

# High-capacity Li-rich Mn-based Cathodes for Lithium-ion Batteries

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**ABSTRACT** Layered Li-rich Mn-based oxides are promising cathode materials for Li-ion batteries due to their high capacity and high operation voltage. However, their commercial applications are hindered by irreversible capacity loss in the first charge-discharge process, voltage decay during cycling, inefficient cyclability and rate capability. Many attempts have been performed to solve such issues, including the mechanism study and strategies to improve the electrochemical performance. This article provides a brief review and future perspective on the main challenges of the high-capacity Li-rich Mn-based cathodes for Li-ion batteries.

**Keywords:** Li-ion batteries, Li-rich Mn-based cathodes, the first charge-discharge process, voltage decay, cyclability, rate capability; DOI: 10.14102/j.cnki.0254-5861.2011-2718

## 1 INTRODUCTION

Recently, the low available specific capacity of traditional cathode materials such as LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiFePO<sub>4</sub> is becoming a bottleneck to the increase of energy densities of the lithium-ion batteries (LIBs) for electric vehicles and electricity grid. Layered Li-rich Mn-based oxide cathode (LMC) materials, a solid solution of Li<sub>2</sub>MnO<sub>3</sub> and LiMO<sub>2</sub> (M = Ni, Mn, Co), are considered as potential candidate cathodes for the next-generation LIBs due to its high specific capacity (> 250 mAh g<sup>-1</sup>), high average discharge voltage (> 3.5 V) and

low cost<sup>[1, 2]</sup> (Fig. 1a and 1b). Nevertheless, commercial applications of Li-rich Mn-based cathode materials are challenged by three main drawbacks. First, a large irreversible capacity loss happens in the first charge-discharge process<sup>[3]</sup> (Fig. 1c). Second, significant voltage decay occurs during cycling<sup>[4]</sup> (Fig. 1d). Third, their cyclability and rate capability are not sufficient<sup>[5, 6]</sup> (Fig. 1e).

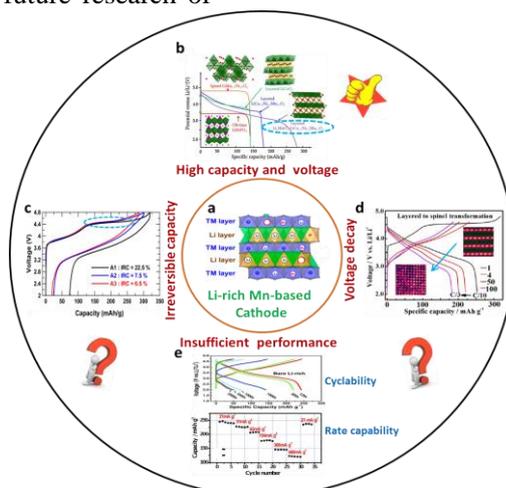
To solve such problems, many researches have been done, including the mechanism study and attempt to improve the electrochemical performance. This article comprehensively presents the challenge and recent progress of high-capacity Li-rich Mn-

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based cathodes from a fundamental perspective and will also provide suggestions for future research of high-energy cathodes.



**Fig. 1.** (a) Structure units of Li-rich Mn-based cathodes (LMC); From ref. [1], copyright of ACS; (b) Capacity and operation voltage comparisons of the present common cathodes for LIBs; From ref. [2], copyright of ACS; (c) Charge-discharge curves showing the irreversible first-cycle charge-discharge process of LMC; From ref. [3], copyright of nature; (d) Charge-discharge curves at different cycle number showing the voltage decay of LMC; From ref. [4], copyright of ACS; (e) The poor cyclability and rate capability of bare LMC; From ref. [5, 6], copyright of Wiley

