A Review on Element Doping in Li-Rich Cathode Materials for Lithium-Ion Batteries

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Abstract. With the growing demand for clean energy, lithium-ion batteries (LIBs) have become essential in applications like electric vehicles due to their high energy density and efficiency. However, conventional cathode materials such as $LiCoO_2$ and $LiFePO_4$ are limited by relatively low specific capacities. To address this, Li-rich Mn-based cathode materials (LRMs) have been proposed as promising alternatives, offering greater specific capacity. Despite their potential, LRMs suffer from challenges like voltage decay, poor rate performance, and safety problems during cycling. This review discusses the use of element doping, such as the introduction of Al, Cr, and Ti, to improve the structural stability and electrochemical properties of LRMs. While significant progress has been made in enhancing capacity and cycle life, issues like voltage fade and long-term stability persist. Future research should focus on optimizing doping strategies, enhancing structural integrity, and reducing costs to facilitate the widespread use of LRMs in energy storage and electric vehicle systems.

1 Introduction

As the demand for clean energy rises, particularly for electric vehicles and sustainable technologies, lithium-ion batteries (LIBs) have become increasingly crucial. LIBs are widely used in portable devices like smartphones and laptops [1], as well as in large-scale applications due to their high energy density and lightweight nature. Nonetheless, the rapid advancements in the energy sector place higher demands on LIBs, including increased capacity, faster discharge rates, and improved safety. Compared to cathodes, anodes are less expensive, with graphite being a particularly cost-effective and commercially viable material. Consequently, the high cost of cathode materials hinders the progress in enhancing specific capacity and reducing overall LIB costs. Traditional cathode materials, such as $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$, although commercially successful, have limitations due to their relatively low specific capacity [2-4]

To overcome these limitations, LRMs have emerged as promising alternatives, offering higher specific capacities [5] and relatively lower costs. In these materials, surplus lithium ions within the Li_2MnO_3 phase occupy one-third of the transition metal layer sites, resulting in the development of a superstructure. Despite their potential, LRMs face challenges such

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as poor rate performance, voltage decay, high initial irreversible capacity, low Coulombic efficiency, and structural transformations from layered to spinel structures [6].

Among various enhancement strategies—including surface coating, ion doping, as well as structural optimization—doping has demonstrated significant promise [7]. This technique involves substituting elements like Al [8], Cr [9], or Ti [10] into the cathode material's crystal lattice, thereby improving structural stability, electronic conductivity, and electrochemical performance.

An overview of recent advancements in doping LIBs will be provided in this review, focusing on improvements in specific capacity, discharge capacity, and cycling life achieved through the introduction of various metals into LRMs.

2 Lithium-rich materials

2.1 Composition and structure

Lithium-rich materials (LRMs) consist of two components: Li_2MnO_3 and $LiMO_2$. Li_2MnO_3, which is part of the monoclinic system with the C/2m space group, shares similarities with $LiMO_2$, characterized by the α-$NaFeO_2$ structure in the hexagonal system (R-3m space group). Both exhibit a similar lithium layer, albeit with some distortion. The key difference lies in the transition metal layer: in Li_2MnO_3, one-third of the transition metal is substituted by lithium ions, whereas $LiMO_2$ contains only transition metals, as illustrated in Fig. 1. The structure of LRMs remains debated; Dr. Haijun Yu and etc propose a two-phase composite of monoclinic and hexagonal crystals [11]. By using atomic-resolution scanning transmission electron microscopy (STEM), their experimental results directly unveil the two-phase coexistence of LiTMO2 and Li2MnO3-like structures. While Karalee A. Jarvis and etc advocate for a single-phase solid solution structure [12]. With the help of XRD and STEM, they conclude that Li [Li0.2Ni0.2Mn0.6]2 composition is integral, but other compositions especially with excess lithium may lead to two-phase coexistence.

