome.

Based on this, unlike previous reports, herein we design a method for the first time to accelerate the phase transformation by tuning the charge upper-limit voltage at a high value, so the phase transformation process can be finished in a few cycles. Then material structure remains stable while cycling at a low upper-limit voltage. By this novel method voltage decay is eliminated significantly.

2. Experimental procedure

2.1. Materials preparation

The Li-rich layered material $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Ni}_{0.14}\text{Co}_{0.14}\text{O}_2$ was synthesized by a coprecipitation process using nickel-cobalt-manganese carbonate as the precursor. Stoichiometric amounts (4:1:1) of $\text{Mn}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Co}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ were dissolved in deionised water to form a mixed solution. In the condition of

vigorous agitation, the PH was adjusted to the range of 7 to 8 by adding aqueous ammonia. Then the obtained precipitated powders were filtered, rinsed and dried in air.

The targeted Li-rich material was prepared by a solid-state reaction of lithium carbonate with nickel-cobalt-manganese carbonate precursor. 5 wt.% excess of Li_2CO_3 is added to compensate its volatilization at high temperature. The resultant mixture was heated in air at 500 °C for 5 h followed by calcination at 850 °C for 10 h to obtain the final product.

2.2. Characterization and Electrochemical Measurement

The crystal structures of the samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance) with Cu Ka radiation at a scan rate of $0.5^\circ \text{ min}^{-1}$. The morphology was characterized using field emission scanning electron microscopy (FE-SEM, Hitachi S4800) and transmission electron microscope (TEM, FEI Tecnai F20). Raman spectra were recorded on a Raman spectrometer (Renishaw inVia Reflex) coupled with microscope in a reflectance mode with a 532 nm excitation laser source.

Electrochemical tests were performed using a CR2032-type coin cell. The working electrode was consisted of 80 wt.% as-prepared material, 10 wt.% carbon conductive agents (super P) and 10 wt.% polyvinylidene fluoride (PVdF) and compressed onto the aluminum foil. The electrode was dried overnight at 80 °C in a vacuum oven prior to use. Cell assembly was performed in a glove box (Superstar 1220/750, Mikrouna) filled with pure argon. Lithium metal was used as counter

electrode and the electrolyte was 1 M LiPF_6 dissolved in a mixed solvent of ethylene carbonate (EC)/ diethyl carbonate (DMC) (3:7 by volume, 53015A, Guotai-Huarong New Chemical Material Co., Ltd). A celgard 2300 membrane was used as the cell separator. Galvanostatic Charge/discharge experiments were performed on a battery test system (LAND CT2001A, Wuhan Jinnuo Electronic Co. Ltd, China) at 0.2 C. Measurements after cycling was performed at a full discharged state.

3. Results and discussion

In order to study the structural evolution and electrochemical characteristics of materials during cycling, these samples after cycling are tested: Sample A: pristine material; Sample B: 2.0-4.6 V for 5 cycles; Sample C: 2.0-4.6 V for 5 cycles + 2.0-4.6 V for 100 cycles; Sample D: 2.0-4.6 V for 5 cycles + 2.0-4.6 V for 200 cycles; Sample E: 2.0-4.6 V for 5 cycles + 2.0-4.4 V for 100 cycles; Sample F: 2.0-4.6 V for 5 cycles + 2.0-4.4 V for 200 cycles

The FE-SEM images of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ pristine materials and materials after electrochemical cycling are revealed in Fig. 1. Morphology of pristine material prepared through co-precipitation method is revealed in Fig. 1(a, b) with different magnification. The material is composed of spheres with diameter in the range of 12-18 μm and 4-8 μm . Primary structure observed in high magnification image is identified as nanoparticles of 80-110 nm in width. Fig. 1(c-g) are pictured by cells after cycling, so spheres are surrounded by super P, and spheres exposed are

mostly in small diameter. After long-term charge/discharge cycling, sphere structure retains well on the whole.

