

Low-Cost Mn-Based Cathode Materials for Lithium-Ion Batteries

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Abstract: Due to a high energy density and satisfactory longevity, lithium-ion batteries (LIBs) have been widely applied in the fields of consumer electronics and electric vehicles. Cathodes, an essential part of LIBs, greatly determine the energy density and total cost of LIBs. In order to make LIBs more competitive, it is urgent to develop low-cost commercial cathode materials. Among all cathode materials, Mn-based cathode materials, such as layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and Li-rich materials, spinel LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, olivine-type LiMnPO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$, stand out owing to their low cost and high energy density. Herein, from the perspective of industrial application, we calculate the product cost of Mn-based cathode materials, select promising candidates with low cost per Wh, and summarize the structural and electrochemical properties and improvement strategies of these low-cost Mn-based cathode materials. Apart from some common issues for Mn-based cathode materials, such as Jahn–Teller distortions and Mn dissolution, we point out the specific problems of each material and provide corresponding improvement strategies to overcome these drawbacks.

Keywords: lithium-ion batteries; Mn-based cathodes; low cost per Wh; high energy density



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1. Introduction

The widespread application of consumer electronics and the urgent requirements of electrical vehicles have greatly promoted the development of lithium-ion batteries (LIBs) [1–3]. Among the main components of LIBs, such as the cathode, anode, electrolyte, and separator, cathode materials, one of the main components of LIBs along with anode materials, liquid electrolytes, and separators, are crucial to the whole energy density and costing of LIBs. This is because of the relatively lower capacity of cathode materials compared with that of anode materials (for example, commercial LiCoO_2 cathode: $\sim 180 \text{ mAh g}^{-1}$; commercial graphite anode: $\sim 350 \text{ mAh g}^{-1}$) and their non-negligibly higher cost (about 40–60% of total LIBs). The high cost of cathode materials has caused the high price of LIBs, which drives up the cost of LIB-based products, especially those that need a large quantity of LIBs, such as electrical vehicles, energy storage devices and electrical tools. As lithium resources are limited and unevenly distributed, LIBs are becoming more and more expensive, which has resulted in the emergence of other competitive batteries, including sodium-ion batteries (SIBs), potassium-ion batteries (KIBs) and magnesium-ion batteries (MIBs). Meanwhile, low-cost lead-acid batteries (LAB) still occupy a large part of the battery market. Under the pressure of traditionally commercial batteries (LABs) and emerging batteries (SIBs, KIBs, MIBs etc.), it is urgent to develop new inexpensive commercial cathode materials for LIBs, so that LIBs can be more competitive in the battery market.

To screen low-cost cathode materials, it is necessary to take the cost into account from the elemental standpoint. At present, cobalt (Co), which is included in commercial LiCoO_2 and ternary materials ($\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$, NCM; $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$, NCA etc.), is the primary element of cathode materials. However, the price of Co is extremely high and keeps rising due to its rare reserve and uneven distribution [4]. Another widely used element for

cathode materials is Ferrum (Fe), which is included in commercial LiFePO_4 for power batteries. However, Fe ions not only have a +2 and +3 valance state, which limits the diversity of Fe-based cathode materials, but also exhibit a low discharge voltage (3.5 V vs. Li/Li^+), which greatly limits the discharge capacity of LiFePO_4 [5]. By comparison, manganese (Mn) is plentiful in the Earth's crust and has been utilized extensively in Ferrum and the steel industry, non-ferrous metallurgy, the chemical industry, electronics, batteries, agriculture, medicine and other fields. Additionally, Mn ions have manifold valance states ranging from +2 to +7, which enables them to produce various cathode materials with different types of crystal structures, such as spinel LiMn_2O_4 , layered LiMnO_2 and olivine LiMnPO_4 . Therefore, Mn-based materials should be the main emphasis when seeking next-generation low-cost cathode materials. Nowadays, LiMn_2O_4 has become a commercial material by virtue of its price advantage and is mainly applied in the two-wheel electric-vehicle industries. Other Mn-based materials, including $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LiMnPO_4 and Li-rich Mn-based materials, will potentially be used as commercial cathode materials for LIBs because of their high energy density and inexpensive price.

There exist several excellent reviews on Mn-based materials which normally focus on a specific type of Mn-based material, such as spinel LiMn_2O_4 [6,7], layered LiMnO_2 [8] and Li-rich Mn-based materials [9,10], and collect recent advances in the academic area; however, they ignore practical industrial applications. Hence, the purpose of this review is to offer an essential understanding of the performance and preparation cost of various types of Mn-based materials. By calculating the preparation cost (raw materials and preparation technology), we selected potential low-cost cathode materials whose cost per Wh is lower than that of present NCM materials. The basic structures, electrochemical performance, and improvement strategies are also elucidated systematically, and their industrial-application prospects are also outlined.

2. Estimation of Energy Density and Cost for Mn-Based Materials

For the industrial application of cathode materials in LIBs, the energy density (gravimetric energy density, GED; volumetric energy density, VED) and cost (production cost, cost per Wh) are vital parameters. The theoretical specific capacity of a cathode material is computed according to the formula $Q = nF/3.6 M_w$, where n is the electron-transfer number, F is the Faraday constant, and M_w is the molecular weight of the cathode material [11]. In order to assess the realistic economic worth of the cathode materials, the data of practical specific capacities, average discharge voltages, and compaction densities of most materials (except $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and $\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$) are obtained from various suppliers of LIB's materials. The material cost is computed according to the average price of raw materials on the CBCIE website (www.cbcie.com) in 2021 and the production cost. The raw materials include the transition-metal salts or transition-metal precursor, lithium salt, phosphate salts for phosphate materials, and additives. The production cost not only includes the cost of electricity, packaging and transportation, but also considers the cost of labor and depreciation of equipment. The GED is generated by multiplying practical specific capacity and average discharge voltage. The VED is generated by multiplying GED and compaction density. The final cost per Wh is the result of material cost/GED. Table 1 summarizes the results from the above.

According to Table 1, LiCoO_2 has the highest VED, implying its widespread application in consumer electrics that provide limited space for batteries. For electric vehicles, the GED and material cost are more important than VED due to its larger space and use of many more batteries to produce much more energy. Although NCM materials, such as $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) have a substantially lower VED than LiCoO_2 , their GED is comparable to that of LiCoO_2 . NCM is widely used in batteries of electrical vehicles due to its significantly cheaper material cost compared to LiCoO_2 [12]. Although LiFePO_4 has a relatively lower GED than NCM and LiCoO_2 , it is still a viable cathode material for electrical vehicles due to its low cost per Wh and extraordinarily extended working life. The cost per Wh of LiFePO_4 is 0.15 CNY Wh^{-1} ,

which is relatively low in present commercial materials, but its energy density is limited to a low level. This paper reviews the low-cost materials with lower cost per Wh than NCM (NCM523: 0.34 CNY Wh⁻¹; NCM811: 0.34 CNY Wh⁻¹). Then, we find that almost all Mn-based materials can meet the aforementioned requirement, and most of them have prices of less than 0.20 CNY Wh⁻¹, with the exception of Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}. Among these low-price Mn-based materials, spinel LiMn₂O₄ and LiNi_{0.5}Mn_{1.5}O₄ demonstrated the lowest cost per Wh at 0.13 CNY Wh⁻¹. LiMn₂O₄ has been applied in two-wheel electric vehicles and electric tools that need higher cost performance and tolerance for relative lower energy density and cycle performance, and it has the potential to replace LABs. The layered LiNi_{0.5}Mn_{0.5}O₂ has a comparable GED to NCM523 and its cost of Wh (0.19 CNY Wh⁻¹) is much lower than that of NCM523, which has the potential to replace NCM materials by virtue of its low price. The cost per Wh for LiMnPO₄ (0.16 CNY Wh⁻¹) and LiMn_{0.5}Fe_{0.5}PO₄ (0.15 CNY Wh⁻¹) is similar to that of LiFePO₄, which has shown a commendable advantage in price. Meanwhile, the higher GED of these two materials make them more attractive, and some material companies are developing them. Li-rich materials, such as layered Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ (0.19 CNY Wh⁻¹, 825.0 Wh kg⁻¹) and rock-salt Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05} (0.30 CNY Wh⁻¹, 1056 Wh kg⁻¹) are becoming research-and-development hotspots for many material companies. Although they do not have a low cost per Wh, they have the highest GEDs among all materials, which can greatly improve the range of electric vehicles.

Table 1. The comparison of various Mn-based materials. Most data are obtained from the materials’ suppliers in China except $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and $\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$. The currency type “CNY” is “Chinese Yuan”.