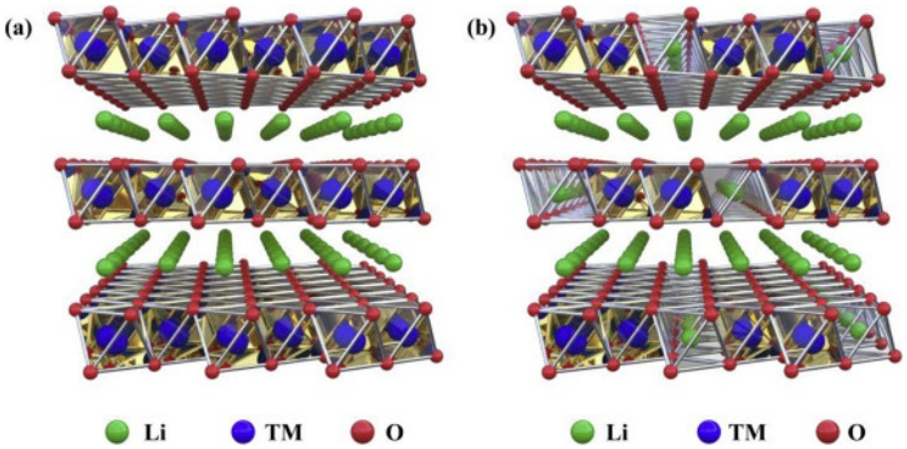

Fig. 1. (a) $LiTMO_2$ composition structure and (b) Li_2MnO_3 composition structure in LRM [13].

2.2 Unique situation

Fig. 2 depicts the lithium-rich oxide material PLLO with a P2-type layered structure, featuring two distinct platforms in its charge-discharge curve. The initial platform, occurring before 4.5 V, resultss from the oxidation of transition metals as lithium ions are deintercalated,

with Co^{3+} and Ni^{2+} oxidizing to Co^{4+} and Ni^{4+}, respectively. The platform at 4.5 V appears only during the first charge, leading to debates regarding its origin. The reversible oxygen redox hypothesis suggests that at this voltage, oxygen ions may partially oxidize (from O^{2-} to O^{-} or O_2^{-}), contributing additional capacity. Furthermore, the migration of transition metals may cause voltage decay. The low initial efficiency of lithium-rich manganese is attributed to an irreversible phase change that produces Li_2O.

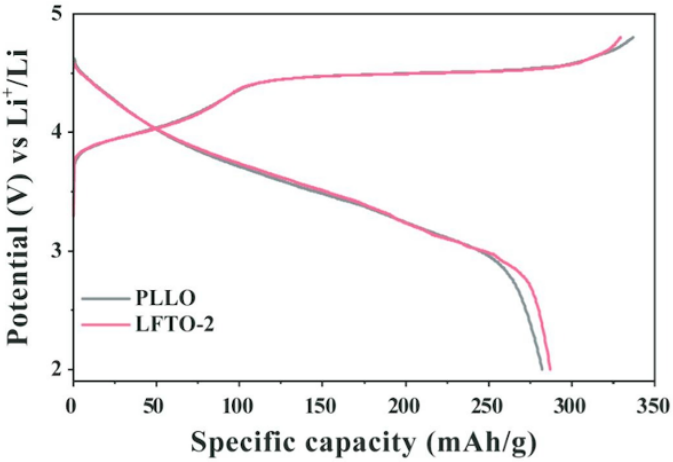

Fig. 2. The initial charge-discharge profiles for PLLO and LFTO-2 at 0.2C (where 1C equals 250 mA/g) [14].

3 Challenge

3.1 Capacity and voltage decay

A primary challenge with lithium-rich manganese (LRM) materials is the degradation of capacity and voltage over time. Voltage decay directly results in capacity decay, making battery life much lower than our requirements. As shown in Figure 3, after 100 cycles, the capacity of LLNMC decreased by 41 mAh/g, retaining only 81.7% of its initial capacity, while the average voltage also dropped significantly. Current research attributes this voltage decay to O_2 release, migration of transition metal ions, and the development of spinel-like phases. So far, this problem still can't be solved perfectly. Despite attempting various new materials, after long-time cycles, either the voltage and capacity decay remains apparent or the cost is high.