Phase transformation can be confirmed vigorously by TEM. Fig. 2 exhibits the HR-TEM images of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ materials after activation between 2.0-4.6 V for 5 cycles and the corresponding Fast Fourier Transform images. In Fig. 2(a), layer structure with space group of R-3m exists after activation. The distance between the adjacent lattice fringes can be assigned to the interplanar distance of hexagonal layered phase, which is $d_{003}=0.47$ nm. The small spots in diffraction pattern indicate the 9R structure, which corresponds to the region marked by blue line. Besides, spinel phase with space group of Fd3m is also found in the same sample, as shown in Fig. 2(b). After activation, cubic spinel has been identified by diffraction pattern along the [111] zone axis. The TEM images confirm phase transformation to spinel has occurred during the activation process.

To further study the structural evolution of Li-rich material during cycling, samples after 200 electrochemical cycles are investigated by TEM, presented in Fig. 3. After 2.0-4.6 V cycling, bulk phase of the material is spinel phase with zone axis [111], as shown in blue frame of Fig. 3(a). Interestingly, Lattice rotation occurs at the surface of the grain, illustrated in red frame. The spinel and layered C2/m structure occurs alternately. Unlike spinel structure is uniform inside the grain, the grain surface is a spinel to layer rotation structure. The black line marks the boundary between these two phases. As to the sample after 2.0-4.4 V cycling shown in Fig. 3(b),

spinel phase with crystal interplanar distance $d=0.29$ nm is also found in the whole grain, but not dominant, and is only found occasionally. In mild cycling condition, layered structure remains steady on the whole, which is much important to resolve voltage decay problem.

Because of the poor statistics of TEM measurements, more accurate measurement on the quantity of layered and spinel structure is carried out. Fig. 4 reveals the Raman spectroscopy of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ pristine material and materials after electrochemical cycling. According to previous reports^{16, 17}, there exist two Raman-active vibrational modes in layered lithium transition metal oxide with R-3m symmetry. They have been described as A_{1g} with the symmetrical stretching of M–O, and E_g with the symmetrical deformation. Curve (a) shows Raman spectrum of pristine material. Two peaks of wave number near 592 cm^{-1} and 479 cm^{-1} are assigned as A_{1g} and E_g respectively. An additional small peak at 430 cm^{-1} originates from the Li_2MnO_3 -like structure of the Mn-rich region due to the reduced local symmetry of $C2/m$ ^{17, 18}.

In order to achieve more convincing and accurate results when analysing Raman spectra data of materials after cycling, Raman peak position of spinel phase is necessary. Pristine Li-rich material is treated with $\text{Na}_2\text{S}_2\text{O}_8$ reagent to deintercalate part of Li ions, and spinel structure is formed at the surface^{19, 20}. Here this material is used to determine the spinel Raman peak position, as shown in curve (b), and denoted as $x\text{MnO}_2 \cdot (1-x)\text{Li}_2\text{MnO}_3$. Spinel peak with $Fd3m$ symmetry emerges at around 622

cm^{-1} , ascribing to A_{1g} peak.

Raman pattern of samples after electrochemical cycling is exhibited in curves (c-g). Coexistence of peaks at 592 cm^{-1} and 622 cm^{-1} indicates strongly the coexistence of both spinel and layered phase. This mixed behavior is in very good agreement with the observation drawn from the HR-TEM images. The mixed peak between 500 cm^{-1} and 700 cm^{-1} can be divided into two single peaks through lorentz fit, as presented in Fig. 4(c-g).

Besides, intensity ratios of these two peaks are calculated for quantity analysis. If we suppose peak intensity ratio of layered to spinel equals their content ratio, the spinel phase content percentage can be estimated, as shown in Table 1. After activation between 2.0-4.6 V for 5 cycles, spinel phase emerges, and its percentage is 37.0%. In subsequent cycles between 2.0-4.4 V, spinel percentage increases a bit, but not much, indicating layered structure remains steady below 4.4 V. In contrast, spinel content increases significantly while cycling between 2.0-4.6 V. After 200 cycles, Raman peak of spinel is quite higher than that of layered phase, achieving 68.0%. In conclusion, phase transformation is countered in mild charge/discharge condition, which is much beneficial to eliminate voltage decay.