Materials		Theoretical Specific Capacity (mAh g ^{−1})	Practical Specific Capacity (mAh g ^{−1}) @ 0.1C	Initial Coulombic Efficiency	Average Discharge Voltage (V)	Compaction Density (g cm ^{−3})	Gravimetricenergydensity (Wh kg ^{−1})	Volumetricenergydensity (Wh L ^{−1})	Material Cost (CNY kg ^{−1})	Cost per Wh (CNY Wh ^{−1})	Main Drawbacks	Cycling Performance	Air Stability
LiCoO ₂		274	210	94%	3.80	3.80	798.0	3032	308.6	0.39	High cost	★★★★☆	★★★★★
NCM523		276	180	88%	3.71	3.45	667.8	2304	226.4	0.34	Relatively low energy density	★★★★☆	★★★★☆
NCM811		275	210	91%	3.66	3.40	768.6	2613	235.2	0.31	Poor stability, bad safety	★★★★☆	★★★☆☆
LiFePO ₄		170	160	98%	3.35	2.20	536.0	1179	81.1	0.15	Low energy density	★★★★★	★★★★☆
Spinel	LiMn ₂ O ₄	148	120	95%	3.80	3.00	456.0	1368	57.5	0.13	Low energy density	★★★☆☆	★★★★☆
	LiNi _{0.5} Mn _{1.5} O ₄	147	133	94%	4.70	3.00	625.1	1875	82.7	0.13	High voltage plateau	★★★★☆	★★★★☆
Layered	LiNi _{0.5} Mn _{0.5} O ₂ [13]	280	199	96%	3.40	/	676.6	/	128.3	0.19	Poor rate capability	★★★☆☆	★★★★☆
	Li _{1.2} Ni _{0.2} Mn _{0.6} O ₂ [14]	378	240	82%	3.45	2.80	845.0	2367	158.3	0.19	Low initial coulombic efficiency	★★★☆☆	★★★★☆
Rock salt	Li _{1.2} Mn _{0.625} Nb _{0.175} O _{1.95} F _{0.05} [15]	353	330	94%	3.20	2.70	1056	2851	319.2	0.30	High production cost	★☆☆☆☆	★★★★☆
Olivine	LiMnPO ₄	171	154	83%	3.90	/	600.6	/	96.5	0.16	Low electronic conductivity	☆☆☆☆☆	★★★★☆
	LiMn _{0.5} Fe _{0.5} PO ₄	170	160	93%	3.72	2.40	595.2	1428	89.1	0.15	Low energy density	★★★★★	★★★★☆

3. Structure, Performance and Improvement Strategies of Mn-Based Materials

The typical low-cost Mn-based materials listed in Table 1 include layered, spinel, rock-salt and olivine structures. Most layered transition-metal oxides often undergo a transformation during cycling, first becoming layered, then spinel, and, finally, forming a rock-salt structure [16,17] (Figure 1). For the layered structure, lithium ions and transition-metal (TM) ions are situated in two independent layers. When some Li sites are replaced with TM, the layered structure can change into a defect spinel/spinel-like structure. After a long cycling process, all metal ions, including Li^+ and TM ions, take up the metal sites randomly, leading to the formation of the rock-salt structure.

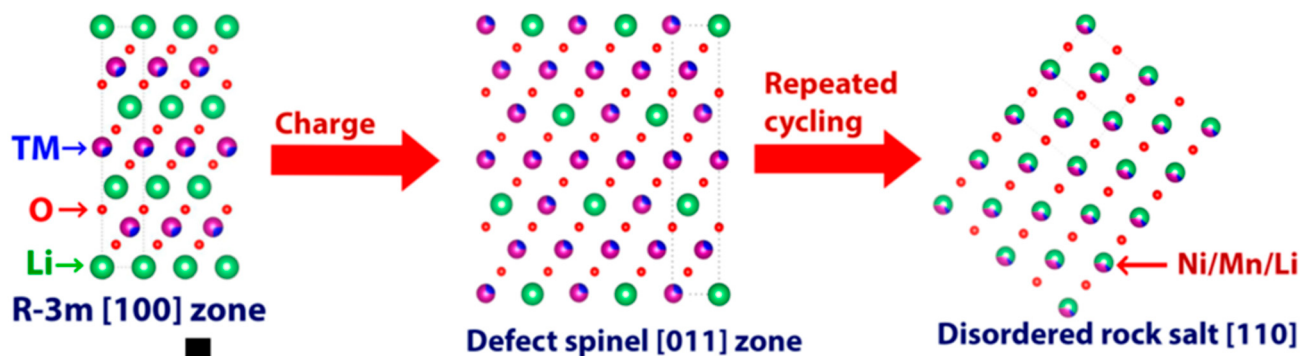


Figure 1. Failure model of layered transition metal oxides (taking Li-rich materials as an example) [16].

3.1. Layered Mn-Based Oxides

LiMnO_2 is the primary Mn-based material, from which many other cathode materials are derived, including $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, LiMn_2O_4 ($\text{Li}_{0.5}\text{MnO}_2$), and Li_2MnO_3 ($\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$). LiMnO_2 has three different types of structures, with space group Pmmn , C2/m and $\text{R}\bar{3}\text{m}$, respectively: orthorhombic, monoclinic and rhombohedral structures [18]. In these, the monoclinic LiMnO_2 with a layered structure can be utilized as a cathode material for LIBs owing to its high theoretical capacity of 285 mAh g^{-1} [19]. However, orthorhombic LiMnO_2 is usually produced during the high-temperature solid-state methods [20], indicating that monoclinic LiMnO_2 (Figure 2a) has a metastable phase. The monoclinic LiMnO_2 is usually synthesized by low-temperature ion-exchange methods [21], which sharply raises the production cost of LiMnO_2 . At present, LiMnO_2 has not been commercialized not only due to the high production cost, but also because of some performance disadvantages, such as Jahn–Teller distortions, Mn dissolution, low electronic conductivity, and structure transformation to spinel phase, which results in low stability [22]. In Mn-based materials, the Jahn–Teller distortion is a common problem which leads to the phase transformation and the disproportionation reaction of Mn^{3+} which generates Mn^{2+} ions and results in Mn dissolution. According to the Jahn–Teller theory, nonlinear molecules with a spatially degenerate electronic ground state tend to experience a geometrical distortion to lower the energy of total molecule. For Mn^{3+} in MO_6 octahedrons, four d orbital electrons will be arranged in two e_g and three t_{2g} orbitals, forming high-spin $t_{2g}^3e_g^1$ or low-spin t_{2g}^4 , which results in an odd number of electrons in d orbitals and Jahn–Teller distortion [18]. To alleviate the Jahn–Teller distortion, various strategies, such as doping, surface modification, and constructing nanostructures with distinctive morphologies have already been used.

3.1.1. $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$

When the Mn cations in LiMnO_2 are partially substituted by Ni cations, a $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ solid solution is formed. The structure of $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ is determined by the ratio of Ni/Mn. When the ratio of Ni/Mn < 1, the spinel structure is formed; otherwise, the $\alpha\text{-NaFeO}_2$ structure with $\text{R}\bar{3}\text{m}$ symmetry (Figure 2b) will be generated [23]. The hexagonal $\alpha\text{-NaFeO}_2$ -structured $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ delivers a discharge specific capacity of about 200 mAh g^{-1} , as well as a plateau potential of 3.8 V [24]. As the valence state of Mn and

Ni ions in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ is +4 and +2, respectively, only the Ni ions undergo the redox reaction from +2 to +4 during the charging and discharging process. The Mn ion keeps the valence state of +4 without the appearance of Mn^{3+} , which can effectively avoid Mn dissolution and the Jahn–Teller distortion [25]. Nevertheless, with the utilization of Ni^{2+} , the Li/Ni cation mixing problem will appear in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, which reduces the Li^+ diffusion rate and the reversible capacity [26].

In order to enhance the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, various strategies were employed, including nanostructure construction, element doping and surface coating. The nano-structured $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ is mainly synthesized using template methods. Yuan et al. [27] carried out an in-situ conversion from $\gamma\text{-MnO}_2$ hollow nanospheres to $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ nanoarchitecture spheres (Figure 2c). In comparison to $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ particles synthesized via a conventional solid-state reaction process, the nanostructured $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ displays a significant improvement in rate performance (121.9 mAh g^{-1} at 3.2 C, 70% of the capacity at 0.2 C), because much faster interfacial kinetics and higher Li^+ insertion/removal rates are realized by reducing the size of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ particles. Later, Yuan et al. [28] utilized cryptomelane-type octahedral molecular sieve manganese dioxide (OMS-2) in the form of dendritic nanostructures as templates to prepare the three-dimensional $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ nanostructures, which also showed improved rate performance.