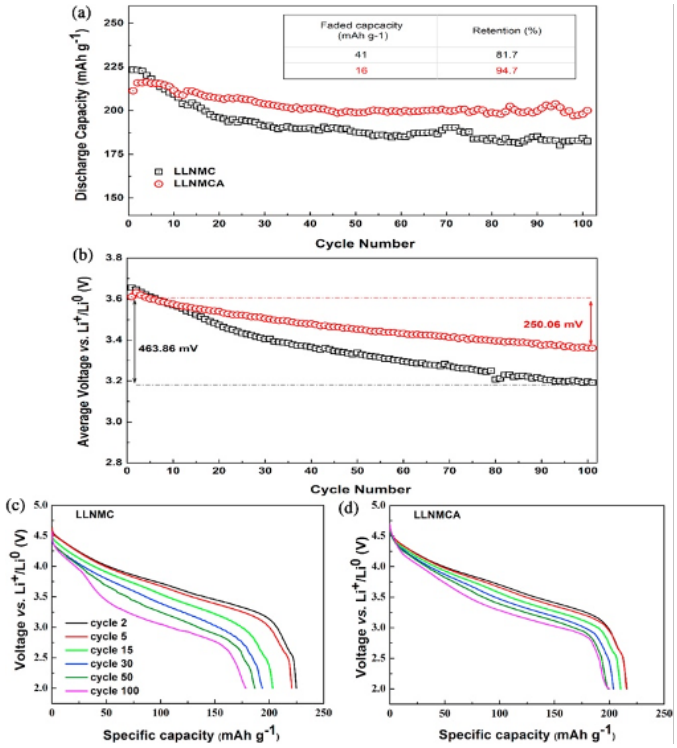

Fig.3. (a) Cycle performance of LLNMC and LLNMCA samples; (b) average discharge voltage as a function of cycle number; (c, d) specific discharge curves for LLNMC and LLNMCA from the second to the one-hundredth cycle[15].

3.2 Low magnification

The rate capability of a battery, defined as the ratio of discharge current to its rated capacity (usually represented as "C"), is critical for performance. Figure 4 illustrates the rate performance of LRMs. Notably, as the discharge rate increases, the specific capacity of the material decreases. The poor rate performance is conditional on various factors. One of them is the intrinsic structure of Li2MnO3 which limits the conductivity of Li+. The irreversible phase change that results in the production of LiMn2O4 further impedes the diffusion of L^{i+} over extended cycle operations. Thus, the secret to enhancing the subpar rate performance is maintaining the integrity of the inner structure.

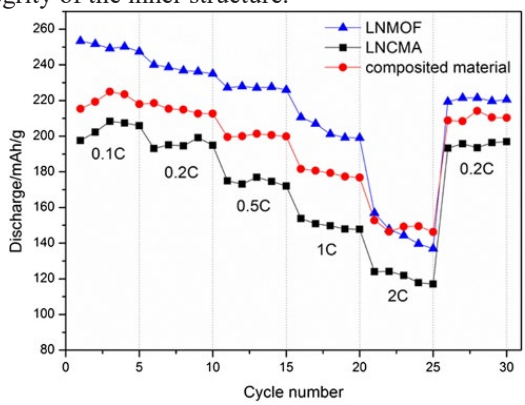

Fig.4. Rate performances of three different materials [16].

3.3 Safety

Lithium-ion batteries pose safety risks, including fire and explosion due to exothermic reactions. The main safety concerns are caused by the use of flammable carbonate and carboxylate solvents in electrolytes, which can break down under high temperature and pressure, leading to thermal runaway. Additionally, lithium dendrites can form on the anode during long-term cycling. Some dendrites may break off as "dead lithium," while others can pierce the separator, causing short-circuits [17].

4 Methods of Improvement

4.1 Surface coating

Active materials in lithium-rich systems are prone to corrosion by the electrolyte during electrochemical reactions, leading to structural degradation. To mitigate this, surface coatings create a protective layer that minimizes electrolyte contact, effectively reducing corrosion under high-voltage conditions. The performance of lithium manganese-based materials can vary based on the coating material, including carbon coating, oxide surface coating (common choices include Al_2O_3[18] and ZnO[19]) and phosphate surface coating. According to studies, these coatings greatly improve the lithium-rich materials' electrochemical characteristics.

4.2 Doping

In LRMs, doping is a commonly used technique to improve conductivity, decrease voltage decay, and improve structural stability. The integrity of the layered structure is directly related to the stability of the voltage and capacity. Structural stability, catalytic activity, and interactions with the electrolyte are all lowered by adding electrochemically inert ions to the lattice, especially at high charge states. This method enhances long-term cycling performance and successfully prevents voltage decay. Depending on the charge characteristics, doping can be classified as cation doping, anion doping, or anion-cation co-doping. Table 1 shows how several common dopants affect particular electrochemical properties.

Table 1. Improvement through the use of doping strategies [15,20,21].