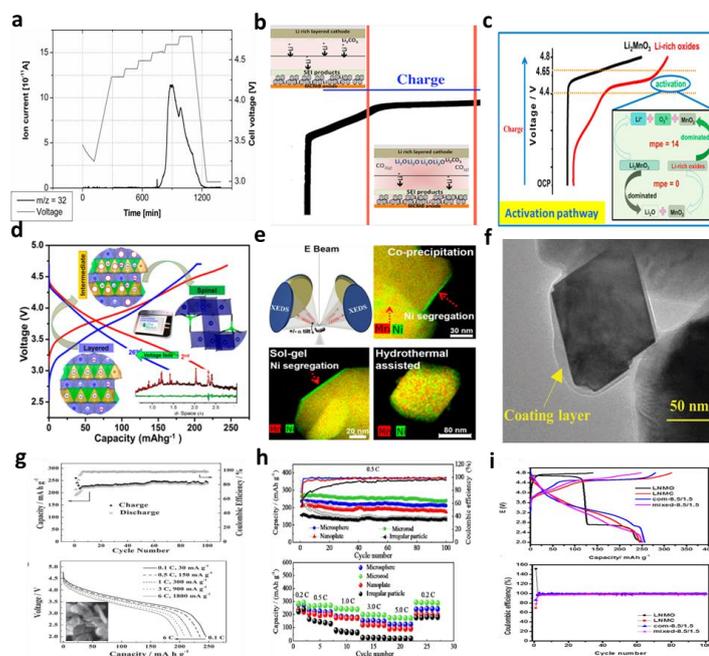
## 2 THE FIRST IRREVERSIBLE CHARGE-DISCHARGE PROCESSES

$\text{Li}_2\text{MnO}_3$  activation is the key and most attractive reaction of Li-rich oxides in the first charge-discharge process, which is the origin of its extra-high capacity<sup>[30]</sup>. Many studies have been done to understand the activation process of  $\text{Li}_2\text{MnO}_3$ . Bruce's group firstly observed the  $\text{O}_2$  release during the first charge process, and proposed an O loss accompanied with  $\text{Li}^+$  extraction mechanism for  $\text{Li}_2\text{MnO}_3$  activation<sup>[31]</sup> (Fig. 2a). Then they re-determined that the  $\text{O}_2$  release is from the electrolyte decomposition at high voltage after ten years<sup>[30]</sup>. Formation of localized electron holes on O atoms ( $\text{O}_2^{2-}$ ) was experimentally observed instead at the  $\text{Li}_2\text{MnO}_3$  activation region, and ex-situ resonant inelastic X-ray scattering (RIXS) was used as detect tool; The  $\text{O}_2^{2-}$ -localized electron holes can reversibly redox during the charge-discharge process<sup>[30]</sup>, and such a behavior was called as "oxygen redox". The reversible oxygen redox phenomenon was supported by Ceder's group using the first-principle calculations<sup>[7]</sup>. Afterwards, Chueh's group adopted ex-situ

scanning transmission X-ray microscope (STXM) and obtained a coupling phenomenon between oxygen redox and transition metal cation migration<sup>[8]</sup>. However, the limitation of these results is that they are achieved using ex-situ methods<sup>[3, 8]</sup> or calculations<sup>[7]</sup>. While *in-situ* Raman was applied for  $\text{Li}_2\text{MnO}_3$  activation study, entirely different  $\text{Li}_2\text{O}$  evolution<sup>[9]</sup> (Fig. 2b) and  $\text{O}^{2-}/\text{O}^-$  redox observation were acquired<sup>[10]</sup>. Besides, Raman and RIXS ( $<100$  nm) can only obtain the surface information of Li-rich materials. To get the real-time bulk information during charge-discharge process, Sun's Group adopted *in-situ* X-ray diffraction (XRD) and electrochemical quartz crystal microbalance (EQCM) to investigate the first-cycle behavior of Li-rich oxides, which can get the bulk structure evolution and mass change<sup>[11, 12]</sup>.  $\beta\text{-MnO}_2$  product and phase transformation of  $\beta\text{-MnO}_2$  to layered  $\text{Li}_{0.9}\text{MnO}_2$  were observed using *in-situ* XRD<sup>[11]</sup>. *In-situ* EQCM results demonstrate that both  $\text{Li}_2\text{O}$  evolution and oxygen redox exist in bare  $\text{Li}_2\text{MnO}_3$  and LMC materials, while  $\text{Li}_2\text{O}$  evolution is dominated in bare  $\text{Li}_2\text{MnO}_3$  and oxygen redox in LMC cathode<sup>[12]</sup> (Fig. 2c). This explains why the Li-rich material ( $0.5\text{Li}_2\text{MnO}_3$  ·