Element doping is an efficacious strategy to enhance the electrochemical properties of cathode materials. Numerous elements have been attempted to dope into $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, such as Al [29,30], Mg [31], Ba [32], Cu [33], Sb [34], Ti [35], Zr [36], Si [37], Mo [38] and F [39]. All these doping ions can suppress the Li/Ni cation mixing in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and further improve the rate capability, specific capacity, and cycling performance. In addition, the special element has particular effects. For instance, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ doped with Al element displayed the highest initial specific capacity of 206 mAh g^{-1} [30] and 215 mAh g^{-1} [29]. This is because Al doping could narrow the size distribution and decrease Li^+ migration resistance with extended lattice parameter of c axle. Ba doping can effectively promote the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ because the Ba–O bond has a greater dissociation energy than the Ni–O bond (563 kJ mol^{-1} vs. $391.6 \text{ kJ mol}^{-1}$), which helps to stabilize the crystal structure [32]. As a result, after 100 cycles, Ba-doped $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ can still operate at 97% of its initial specific capacity. Cu doping could extend the migration channels of lithium ions in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, which, in turn, improves the rate performance effectively [32]. In addition to single-element doping, the double-element co-doping is applied in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, which has shown better improvement than single-element doping. Jia et al. [40] realized a Na–Al dual-doped $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ material, improving the reversible capacity, cycling stability, and the stability of discharge midpoint potential (Figure 2d). Na^+ successfully entered into the lithium layer and played a “pillar” role to promote the structural stability, as opposed to hindering the diffusion of Li^+ . The Al–O bond with a higher bond dissociation energy further reinforced the crystal structure. As a result, the Na–Al dual-doped $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ displayed a high initial specific capacity of 216 mAh g^{-1} and a capacity retention of 90.56% after 180 cycles (Figure 2e).

Surface coating can function as a barrier between cathode materials and liquid electrolytes, preventing direct contact and further enhancing the interface stability. Meanwhile, the conductivity of cathode materials can also be promoted by coating a conductive layer. Hashem et al. [41] prepared carbon-coated $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using an oxalate coprecipitation method, with table sugar as a carbon source. In comparison to pristine $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, the as-prepared sample exhibited superior capacity retention (92% after 50 cycles vs. 75% after 30 cycles). Jia et al. [42] coated a stable, 10 nm thick, and lithium super conductive Li_2TiO_3 layer on the surface of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, which effectively enhanced the Li^+ diffusion rate, protected the particle morphologies, and helped to maintain a better structure stability, by reducing side reactions between the cathode materials and liquid electrolytes. In order to further improve the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, element doping and surface coating were combined, such as Sb-doped and Sb_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [34], and Zr-doped and Li_2ZrO_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [36]. In these, element doping could

enhance structural stability by reducing the degree of Li/Ni cation mixing, while surface coating could efficaciously shield the active material from direct contact with liquid electrolytes, and increase the Li^+ diffusion rate at the interface between electrode and electrolyte. However, present methods for these materials usually follow two steps: preparation of precursors (without doping agents) and preparation of final materials. Since the doping ion is diffused from surface to bulk, resulting in a low doping amount [36], it is important to investigate how to add a doping agent to the precursor.

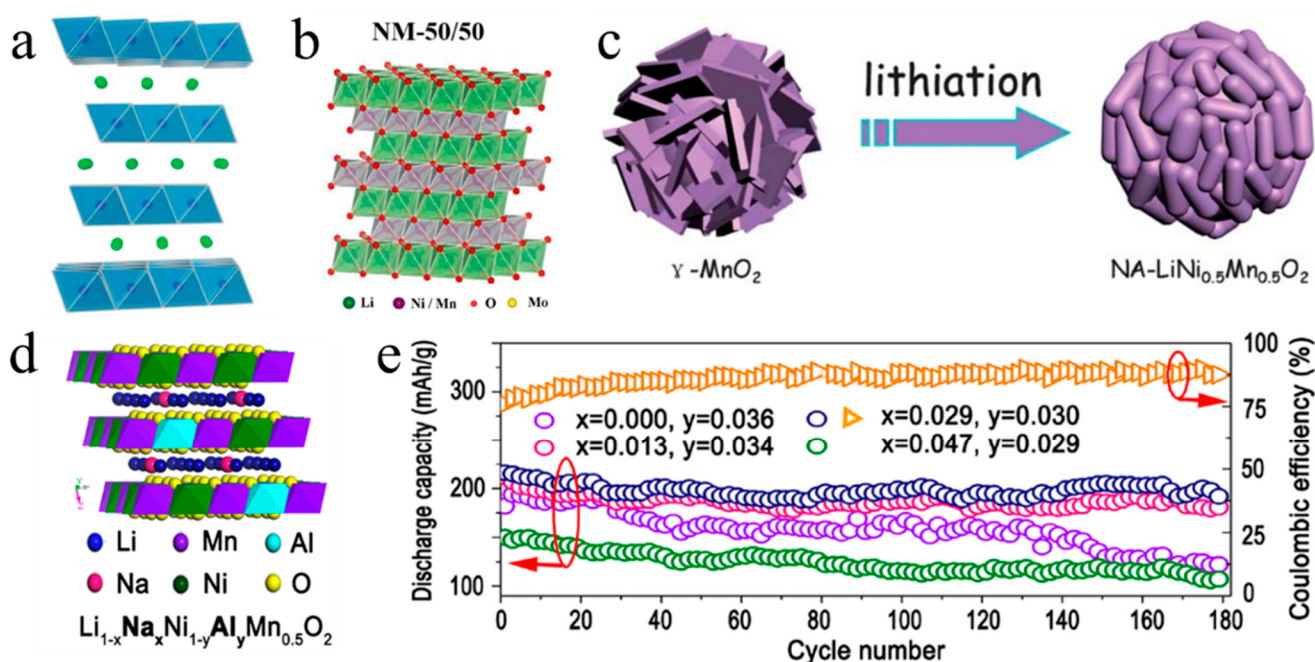


Figure 2. (a) Crystal models of monoclinic LiMnO_2 (blue: MnO_6 octahedron, green: Li) [23]. (b) Crystal models of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [35]. (c) Schematic diagram of the synthesizing nanostructured $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ derived from the in-situ conversion of $\gamma\text{-MnO}_2$ hollow nanospheres [27]. Schematic diagrams (d) and cycling performance (e) of crystal structure of $\text{Li}_{1-x}\text{Na}_x\text{Ni}_{0.5-y}\text{Al}_y\text{Mn}_{0.5}\text{O}_2$ [40].

3.1.2. Li-Rich Mn-Based Oxides

Owing to their high specific capacity ($>250 \text{ mAh g}^{-1}@0.1\text{C}$), low cost, and outstanding safety, Li-rich Mn-based (LRM) layered oxides are regarded as the most promising candidate of cathode materials for the next-generation high-specific-energy LIBs. The main component of LRM cathode materials is the inexpensive Mn element; low Co content ($< 10 \text{ mol\%}$) or no Co content is the main way to reduce the material cost of LRM. The low cost of LRMs combined with the high energy density can significantly reduce the cost per Wh. Since Numata et al. [43] reported $\text{LiCoO}_2\text{-Li}_2\text{MnO}_3$ for the first time in 1997 and Gopukumar et al. [44] originally used Li_2MnO_3 as a cathode material for LIBs in 1999, numerous studies have been conducted on LRM cathode materials. However, the structure of LRMs has not been figured out yet; there are still two arguments about their structure, one is a two-phase nanodomain ($x\text{Li}_2\text{MnO}_3 \bullet (1-x) \text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$), and the other one is a single-phase solid solution ($\text{Li}_{1+x}\text{Ni}_y\text{Co}_z\text{Mn}_{1-x-y-z}\text{O}_2$) [10]. Nevertheless, both nano-domain and solid-solution structures are composed of monoclinic Li_2MnO_3 (C2/m) and trigonal LiMO_2 ($\text{R}\bar{3}\text{m}$) (Figure 3a).

Although LRM show great potential as cathode materials for LIBs due to their high specific capacity, their low initial coulombic efficiency, serious voltage fading, bad cycling and rate properties have limited their practical utilization. Several studies have focused on the causes of the LRM's poor initial coulombic efficiency. Oxygen activation brought about by the Li-O-Li configuration (Figure 3b) is not only the cause of LRMs' high specific capacity [45], but also the main origin of the problems of oxygen loss and transition

metal migration. During the initial charging/discharging process, O₂ gas is generated and released due to the oxidation of some active O, causing an amount of irreversible capacity. Meanwhile, some TM ions will transfer from TM sites to Li sites and form an irreversible spinel phase in the first cycle because the irreversible oxygen release reduces the binding energy of TM ions and oxygen, which further increases irreversible capacity loss. The continuous structural transition from layered to spinel phase has been considered as the cause of the voltage decay and poor cycling performance during cycling [46,47]. In addition, some researchers found that the capacity and voltage decay are caused by the decrease in the redox couple of TM ions [48]. The diffusion kinetics of Li⁺ in the crystal structure often sets a limit on the rate performance of LRMs. The pristine structure of cathode materials is destroyed during the phase transition from the layered to spinel structure, leading to a poor rate performance [49,50]. Interestingly, some scholars have explored how the Li⁺ content affects the structure of LRM cathode materials. LRMs with lower lithium content had more chemical ordering defects, while the spinel-structured surface had no obvious structural change with the change in lithium content [51]. Some advanced characterization methods are used to reveal the failure mechanism of LRM positive electrode during the cycle [52,53]. Li/Ni and Li/Mn anti-site defects were also discussed in the case of LiNi_xCo_yMn_(1-x-y)O₂ and Li₂MnO₃ cathode materials [54]. In order to avoid the anti-site defects, LiNi_xCo_yMn_(1-x-y)O₂ and Li₂MnO₃ were prepared under Ni-rich condition and under O-rich and Mn-poor conditions, respectively.