Materials	Elements	Initial discharge capacity (mAh g^{-1}/C)	Initial coulombic efficiency	Capacity retention percentage (%/cycles/C)
$Li_{1.14}$ ($Ni_{0.136}Co_{0.136}Mn_{0.544}$)O_2	Al	225/0.1	72%	82%/100/0.1
		212/0.1(Al)	73%	95%/100/0.1
	Mg	286/0.1	84%	61%/100/0.1
$Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$		273/0.1(Mg)	78%	82%/100/0.1
		160/0.1(Mg)	64%	150%/100/0.1

$Li_{1.20}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$		261/0.1	75%	52%/300/1
	Na	276/0.1	77%	81%/300/1
	F	282/0.1	78%	76%/300/1
	Na+F	291/0.1	82%	85%/300/1

Even if the modification technique helps lithium-rich batteries operate better electrochemically, there are currently many difficulties in the widespread application of lithium-rich batteries. Therefore, further innovation and breakthroughs are still needed. For example, when using the doping modification method, researchers found that only doping with a certain element can only improve the electrochemical performance of one aspect, and another element can improve the electrochemical performance of another aspect, so a co-doping method was adopted. From a microscopic point of view, for positive electrode materials, how to increase the diffusion rate of lithium ions and maintain the stability of the layered structure is crucial. Therefore, a deeper understanding of the reasons for the weakening of electrochemical performance and using the existing technologies are needed. After understanding the mechanism of the modification method, there will be more direction and research efficiency for further.

5 Conclusion

LRMs are regarded highly promising for next-generation lithium-ion batteries due to their high energy density and unique electrochemical properties. However, they encounter major challenges, including low initial Coulombic efficiency, poor rate performance, and decay of capacity and voltage. Additionally, large-scale industrial use is limited by issues like oxygen release and structural transformations during charge and discharge. This review systematically examines the structure, working mechanisms, and electrochemical behavior of Li-rich Mn-based cathodes, offering modification strategies like doping and surface treatments to address these challenges.

Looking ahead, future research should focus on optimizing these strategies and developing new techniques, such as co-doping and multi-layer coatings, to improve performance. This work will guide future studies and support industrial applications, particularly in electric vehicles and energy storage systems. Collaboration among chemists, physicists, and materials scientists will be crucial for addressing interface and surface issues, ensuring that these materials meet the growing demands for high-efficiency energy storage.

References

1. P. Peng, Y. Chen, Q. Zhou, L. Shen, Y. Wen, F. Du, Y. Chen, J. Zheng, J. Tructure Engineering with Sodium Doping for Cobalt-Free Li-Rich Layered Oxide toward Improving Electrochemical Stability. Colloid Interface Sci. **676**, 847-858 (2024)
2. Y. Zhang, H. Xie,H. Jin, Q. Zhang, Y. Li, X.Li, K. Li, C.Research Status of Spinel Limn2o4 Cathode Materials for Lithium Ion Batteries. Bao, IOP Conf. Ser.: Earth Environ. Sci. **603**, 12-51 (2020)