XRD patterns of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ materials before and after electrochemical cycles are presented in Fig. 5. All the diffraction peaks, except weak peaks between $2\theta = 20\text{--}25^\circ$, are indexed to $\alpha\text{-NaFeO}_2$ hexagonal type structure with a space group symmetry of R-3m. Weak peaks located between $2\theta = 20\text{--}25^\circ$ show the

presence of monoclinic Li_2MnO_3 phase with $C2/m$ symmetry. These peaks are attributed to the short-range Li–Mn cation ordering in the transition metal layers^{5, 21, 22}. In addition, the enlargement of the XRD patterns in the range of $2\theta = 18^\circ$ - 19° is also displayed in Fig. 5. For pristine material, diffraction peak at $2\theta = 18.67^\circ$, which corresponds to the (003) crystal plane, is a characteristic peak of as-prepared Li-rich material. After cycling at 2.0-4.6 V and 2.0-4.4 V for 200 cycles, the peak position shifts to 18.57° and 18.55° respectively. The shifting to low angles is caused by two reasons: one is phase transformation from layered to spinel, and the other is expansion of crystal lattice during intercalation/extraction of Li ions. Unfortunately, the contribution of these two causes is not distinguishable here.

Fig. 6 depicts the charge/discharge curves of pristine Li-rich material and corresponding discharge average voltage of the initial five cycles, i.e. electrochemical activation process. The discharge capacity of the 1st cycle is 247.2 mAh/g, and the value increases to 260.4 mAh/g gradually, which means Li_2MnO_3 is activated continuously at 2.0-4.6 V cycling. Specific discharge energy is divided by specific capacity to calculate the average voltage. The 1st cycle discharge average voltage is 3.6155 V, and the value decreases to 3.5671 V for the 5th cycle. The average voltage decay is 9.6800 mV, and the rapid decay is mostly caused by layered structure transformation to spinel structure, which is accordance with TEM and Raman results.

In the sequent cycling procedure, electrochemical characteristics are different while cycling at different charging cut-off voltages, as revealed in Fig. 7. R1 peak is

attributed to the reduction reaction of nickel and cobalt ions in the LiMO_2 component⁷,²³. The individual peaks from nickel and cobalt ion contributions are not distinguishable in these plots. R2 and R3 peaks are from reducing manganese ions in layered type and layered-spinel combined structures, respectively^{7, 8}. At the 6th cycle's dQ/dV plot, R3 peak appears at around 3.2 V, illustrating the formation of spinel phase. The dQ/dV peaks after 2.0-4.6 V cycling shift to lower position significantly, as shown in Fig. 7(a, b). R2 peak becomes very small, indicating the layered structure diminishes a lot. R3 peak shifts to about 3.0 V at the 106th cycle, and further to 2.8 V at the 206th cycle. The peak position change verifies the phase transformation continues during the whole 2.0-4.6 V cycling process. On the contrary, after long-term cycling at 2.0-4.4 V for 100 and 200 cycles, the position of R2 and R3 peaks remain steady. This is a strong evidence that layered structure hardly converts to spinel phase any further.

To get a better understand on the structural evolution of the material while Li-ions intercalate/extract at different charging cut-off voltages, the schematic image of ion migration is presented in Fig. 8. After 2.0-4.6 V activation, Li-ions extract from Li layer and transition metal (TM) layer, forming Li-ion vacancy. Then the TM ions migrate to the Li-ion vacancy, and that's the origin of spinel phase. In the sequent cycling process at 2.0-4.6 V, TM ion migration continues so spinel content increases, leading to severe voltage decay. While in milder condition of the 2.0-4.4 V charge/discharge situation, Li-ion extraction extent is lower. The residual Li-ions can

support the structure and no more TM ions diffuse into Li-ion vacancy. So the average voltage can retain during a long term.