In order to solve the above problems, the main strategies are doping, coating and surface modification. The elements that are usually utilized to dope cations at TM sites have a stronger bond with oxygen than Ni, Co, and Mn, which can efficaciously inhibit the structural shift from layered to spinel [55]. Surface coating is utilized in LRMs to keep the structural stability of the electrode/electrolyte interface and reduce voltage fading [55]. However, doping and coating are unable to address the issue of oxygen loss, which is the essential problem of LRMs. One present effective strategy to reduce the oxygen loss is creating defects/vacancies which is mostly realized by surface modification. For example, Qiu et al. [56] modified the Li[Li_{0.144}Ni_{0.136}Co_{0.136}Mn_{0.544}]O₂ with CO₂ by gas–solid interface reaction (GSIR) to form a layer of oxygen vacancy with a thickness of 10–20 nm on the surface of material (Figure 3c). Oxygen vacancy can effectively inhibit the release of lattice oxygen; hence, the obtained sample has shown an improved initial coulomb efficiency of 93.2% and cycling performance; Peng et al. [57] treated the LRM with oleic acid to manufacture cation and anion double defects and an in-situ surface reconstruction layer to reduce oxygen release and improve structural stability, which can enable precise control of the ICE from 84.1% to 100.7%. At the same time, this sample presents a high specific capacities of 330 mAh g^{−1} at 0.1 C with a large energy density of 1143 Wh kg^{−1}, and 276 and 250 mAh g^{−1} at 1 and 5 C due to the fast kinetics of Li⁺ and its electron (Figure 3d). In contrast to the surface modification, Zhu et al. [58] developed the method of molten molybdate-assisted LiO extraction to create gradient Li-rich single crystals, which can inhibit oxygen loss. Lithium is rich in the core of the particle, poor on the surface, and continuous in between (Figure 3e). The prepared material shows a good voltage and cycling stability with high discharge specific capacity of 250.4 mAh g^{−1} and high average voltage of 3.368 V after 200 cycles at 0.2 C.

Since the price of Cobalt salts has increased sharply in recent years, LRMs with low Co content or without Co are more attractive in industrial application due to their relatively low cost. However, LRMs with less Co (<10%) show poor structure stability and ionic/electron conductivity, such as Li_{1.2}Ni_{0.2}Mn_{0.6}O₂. To enhance the electrochemical properties, Chen et al. [59] prepared a hierarchical Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ quasi-sphere with a plane-based surface, in which the electrochemical active planes allow for fast Li⁺ transport kinetics due to efficient ion and electron transport (Figure 3f). The as-prepared Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ displayed improved cycling and rate performance. On the surface of the Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ microsphere, Ding et al. [14] pyrolyzed urea to form a multifunctional surface modification, which could simultaneously construct oxygen vacancy, integrated spinel phase and N-

doped carbon nanolayer (Figure 3g). The integration of oxygen vacancy and spinel phase could not only inhibit the irreversible release of O_2 but also promote the diffusion of Li^+ . Meanwhile, the N-doped carbon nanolayer with high electrical conductivity could promote electron transport and reduce electrolyte corrosion. The electrochemical results show that the surface-modified $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ can retain its initial specific capacity up to 89.9% after 500 cycles at 1 C, and its voltage decay rate per cycle is merely 1.09 mV (Figure 3h), which significantly inhibits the capacity and voltage decay.

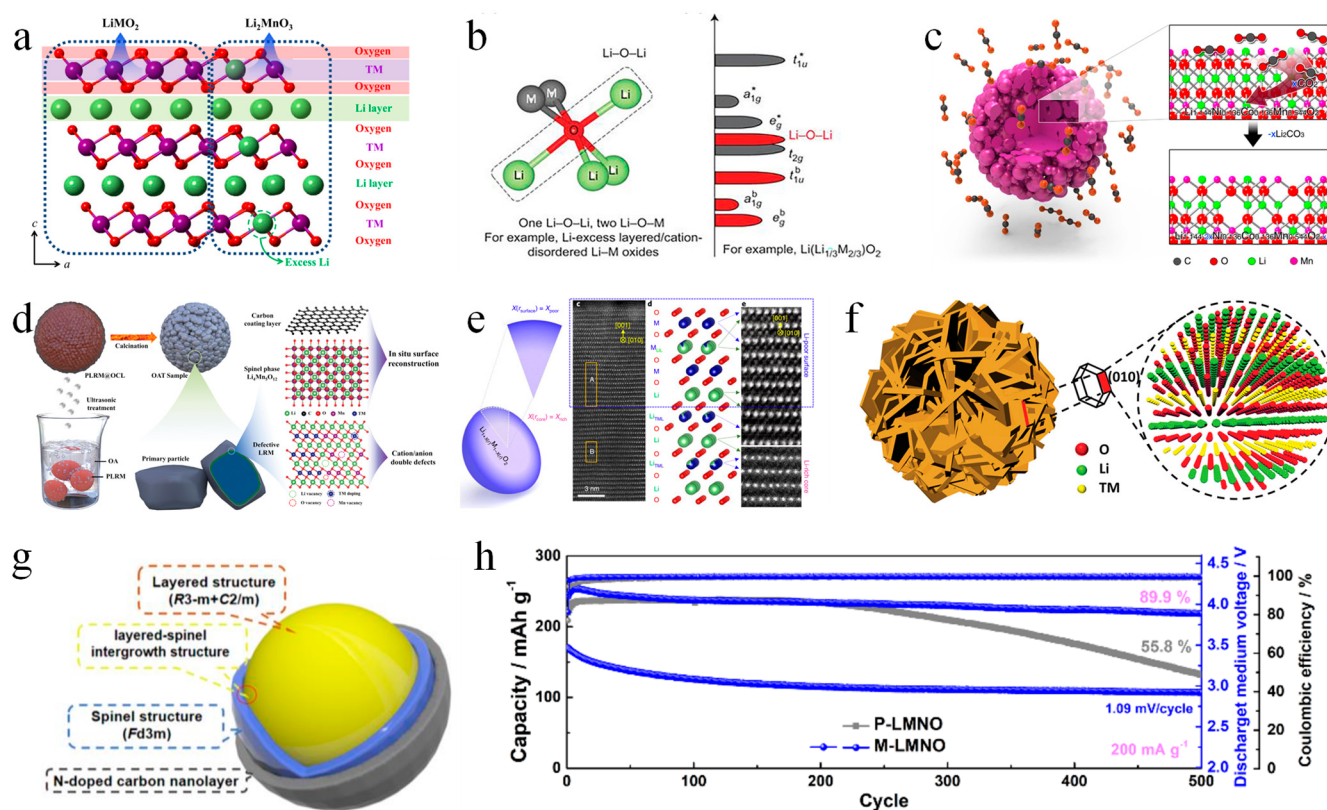


Figure 3. (a) Schematic diagram of Li-rich materials [10]. (b) Structural origin of the preferred oxygen oxidation along the Li–O–Li configuration [45]. (c) Schematic diagram of gas–solid interface reaction (GSIR) between Li-rich layered oxides and carbon dioxide [56]. (d) Schematic diagram of oleic acid–assisted interface engineering [57]. (e) Schematic of the Li gradient Li-rich material [58]. (f) Schematic illustration of hierarchical structured $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ material [59]. (g) Schematic illustration and cycling performance (h) (blue lines) of $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by three-in-one surface modification [14].

3.2. Spinel Mn-Based Oxides

Spinel Mn-based oxides show great structural stability and have been widely applied in LIBs, MIBs [60,61], and so on. $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ are, at present, the main spinel Mn-based oxides for lithium batteries. Although their theoretical specific capacity is only about half that of layered Mn-based oxides, their more stable structures and quicker Li^+ diffusion compared with layered forms have attracted much attention in scientific research and industrial application. $LiMn_2O_4$ has become the most mature commercial material in Mn-based cathode materials, while $LiNi_{0.5}Mn_{1.5}O_4$ was originally prepared and investigated as one of the metal-substituted $LiMn_2O_4$ derivatives. Since the low valance state of Ni^{2+} can increase the valance state of Mn and further prevent the Jahn–Teller effect and Mn dissolution, Ni^{2+} doping can stabilize the crystal structure [62]. Similar to the aforementioned $LiNi_{0.5}Mn_{0.5}O_2$, the valance state of Mn in $LiNi_{0.5}Mn_{1.5}O_4$ is +4, so only Ni ions undergo oxidation and reduction during cycling. Compared with $LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$ has a comparable cost per Wh (0.13 CNY Wh^{-1}), but a higher potential

plateau of ~ 4.7 V as well as a higher energy density of 650 Wh kg^{-1} . When matched with a suitable high-voltage electrolyte, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has great potential to be widely applied.