3. Y. Ding, D. Mu, B. Wu, R. Wang, Z. Zhao, F. Wu, Recent Progresses on Nickel-Rich Layered Oxide Positive Electrode Materials Used in Lithium-Ion Batteries for Electric Vehicles. Appl. Energy **195**, 586-599(2017)
4. Y. Wang, P. He, H. Zhou, Olivine Lifepo 4: Development and Future. Energy Environ. Sci. **4** (3), 805-817 (2011)
5. M. M. Thackeray, S. H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek, S. A. Hackney, Li2mno3-Stabilized Limo2 (M = Mn, Ni, Co) Electrodes for Lithium-Ion Batteries. J. Mater. Chem. **17** (30), 3112 (2007)
6. Y. Li, Z. Li, C. Chen, K. Yang, B. Cao, S. Xu, N. Yang, W. Zhao, H. Chen, M. Zhang, Recent Progress in Li and Mn Rich Layered Oxide Cathodes for Li-Ion Batteries. Energy Chem. **61**, 368-385 (2021)
7. P. Oh, J. Yun, S. Park, G. Nam, M. Liu, J. Cho, Recent Advances and Prospects of Atomic Substitution on Layered Positive Materials for Lithium-Ion Battery Adv. Energy Mater. **11** (15), 2003197 (2021)
8. W. Yan, C.; Y. Xie, J. C. Jiang, D. Y. Sun, X. D. Ma, Z. G. Lan, Y. C.Enhanced Rate Performance of Al-Doped Li-Rich Layered Cathode Material Via Nucleation and Post-Solvothermal Method. Jin, ACS Sustain. Chem. Eng. **6** (4), 4625 (2018)
9. B. Song, C. Zhou, H. Wang, H. Liu, Z. Liu, M. O. Lai, L. Lu, Advances in Sustain Stable Voltage of Cr-Doped Li-Rich Layered Cathodes for Lithium Ion Batteries. Electrochem. Soc. 2014, **161** (10), A1723-A1730 (2014)
10. Y. Wang, S. Liu, X. Guo, B. Wang, Q. Zhang, Y. Li, Y. Wang, G. Wang, L. Gu, H. Yu, Elements Gradient Doping in Mn-Based Li-Rich Layered Oxides for Long-Life Lithium-Ion Batteries. Mater. Sci. Technol. **207**, 266-273 (2025)
11. H. Yu, R. Ishikawa, Y.-G. So, N. Shibata, T. Kudo, H. Zhou, Y. Ikuhara, Cathode Material for Lithium-Ion Batteries. Angew. Chem. Int. Ed. **52** (23), 5969-5973 (2013)
12. K. A. Jarvis, Z. Deng, L. F. Allard, A. Manthiram, P. J. Ferreira, Atomic Structure of a Lithium-Rich Layered Oxide Material for Lithium-Ion Batteries: Evidence of a Solid Solution. Chem. Mater. **23** (16), 3614-3621 (2011)
13. H. Zheng, X. Han, W. Guo, L. Lin, Q. Xie, P. Liu, W. He, L. Wang, D. -L. Peng, Mater. Recent Developments and Challenges of Li-Rich Mn-Based Cathode Materials for High-Energy Lithium-Ion Batteries. Today Energy. **18**, 100518 (2020)
14. S. Wang, J. Suo, Y. Liu, W. Guo, G. Gao, X. Han, M. Fan, R. Wu, D.-L. Peng, Q. Xie, Enhancing the Electrochemical Properties of Li-Rich Layered Oxide Cathodes by a Facile Fe/Ti Integrated Modification Strategy. Chem. Eng. J. **497**, 154387 (2024)
15. H. Guo, Y. Xia, H. Zhao, C. Yin, K. Jia, F. Zhao, Z. Liu, Stabilization Effects of Al Doping for Enhanced Cycling Performances of Li-Rich Layered Oxides. Ceram. Int. **43** (16), 13845-13852 (2017)
16. H. Zhu, Y, Xiao, J. Dong, D. Zhang, C. Chang, New Composite Li1.4mn0.61ni0.18co0.18al0.03o2.4 and Lini0.5mn1.5o3.9f0.1 Cathode Material with Higher Specific Capacity and Better Capacity Retention. Ionics **26** (8), 3749-3760 (2020)
17. H. K. Hu, W. D. Xue, Y. Li, P. Jiang, Safety Protection Measures for Lithium Ion Batteries: An Overview and Outlook. Acta Polym. Sin. **53** (5), 457-473 (2022)
18. Y. Zhou, P. Bai, H. Tang, J. Zhu, Z. Tang,Chemical Deposition Synthesis of Desirable High-Rate Capability Al2o3-Coated Li1.2mn0.54ni0.13co0.13o2 as a Lithium Ion Battery Cathode Material. Electroanal. Chem. **782**, 256-263 (2016)

19. G. Singh, R. Thomas, A. Kumar, R. S. Katiyar, A. Manivannan, Electrochemical and Structural Investigations on Zno Treated 0.5 Li 2mno 3-0.5limn 0.5ni 0.5o 2 Layered Composite Cathode Material for Lithium Ion Battery. Electrochem. Soc. **159** (4), A470-A478 (2012)
20. P. K. Nayak, J. Grinblat, E. Levi, M. Levi, B. Markovsky, D. Aurbach, Understanding the Influence of Mg Doping for the Stabilization of Capacity and Higher Discharge Voltage of Li-and Mn-Rich Cathodes for Li-Ion Batteries. Phys. Chem. Chem. Phys. **19** (8), 6142-6152 (2017)
21. P. Zhang, X. Zhai, H. Huang, J. Zhou, X. Li, Y. He, Z. Guo, Synergistic Na+ and F− Co-Doping Modification Strategy to Improve the Electrochemical Performance of Li-Rich Li1·20mn0·54ni0·13co0·13o2 Cathode. Ceram. Int. **46** (15), 24723-24736 (2020)