0.5LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>) has a higher capacity than the mean value of Li<sub>2</sub>MnO<sub>3</sub> and LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>. However, the real species of Li<sub>2</sub>O and O<sub>2</sub><sup>2-</sup> were not observed using other direct tools. From above, there is still controversy about the first charge-discharge process of LMC cathodes. One possible reason for the inconsistency of different groups' work is the

composition difference of LMC cathodes they used. And *in-situ* methods development, which can get both the surface and bulk information, is vital to unravel the internal first charge-discharge mechanism. This is further benefit to reduce the irreversible capacity in the first cycle.



**Fig. 2.** (a) Operando mass spectrometry showing the first-cycle oxygen release at high voltage; From ref. [31], copyright of nature; (b) Scheme of the Li<sub>2</sub>O evolution during the first cycle; From ref. [9], copyright of ACS; (c) Scheme of different activation ways of bare Li<sub>2</sub>MnO<sub>3</sub> (Li<sub>2</sub>O evolution domination) and Li<sub>2</sub>MnO<sub>3</sub> component in LMC (oxygen redox domination); From ref. [12], copyright of ACS; (d) Scheme of the voltage decay mechanism showing metal cations migration for layered-to-spinel conversion; From ref. [1], copyright of ACS; (e) EDS mapping showing the different Mn/Ni distribution in Li-rich particles obtained by different synthesis methods; From ref. [16], copyright of ACS; (f) TEM image showing the guar gum (GG) binder coated on LMC particle; From ref. [19], copyright of RSC; copyright of ACS; (g) Cyclability and rate performance of crystal habit-tuned LMC nanoplates; SEM image of the LMC nanoplates is insert; From ref. [21], copyright of Wiley; (h) Structure-dependent cyclability and rate capability of LMC cathodes; From ref. [22], copyright of Elsevier; (i) Initial charge-discharge profiles and Coulombic efficiencies of Li-rich, spinel, Li-rich layered/spinel composite and physical mixture of Li-rich and spinel; From ref. [25], copyright of ACS

### 3 VOLTAGE DECAY

The Li-rich cathodes suffer voltage decay during cycling, which means average discharge voltage decreases with the cycling number. The voltage decay mechanism was always attributed to layered-to-spinel phase transformation and migration of Mn and Li between transition metal layer and lithium

layer<sup>[1, 4]</sup> (Fig. 2d), which are obtained using ex-situ transmission electron microscope (TEM) and neutron powder diffraction. Some more detailed work revealed that the layered-to-spinel phase transformation prefers to take place in lattice defect<sup>[13]</sup>; *In-situ* XRD and Mass spectroscopy (MS) results demonstrated that a low Co/Ni ratio LMC released no lattice oxygen at the first cycle, which leads to a

milder voltage decay behavior<sup>[14]</sup>. Based on this mechanism, it is reasonable that doping and structure modulation can remit voltage decay, e.g. Al<sup>3+</sup> doping<sup>[15]</sup> and metal ions distribution regulation<sup>[16]</sup> (Fig. 2e). The conventional oxides coatings, such as Al<sub>2</sub>O<sub>3</sub>, LiAlO<sub>x</sub>, ZrO<sub>2</sub> and so on have been proved that they have little-to-zero effect on voltage decay mitigation<sup>[17]</sup>. Some functional coatings (e.g. LiFePO<sub>4</sub><sup>[18]</sup>) partly suppress voltage decay, but the reason was ascribed to bulk metal ion doping of core Li-rich materials caused by surface modification. But when organic guar gum (GG), which only includes C, H, O elements and lack of metal ions, was applied as the binder of LMC cathode electrode, a coating layer on LMC particles was observed after cycling<sup>[19]</sup>. Such a coating layer is composed of GG and solid electrolyte interphase (SEI), leading to an abnormal voltage fade remission<sup>[19]</sup>. To the best of our knowledge, there are no reports that electrolyte decomposition produced SEI can induce bulk doping of particles<sup>[26, 27]</sup>. And it is infeasible that an organic GG binder can induce bulk doping. The extraordinary voltage decay mitigation by GG binder indicates an in-depth mechanism existing. But Sun's work doesn't reveal the specific role of water-soluble GG binder<sup>[19]</sup>. Further studies still need to be done to reveal the root origin of voltage decay, especially using *in-situ* methods, and strategies to eliminate voltage decay of LMC cathodes are urgent to develop.