LiMn_2O_4 is a cubic spinel with an $Fd3m$ space group, and can be synthesized via a simple solid-state reaction in an air atmosphere at a high temperature. In the spinel structure of LiMn_2O_4 , the Li^+ , Mn ions and O ions are situated at the 8a tetrahedral sites, 16d octahedral sites and 32e positions, respectively. O ions are cubic-close-packed [63] (Figure 4a). The edge-shared MnO_6 octahedrons can construct a continuous three-dimensional cubic array, and, further, cause the formation of the robust Mn_2O_4 spinel framework, in which fast diffusion of Li^+ is realized. Since the theoretical specific capacity and average discharge voltage of LiMn_2O_4 is relatively low (146 mAh g^{-1} , ~ 3.8 V), it exhibits a relatively low energy density. When the discharge voltage is lower than 3 V, the lithiation of LiMn_2O_4 occurs, which leads to irreversible phase transformation from spinel to rock-salt ($\text{Li}_2\text{Mn}_2\text{O}_4$) [63]. Besides the low energy density, another problem of LiMn_2O_4 is its poor cycling performance due to its Mn dissolution, especially at high temperatures. In LiMn_2O_4 , the average valance state of Mn ions is $+3.5$, mostly composed of Mn^{3+} and Mn^{4+} . Mn dissolution has been mainly ascribed to the dissolution of Mn^{2+} , which originates from the disproportionation of Mn^{3+} ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) [64,65]. Meanwhile, the currently used LiPF_6 -based carbonate electrolyte will produce large amounts of hydrofluoric acid (HF) with the presence of trace water, which accelerates the dissolution of Mn^{4+} . Surface coating can also effectively promote the electrochemical performance of LiMn_2O_4 [66–70]. Coating with solid electrolytes can avoid the Mn reactions of LiMn_2O_4 in the case of liquid electrolytes. $\text{Li}_{6.375}\text{La}_3\text{Zr}_{1.375}\text{Nb}_{0.625}\text{O}_{12}$ (LLZNO) electrolytes were used by Bi et al. [71] to coat LiMn_2O_4 , which not only suppressed Mn reactivity but also enhanced the interface between $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) and LiMn_2O_4 . After 100 cycles at 0.2C and 55°C , the solid battery with LMO@LLZNO cathode, LLZTO electrolyte, and Li metal showed a high discharge capacity retention of 81.3%.

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, one of the most significant LiMn_2O_4 derivatives, was originally synthesized in 1996 via substituting part of Mn sites with Ni. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ contains two types of spinel crystal structures, one is face-centered cubic ($Fd3m$) with disordered TM ions, and the other is primitive simple cubic ($P4_332$) with ordered TM ions [72] (Figure 4b,c). In the $Fd3m$ space group, Li^+ occupies tetrahedral 8a sites, Mn/Ni ions occupies octahedral 16d sites randomly, and O^{2-} occupies 32e sites. In $P4_332$ space group, Li^+ occupies tetrahedral 8a sites, Mn^{4+} occupies 12d sites, Ni^{2+} occupies 4b sites, and O^{2-} occupies 24e and 8c sites. It is worth noting that Ni^{2+} replaces part of Mn^{4+} sites orderly in the $P4_332$ space group, different from that in the $Fd3m$ space group. Compared with $P4_332$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the $Fd3m$ space group exhibits outstanding electrochemical performance and structural reversibility. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been deemed as one of the most promising cathode materials for LIBs, owing to its high working voltage (4.7 V), high specific capacity (146.7 mAh g^{-1}), high energy density, low cost, and good cycle stability [73,74]. However, in addition to some common obstacles for Mn-based cathode such as TM ions' dissolution and the Jahn–Teller effect of Mn^{3+} , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also has great side reactions with liquid electrolytes due to its high voltage plateau [75].

To solve the above problems of LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, various strategies, including element doping, surface coating, an appropriate synthesis method, and electrolyte modification, etc., are proposed to improve their electrochemical performance. Element doping can restrain the Mn^{3+} disproportionation reaction and Jahn–Teller distortion for spinel Mn-based oxides. Present doping ions can be divided into two categories, cations and anions. Present doping cations include Al, Cr, Co, Ga, Pr, Gd, La, Ce, Nd, Sm, Sc, Y, Tb, Er, B, Fe, Mg, Ti, Ru, Si, Ni, Zn, Cu, Sn, Li, and Na ions, etc., and anions include F, Cl, Br S, and PO_3 ions, etc., which have been summarized by Cui et al. [7]. Among the various single cation doping options, Al doping has shown the best improvement effect on the cycling performance of LiMn_2O_4 . Sun et al. [75], Xia et al. [76] and Xiao et al. [77] synthesized the Al-doped samples, which show excellent cycling performances with capacity retentions of 98.5%, 99.34% and 99.3% after 50 cycles at $\sim 50^\circ\text{C}$,

respectively. The improvement effects can be summarized as: (1) an Al–O bond with a higher bonding energy than Mn–O (512 kJ mol^{-1} vs. 402 kJ mol^{-1}) could enhance the stability of the spinel structure during insertion/de-insertion of lithium; (2) the smaller lattice parameter of Al-doped LiMn_2O_4 alleviates the dissolution of the active material and maintains its structural integrity. Meanwhile, a multi-doped strategy with three elements also shows potential to greatly enhance the electrochemical properties of LiMn_2O_4 . Sun et al. prepared the Li, Co, Gd multi-doped LiMn_2O_4 , which shows an outstanding capacity retention of 98.3% after 100 cycles at 25°C due to its improved structure stability [78]. Manthiram et al. synthesized several Li-M-F (M = Ti, Ni, Cu, Fe, Co, Zn) multi-doped LiMn_2O_4 with excellent electrochemical performance. In these samples, Li^+ and Ni^{2+} are used to prevent Mn dissolution which is caused by a much smaller lattice-parameter difference between the two cubic phases formed during the charge–discharge process. However, the low-valence-state ion doping will increase the valence state of Mn, causing low specific capacity ($<100 \text{ mAh g}^{-1}$). Then, F doping was applied to decrease the valence state of Mn in the Li-Ni co-doped LiMn_2O_4 . Among these materials, $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Zn}_{0.075}\text{O}_{3.85}\text{F}_{0.15}$ displayed a high specific capacity of 113 mAh g^{-1} , good cycling performance with a capacity retention of 94.6% after 50 cycles at 60°C , and excellent rate capability with a retention of 96% at 4 C of its initial specific capacity at 0.1 C [79]. Anion doping can also inhibit the structural changes during the charging/discharging process, thereby improving the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Previous research has shown that doping with F can suppress the generation of NiO impurity, reducing TMs dissolution and improving the rate performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. It is a pity that doping is unable to prevent undesired side reactions between $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and liquid electrolytes [80].

Coating can effectively inhibit side reactions by impeding the direct contact between cathodes and liquid electrolytes. Ideal coating materials for spinel Mn-based oxides should have a good match with the spinel lattice and good diffusion ability of Li^+ and electrons. Chong et al. [81] synthesized Li_3PO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by solid-state reaction. With the Li_3PO_4 layer ($<6 \text{ nm}$), coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ had a disordered crystal structure, protected cathode-electrolyte interface, and dramatically enhanced cycling performance. Jang et al. [82] synthesized LiFePO_4 -modified spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ through a single-step coating process. LiFePO_4 coating greatly improved the thermal stability and high temperature performance, with negligible discharge-capacity reduction. Fang et al. [83] employed atomic layer deposition (ALD) to coat an ultrathin Al_2O_3 layer onto $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles (Figure 4d). Al_2O_3 coating protected $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ from direct exposure to liquid electrolytes, which improved the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The Al_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed 63% capacity retention after 900 cycles (Figure 4e), whereas the bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ maintained 75% of the original capacity after 200 cycles. Apart from inorganic coating, organic materials such as polyimide (PI) [84] and polypyrrole (PPy) [85] can also improve the electrochemical performance of spinel Mn-based oxides. Kim et al. [86] utilized thermal polymerization to produce PI coating from polyamic acid and found that 0.3 wt % PI coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered excellent cycle ability with capacity retention of $>90\%$ at 55°C .

Choosing an appropriate synthesis method can also improve the electrochemical properties of spinel Mn-based oxides, especially $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The solid-phase method, sol-gel method, and molten-salt method are the three main methods to synthesize $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, while each technique has its own advantages and problems. The solid-phase method is a simple, economical and time-saving method [87]. However, the produced $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ not only has a lot of oxygen defects and impurities such as NiO, but also uneven particle-size distribution and severe agglomeration of particles. Oxygen defects usually lead to the generation of more Mn^{3+} , which will have Jahn–Teller distortion, a disproportionation reaction to producing soluble Mn^{2+} , and, thereby, impair the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [88]. Rosedhi et al. [89] synthesized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via ball-milling and following calcination at 750°C . The as-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ displayed an initial discharge capacity of 81 mAh g^{-1} and 86 mAh g^{-1} after 100 cycles at 1C. The widely used

sol-gel method can synthesize $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with good crystallization, small particle size, homogenous dispersion, and outstanding electrochemical performance [90]. In comparison to other synthetic methods, the sol-gel method is much more complicated, time-consuming, and relatively expensive. Cui et al. [91] synthesized nanosized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with an average particle size of 80–100 nm, via a high-oxidation-state manganese sol-gel method. The produced $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ materials not only have an impurity-free cubic spinel structure, but also exhibit excellent dispersion. Both the solid-phase method and sol-gel method need a high-temperature annealing process, which will easily cause impurities and oxygen defects. The molten-salt method is a simple method for preparing complex oxides with pure phase in a low-melting point flux [92]. Wen et al. [93] synthesized spherical $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ materials using the molten-salt method. The as-prepared material displayed a high discharge capacity of 129 mAh g^{-1} in the first cycle and 127 mAh g^{-1} after 50 cycles. The good retention of capacity is credited to significantly fewer impurity phases than that prepared via a solid-state reaction.