The detailed discharge capacity and discharge average voltage curves are given in Fig. 9. The material delivers 259.8 mAh/g at the 6th cycle of the 2.0-4.6 V cycling, and remains 210.4 mAh/g at the 206th cycle, leading to a capacity retention of 81.0%. The discharge average voltage decreases from 3.5719 V at the 6th cycle to 3.2236 V at the 206th cycle, thus the value of voltage decay is 1.7415 mV per cycle. As regards to the 2.0-4.4 V situation, cycling capacity and average voltage possess much higher stability. The discharge capacity of the 6th cycle is 228.4 mAh/g, and the value remains at 192.4 mAh/g at the 206th cycle, corresponding to a capacity retention of 84.2%. The discharge average voltage of the 6th cycle is 3.5293 V, after cycling at 2.0-4.4 V for 200 cycles, it declines to 3.4718 V, and the voltage decay velocity is 0.2875 mV per cycle. The voltage decay speed of 2.0-4.6 V is 6.06 times of that of 2.0-4.4 V condition. In milder charging cut-off voltage, layered-spinel structure remains stable and so does the electrochemical plateau.

4. Conclusions

In summary, Li-rich cathode material $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ with uniform spherical shape has been fabricated through a co-precipitation method and calcination procedure. A facile method of tuning the charge/discharge cut-off voltage has been developed to eliminate the voltage decay during electrochemical cycling process.

Spinel phase occurs after 5 cycles' activation at 2.0-4.6 V. After sequent long term cycling at 2.0-4.6 V, spinel phase percentage increases gradually. However in milder condition of 2.0-4.4 V, spinel content remains steady and is not dominant even after 200 cycling. In milder condition, the residual Li-ions can maintain the layered-spinel combined structure and no more TM ions diffuse to Li-ion vacancy to form more spinel. As a result, during 200 charge/discharge cycles, voltage decay per cycle is 0.2875 mV, while the value of 2.0-4.6 V is as high as 6.06 times of that of 2.0-4.4 V. Therefore, we believe that such a small voltage decay of Li-rich material can satisfy the demand of control ability and homogeneity of electric vehicle batteries.

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Figure captions

Fig. 1 FE-SEM images of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ materials before and after electrochemical cycles: (a, b) pristine material, (c) Sample B, (d) Sample C, (e) Sample D, (f) Sample E, (g) Sample F

Fig. 2 HR-TEM images of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ materials after 2.0-4.6 V for 5 cycles and the corresponding Fast Fourier Transform images: (a) R-3m layered structure; (b) Fd3m spinel structure

Fig. 3 HR-TEM images of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ materials after cycling at different voltage range and the corresponding Fast Fourier Transform images: (a) 2.0-4.6 V; (b) 2.0-4.4 V

Fig. 4 Raman spectra of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ materials before and after electrochemical cycles: (a) pristine material, (b) spinel $x\text{MnO}_2 \cdot (1-x)\text{Li}_2\text{MnO}_3$, (c) Sample B, (d) Sample C, (e) Sample D, (f) Sample E, (g) Sample F

Fig. 5 XRD patterns of the $\text{Li}_{1.14}\text{Mn}_{0.54}\text{Co}_{0.14}\text{Ni}_{0.14}\text{O}_2$ materials before and after electrochemical cycles: (a) pristine material, (b) Sample B, (c) Sample C, (d) Sample D, (e) Sample E, (f) Sample F

Fig. 6 (a) the charge/discharge curves of pristine material of the initial five cycles and **(b)** corresponding discharge average voltage

Fig. 7 the charge/discharge curves of pristine material of the 1st, 6th, 106th, 206th cycles and corresponding discharge dQ/dV plots: (a, b) 2.0-4.6 V; (c, d) 2.0-4.4 V

Fig. 8 schematic image of the ion migration and structural evolution of the material

while cycling at different charging cut-off voltages

Fig. 9(a) cycling discharge capacities at different cut-off voltages and **(b)** corresponding average voltage.

Table 1 estimated spinel phase content percentage

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Fig. 3 HR-TEM images of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$ materials after cycling at different voltage range and the corresponding Fast Fourier Transform images: (a) 2.0-4.6 V; (b) 2.0-4.4 V

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Table 1 estimated spinel phase content percentage

	$I_{\text{layered}} : I_{\text{spinel}}$	Spinel percentage
Sample B	1.70	37.0%
Sample C	0.60	62.5%
Sample D	0.47	68.0%
Sample E	1.63	38.0%
Sample F	1.57	38.9%