#### 4 CYCLABILITY AND RATE CAPABILITY IMPROVEMENT

Li-rich cathode materials suffer capacity fade during cycling, and its rate capability is still not enough for commercial applications due to its structure instability, side reactions with electrolyte and low Li<sup>+</sup> conductivity<sup>[20]</sup>. To improve the cyclability and rate capability of Li-rich materials, the most common methods were doping, surface modification, structure regulation and composition adjustment<sup>[20-25]</sup>. Doping and surface modifications

always need to introduce inert metal ions or coatings, such as Mg<sup>2+</sup>, Ti<sup>3+</sup>, ZrO<sub>2</sub>, etc.<sup>[20, 28]</sup>, which results in capacity decrease of Li-rich materials. In comparison, structure regulation and composition adjustment only simply require synthesis condition and raw materials ratio controlling, such as tuning the thermodynamic and kinetic conditions<sup>[29]</sup>, optimizing the particle shape, particle size, crystal orientation, morphology and layered/spinel ratio, and so forth<sup>[21-25]</sup>. And such simple structure regulation and composition adjustment methods can improve the cyclability, rate capability, and initial Coulomb efficiency while keeping capacity<sup>[21-25]</sup>.

For example, Sun's group prepared crystal habit-tuned nanoplates with increased (010) nanoplate, which exhibit excellent cyclability and rate performance<sup>[21]</sup> (Fig. 2g); High rate-capability Li-rich cathodes with hierarchical micro/nanostructure were synthesized by solvothermal and coprecipitation methods<sup>[22]</sup>; The relationship between the morphologies and electrochemical properties were also revealed<sup>[23]</sup> (Fig. 2h). Layered/spinel composite materials with spinel Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> composition were obtained using one-step solvothermal and Pechini methods, respectively<sup>[24, 25]</sup>; The cyclability, rate capability and first-cycle Coulomb efficiency were improved in the same time, while the capacity was well kept, compared to the bare layered Li-rich cathodes<sup>[24, 25]</sup>. A comparison of bare Li-rich, spinel, Li-rich layered/spinel, physical mixture of Li-rich and spinel indicate the positive role of integrated spinel in electrochemical performance improvement (Fig. 2i).

#### 5 SUMMARY AND PERSPECTIVE

In summary, three main drawbacks hindering the commercial applications of Li-rich Mn-based cathode materials for LIBs were briefly reviewed. Based on the existing experimental and theoretical results, some solid conclusions and perspectives are as follows: 1) Developing *in-situ* research techniques, which can obtain both surface and bulk information,

is vital to clarify the unclear first charge-discharge process and voltage fade mechanism, especially the origin of extra-high capacity of LMC cathodes and the function of organic coating layer on voltage decay mitigation; 2) The different compositions of Li-rich materials used in different groups' research may be part of the reason why different results were obtained, even using the same characterization method; It is urgent to build a quantitative composition-mechanism-performance relationship of Li-rich cathodes, which can guide the future research and applications; 3) Structure regulation and composition

adjustment can provide a simple and valid way to achieve efficient cyclability, rate capability and the first-cycle Coulombic efficiency; Unclear first charge-discharge process and voltage decay are the present key issues hindering the applications of LMC cathodes; Overall, we believe Li-rich Mn-based cathodes will play a vital role in next-generation LIBs due to its unique advantages of high capacity, high operation voltage and low cost. And further studies need to be focused on the charge-discharge mechanism and elimination of voltage fade during cycling.

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