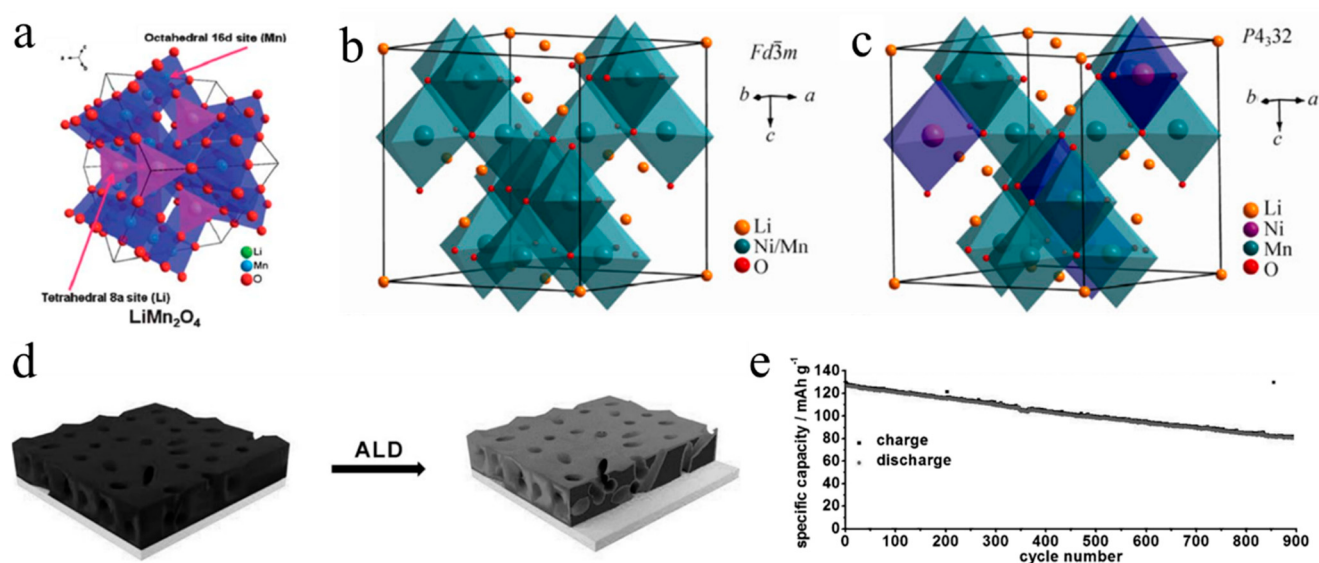


Figure 4. Crystal structure of LiMn_2O_4 (a) [62], $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with $Fd\bar{3}m$ space group (b) and $P4_332$ space group (c) [72]. Diagram showing (d) and long-term cycling performance (e) of ALD-based Al_2O_3 coating $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [83].

For $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the high working voltage at around 4.7 V makes it promising due to its high theoretical energy density ($\approx 690 \text{ Wh kg}^{-1} = 147 \text{ mAh g}^{-1} \times 4.7 \text{ V}$), but it greatly limits the compatibility of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with conventional liquid electrolytes. The mainstream liquid electrolyte is prepared by mixing organic carbonate esters and LiPF_6 and will undergo a continuous decomposition above 4.5 V versus Li^+/Li , resulting in increased thickness of solid electrolyte interphase (SEI), aggravated dissolution of Mn ions, and destroyed electrode structure [94]. Hence, electrolyte additives, fluorinated electrolytes and solid electrolytes are utilized to improve the compatibility between high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and electrolytes. Some additives can be polymerized to form a protective layer and thereby suppress the side reaction between material and electrolytes, prior to the decomposition of electrolyte. For example, Li et al. [95] utilized lithium bis(2-methyl-2-fluoromalonato)borate (LiBMFMB) as an electrolyte additive for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. With the addition of LiBMFMB, a thinner and stabler SEI was formed to prevent further decomposition of the carbonate solvent. Johannes et al. [96] synthesized a novel electrolyte with γ -Butyrolactone (GBL) as solvent, fluoroethylene carbonate (FEC) as solid electrolyte interphase (SEI) additive, and lithium tetrafluoroborate (LiBF_4) as electrolyte salt, and its cutoff potential was increased to 4.6 V [97,98]. Apart from the continuous side reactions between electrolytes and cathode materials, the reactions between LiPF_6 and trace water will produce HF, which will corrode the cathodes and then cause the TMs dissolution [99].

To solve the above-mentioned problems, additives that have strong bonding with HF, F⁻, and H⁺ have been utilized to scavenge the detrimental HF. Li et al. [100] utilized pentafluorophenyltriethoxysilane (TPS) as an additive to improve the cycling stability of LiNi_{0.5}Mn_{1.5}O₄. TPS not only constructed an ionically conductive cathode electrolyte interphase (CEI) film, but also captured detrimental species in electrolytes. As a result, after 400 cycles at 1 C, LiNi_{0.5}Mn_{1.5}O₄ presented an improved discharge capacity retention from 28% to 85%, with the addition of 1 wt % TPS. In addition, fluorinated electrolytes can promote the capacity of LiNi_{0.5}Mn_{1.5}O₄ because of their high oxidation potential. Zhang et al. [101] substituted ethyl methyl carbonate (EMC) and (ethylene carbonate) EC with fluorinated EMC and fluorinated cyclic carbonate (F-AEC) and found that fluorinated electrolytes greatly improve the voltage limits of the electrolyte, and thereby enhance the electrochemical properties of full batteries at elevated temperatures. Developing solid electrolytes can completely solve the decomposition and side reactions of liquid electrolytes, because some solid electrolytes show a wide voltage window beyond 5 V [102]. Li et al. [103] realized high-voltage cycling in solid-state systems using LiNi_{0.5}Mn_{1.5}O₄ cathode, Lipon solid electrolyte, and Li anode. The solid-state high-voltage battery delivered a remarkable capacity retention of 90% over 1000 cycles, a high coulombic efficiency of 97% and a round-trip energy efficiency of 97%.

3.3. Cation-Disordered Rock-Salt Mn-Based Li-Rich Materials

The cation-disordered rock-salt (DRX) structure is mostly considered to be the product of material that has lost its electrochemical activity after cycling. As opposed to the layered structure's ordered arrangement of metal ions, Li and TM ions of DRXs are randomly mixed in each other's positions [104]. Therefore, the DRX structure was thought to be harmful to Li⁺ transport and incapable of providing reversible capacity, until Ceder et al. discovered the electrochemical activity of Li_{1.211}Mo_{0.467}Cr_{0.3}O₂ in 2014 [105]. In the DRX structure, the Li⁺ diffusion between two octahedral (o) sites must undergo an intermediate tetrahedral (T_d) site, known as o-t-o diffusion. The intermediate tetrahedral (Td) site has four face-sharing octahedrons that can be filled with Li or M, which forms a "tetrahedral cluster", generating five possible situations: Li₄ (0-TM), Li₃M (1-TM), Li₂M₂ (2-TM), LiM₃ (3-TM) and M₄ (4-TM) [104] (Figure 5a). The o-t-o Li⁺ diffusion needs a minimum of two Li⁺, making a Li₄, Li₃M, Li₂M₂ environment possible through Li⁺ diffusion pathways. However, the Li⁺ mobility in structures that only contain 1-TM channel or 2-TM channels would be negligible in DRX compounds. Then, in order to guarantee the Li⁺ diffusion in DRX compounds, sufficient 0-TM channels are required to form the 0-TM percolating network [105], which can be constructed by excess Li⁺ in a DRX structure (Figure 5b,c). Therefore, the investigations of DRX compounds mainly focus on the Li-rich materials.

Since Ni, Co and Mn will not migrate to Li sites when a significant amount of Li is removed, causing further structural change, they are the main elements in the majority of layered cathode materials [106]. In contrast, the DRX Li-rich materials show an important advantage of using a large range of TM species, such as V, Mn, Nb, Mo, Ti, Cr and so on. Another advantage of DRX Li-rich materials is the higher specific capacity (>250 mAh g⁻¹), compared with present NCM materials [104]. Meanwhile, the intrinsic cation disorder can cause a small volume change in the DRX structure which, in principle, is advantageous for the cycling of cathode materials. Even the nearly zero-strain Li-ion cathodes of Li_{1.3}V_{0.4}Nb_{0.3}O₂ and Li_{1.25}V_{0.55}Nb_{0.2}O_{1.9}F_{0.1} have been designed and synthesized by Ceder et al. in order to enhance the cycling of cathode materials [107] (Figure 5d). However, the rate capability and cycling performance of DRX Li-rich materials are extremely poor and far from that of today's commercial cathode materials. What is worse, only few of the improvement strategies are effective at promoting the electrochemical properties of DRX materials, such as fluorination.

Among various DRX Li-rich cathodes, the Mn-based materials have shown many advantages, including low cost, resource friendliness, and high energy density (about 1000 Wh kg⁻¹) [108,109], demonstrating great potential as low-cost high-energy-density

materials. The Mn-based Li-rich $\text{Li}_2\text{Mn}_{2/3}\text{Nb}_{1/3}\text{O}_2\text{F}$ and $\text{Li}_2\text{Mn}_{1/2}\text{Ti}_{1/2}\text{O}_2\text{F}$ materials were synthesized via high-energy ball-milled methods and exhibited a high specific capacity of $>300 \text{ mAh g}^{-1}$ and high energy density of around 1000 Wh kg^{-1} without the use of O redox [108]. Another series of Mn-based $\text{Li}_x\text{Mn}_{2-x}\text{O}_{2-y}\text{F}_y$ compounds with a high capacity of 350 mAh g^{-1} was also synthesized using ball-milling methods [109] (Figure 5e). Although the high-energy ball-milling process is a good method to produce DRX compounds even for materials whose disorder cannot be accessed thermally, its high energy consumption and low productivity make it unsuitable for industrial application. To realize the industrial product of Mn-based DRX compounds, the traditional solid-state method has been employed. However, these Mn-based DRX compounds must contain d0 element to stabilize the disordered structure, and Nb^{5+} is often used. For instance, Ceder et al. [110] and Tong et al. [15] prepared Li-Mn-Nb-O-F compounds by sintering at 1000°C under an argon atmosphere for 7h using Li_2CO_3 , MnO_2 , Nb_2O_5 and LiF as raw materials. The as-prepared $\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$ showed a high specific capacity of 330 mAh g^{-1} and high average discharge voltage of 3.2 V. However, to improve its electrochemical performance, fluorinated DRX needs a larger F content since the F solubility in DRX using LiF as the F source is limited at 7.5 at%. Chen et al. [111] synthesized the Li-Mn-Nb-O-F compounds using a solid-state calcination method using poly(tetrafluoroethylene) (PTFE) as an F source; the incorporation of F content was up to 12.5 at%. In this, the Li-Mn-Nb-O-F compound with 10 at% of F substitution displays a reversible discharge capacity of $\approx 255 \text{ mAh g}^{-1}$ and good cycling performance (123% capacity retention after 30 cycles) (Figure 5f).

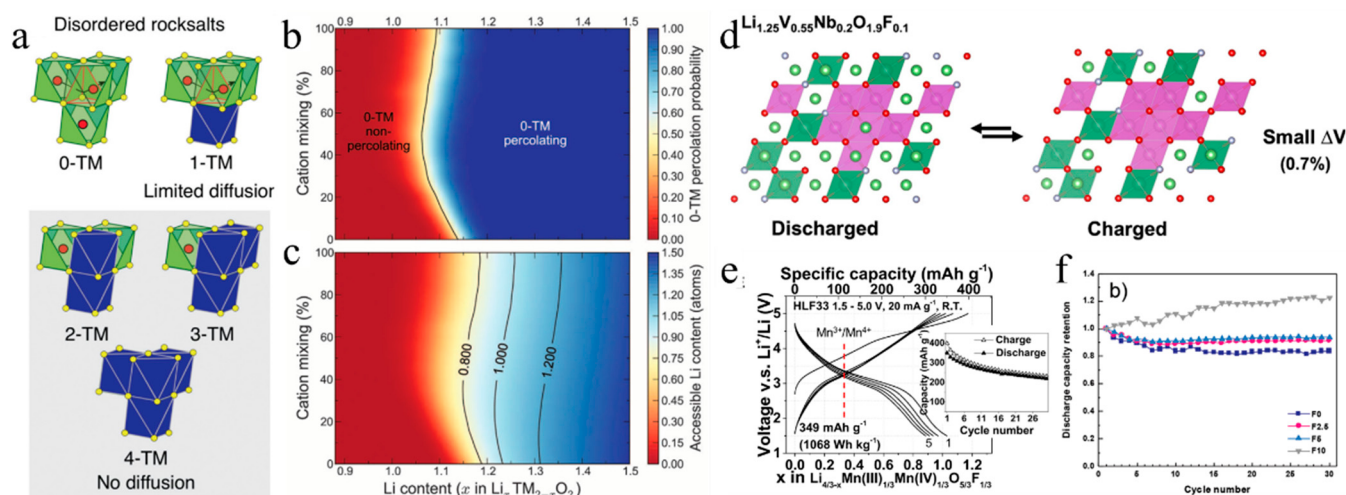


Figure 5. (a) Cation disorder causes the formation of all varieties of tetrahedral clusters (0-TM, 1-TM, 2-TM, 3-TM and 4-TM channels) [104]. (b) Computed probability of discovering a percolating network of 0-TM channels versus Li content (x in $\text{Li}_x\text{TM}_{2-x}\text{O}_2$) and cation mixing ($\text{TM}_{\text{Li layers}}/\text{TM}_{\text{TM layers}} \times 100\%$) [105]. (c) Accessible Li content by a percolating 0-TM network versus Li content and cation mixing [105]. (d) Structure change of $\text{Li}_{1.25}\text{V}_{0.55}\text{Nb}_{0.2}\text{O}_{1.9}\text{F}_{0.1}$ during charging and discharging [107]. (e) Electrochemical performance of $\text{Li}_{1.3333}\text{Mn(III)}_{0.3333}\text{Mn(IV)}_{0.3333}\text{O}_{1.6667}\text{F}_{0.3333}$ (HLF33) [109]. (f) Capacity retention of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Nb}_{0.2}\text{O}_2$ (F0), $\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$ (F2.5), $\text{Li}_{1.2}\text{Mn}_{0.65}\text{Nb}_{0.15}\text{O}_{1.9}\text{F}_{0.1}$ (F5), and $\text{Li}_{1.2}\text{Mn}_{0.7}\text{Nb}_{0.1}\text{O}_{1.8}\text{F}_{0.2}$ (F10) cathodes [111].

3.4. Phospho-Olivine Mn-Based Compounds

Since the groundbreaking investigation of Goodenough et al. in 1996 [112], the Phospho-olivine LiMPO_4 compound (where $M = \text{Fe, Mn, Co or Ni}$) has been recognized as a viable cathode material for LIBs. Among the olivine phosphate family, LiMnPO_4 and $\text{LiFe}_x\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4$ are excellent candidates for stable and high-energy-density cathode materials. Phospho-olivine LiMnPO_4 is made up of a hexagonal close-packed (hcp) framework of oxygen with Pnma space group, where Mn and Li occupy octahedral Figure 4a,c

octahedral sites, and P atom being in Figure 4c tetrahedral site, respectively (Figure 6a). $\text{LiFe}_x\text{Mn}_{1-x}\text{Fe}_x\text{PO}_4$ has a similar crystal structure, with Li and Mn/Fe atoms located in the octahedral Figure 4a,c sites, respectively, while the tetrahedral Figure 4c position harbors the P atoms [113]. LiMnPO_4 is attractive due to its high theoretical discharge capacity ($\approx 170 \text{ mAh g}^{-1}$), high operating voltage (4.1 V vs. Li/Li^+), high structural stability during the charging/discharging process, superior theoretical energy density ($\approx 701 \text{ Wh kg}^{-1} = 171 \text{ mAh g}^{-1} \times 4.1 \text{ V}$), and high safety due to its strong P–O covalent bond. Additionally, LiMnPO_4 shows low toxicity, environmental friendliness and low cost. However, the low electronic conductivity ($< 10^{-10} \text{ S cm}^{-1}$) and low lithium-ion diffusion ($< 10^{-16} \text{ cm}^2 \text{ s}^{-1}$) of LiMnPO_4 significantly affects its rate capability and cycling performance at high rates and limits its industrial application [114]. $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ is a solid-solution material between LiMnPO_4 and LiFePO_4 with uniform distribution of Mn and Fe elements [115–117]. Fe^{2+} doping can reduce electrochemical polarization, leading to an enhancement in aspects such as the reversibility of electrodes, the ability of de-lithiation/lithiation and the diffusion of Li^+ . Moreover, Jahn–Teller lattice distortion of Mn^{3+} ions will hinder the lithium extraction/insertion process in LiMnPO_4 , which will further cause a large volume change and interface strain between the LiMnPO_4 and MnPO_4 phases [118]. In order to overcome these problems, several methods have been applied to improve the electrochemical properties of LiMnPO_4 and $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$, including particle-size reduction, carbon coating, ion doping, and an optimized synthesis process.

Reducing particle size to a nanometer scale can efficaciously enhance the electrochemical properties of phospho-olivine materials, such as nanoparticles [119] and nanosheets [120–122], because nanoparticles can provide shorter diffusion pathways and larger surface-area contact with electrolytes for electron and ion transfer [123]. Particle size and shape may be greatly controlled via synthesis methods. Common preparation methods include the solid-phase method, sol-gel method, hydrothermal/solvothermal method, precipitation method, spray pyrolysis method, polyol synthesis and so on. The solid-phase method is a conventional and economical synthesis method, which heats a mixture of lithium, manganese and phosphorus sources at a high temperature to form olivine-phase products [124]. This method can be easily scaled up for commercial use. However, the solid-phase method not only needs a high-temperature environment, but also produces large or agglomerated particles with poor electrochemical performance [125]. In comparison to the solid-phase method, the liquid-phase method is beneficial for controlling particle morphology and synthesizing nanoparticles. For example, powders produced using the sol-gel method have high purity, uniformity, increased crystallinity, accurate stoichiometric control, and minimal size [126]. Sol-gel synthesis is a low-temperature wet chemical method which involves the formation of sols, the gelation of sols into gels, the drying of gels into “xerogels” with reduced volume, and the densification to obtain final powder products [127]. The sol-gel method can adjust the product’s structure and morphology within the nanometric range, by controlling reaction time, pH value, calcination temperature, concentration, viscosity and so on. Kwon et al. [128] studied the influence of calcination temperature on particle size and successfully synthesized LiMnPO_4 nanoparticles with a diameter of $130 \pm 10 \text{ nm}$ via a glycolic-acid-assisted sol-gel approach and this sample showed a reversible capacity of 134 mAh g^{-1} at 0.1 C. Liu et al. [129] synthesized carbon-coated nano-sized LiMnPO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ of 100–150 nm in width and 200–400 nm in length using a high-energy ball-milling-assisted sol-gel method (Figure 6b,c). The as-prepared $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ attained considerable electrochemical performance with initial discharge capacities of 128.6 mAh g^{-1} and capacity retentions of 93.5% and 90.3% after 100 cycles at 1 C and 2 C rates, respectively (Figure 6d). Although nanoparticles provide shorter diffusion lengths and better electrochemical performances, they have low tap density because of their high surface area, which causes low tap density and loading of active material in electrodes [130]. Since spherical particles have the largest tap density, it is crucial to control the particle morphology. The hydrothermal/solvothermal method can produce homogenous and morphology controllable particles. Hydrothermal/solvothermal method involves wet chemical

processes that take place in an aqueous solution of mixed precursors above the solvent's boiling temperature [131]. Cao et al. [132] synthesized LiMnPO_4 particles with good sphericity and high tap density using the hydrothermal method with Li_3PO_4 as the precursor (Figure 6e). This sample exhibited excellent cycling performance with capacity retention of 95.55% after 500 cycles (Figure 6f). Luo et al. [133] synthesized a $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocrystal using a facile solvothermal reaction and studied the transformation law of morphology from nanosheet to nanoellipsoid. By modifying pH value and precursor ions, nanoellipsoid S-2.6 delivers excellent cycling performance and chemical stability.

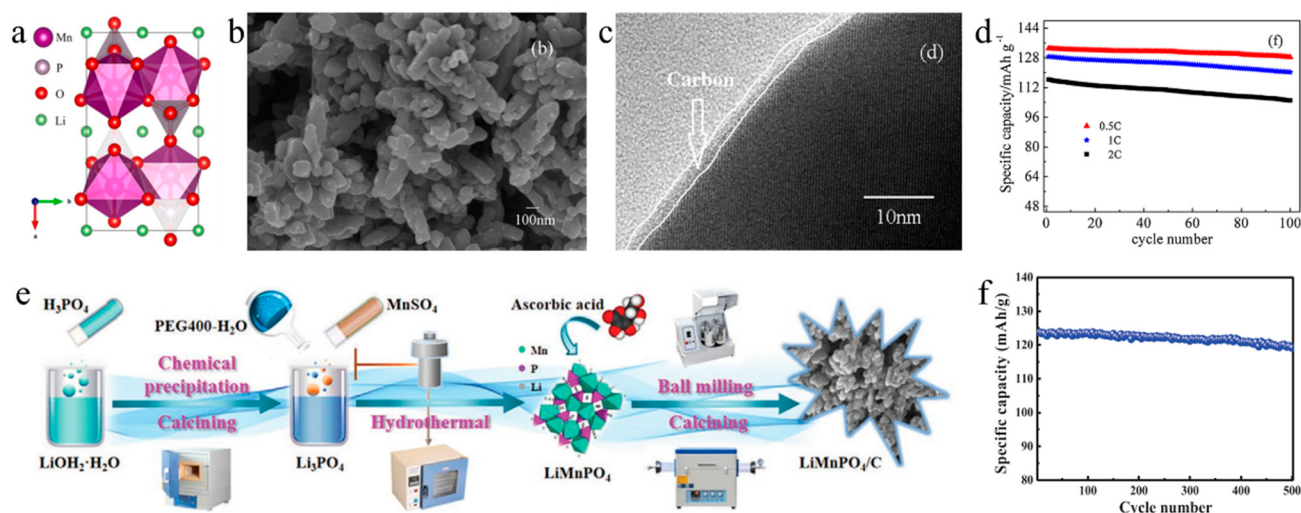


Figure 6. (a) Crystallographic structures of LiMnPO_4 . SEM images (b), TEM images (c) and cycling performance (d) of nano-sized $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ [129]. Process diagram (e) and cycling performance (f) of LiMnPO_4/C synthesized by hydrothermal method [132].

Ion doping at Li, Mn, and O sites can also enhance the electrochemical performances of LiMnPO_4 . Li-site doping can reduce the charge transfer resistance and broaden the one-dimensional diffusion channels of Li^+ [134], but the transition metal in the Li layer will hinder Li^+ diffusion to a certain extent [135]. Thus, Mn-site doping has received a lot of attention, such as doping with Fe [136], V [137], Mg [138], Ni [139], Cu [140], Cr [141], and Zn [135]. Oukahou et al. [136] synthesized $\text{LiMn}_{1-x}\text{M}_x\text{PO}_4$ ($\text{M} = \text{Ni}, \text{Fe}$) with improved electronic conductivity and reduced Li^+ diffusion energy barrier, by doping Ni^{2+} and Fe^{2+} cations at Mn sites. Hu et al. [142] synthesized Fe-doped LiMnPO_4 nanoparticles through the solvothermal method, and found that Fe doping can significantly increase the initial reversible capacity, cycle performance and rate capacity. $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ exhibits a high discharge capacity of 147 mAh g^{-1} and nearly 100% capacity retention after 100 cycles at 1 C. Anion doping at O sites can also enhance the electrochemical properties of LiMnPO_4 by facilitating Li^+ migration of lithium ions in the diffusion channels and enhancing electronic conductivity [134]. Zhang et al. [129] prepared Sulphur-doped $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ via a one-step solvothermal process. Since doping Sulphur with a less electronegative atom is advantageous for increasing electronic conductivity, the as-prepared cathode material delivers a high specific discharge capacity of $166.83 \text{ mAh g}^{-1}$ at 0.1 C.

Carbon coating is a common method to increase the conductivity of phospho-olivine materials by enhancing the electron conductivity between particles [143] and improving the contact between the active material and liquid electrolyte. The most important thing for carbon coating is to select high-quality and low-cost carbon sources. Mizuno et al. [144] studied the discharge capacities of LiMnPO_4 coated with carbon prepared from different carbon sources and found that LiMnPO_4 with carbon obtained from carboxymethyl cellulose exhibits the highest discharge capacity of 94 mAh g^{-1} at 0.01 C. However, this method needs additional heat treatment to form a carbon coating. The polyol method can efficaciously prepare nanosized particles with in-situ carbon coating. The polyol method

includes four main steps, in which the polyol acts as solvent, fuel, energy supplier and carbon source, respectively [145]. Long et al. [146] synthesized LiMnPO_4 with a carbon coating using a microwave-assisted polyol method at 130 °C for 30 min. The obtained LiMnPO_4/C sample contains a 2 nm thick carbon layer and delivers a discharge capacity of 126 mAh g^{-1} with a capacity retention of ~99.9% after 50 cycles at 1 C. By using a two-step mechanochemically assisted solid-state synthesis, Podgornova et al. [147] synthesized carbon-coated $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ cathode materials. They found that the capacity and rate capability of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ improved owing to the good graphitization of the carbon coating and the tight combination between the carbon coating and $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$. Although these aforementioned methods can enhance the electrochemical performances of LiMnPO_4 and $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$, obtaining all these desired properties is still challenging. To prepare LiMnPO_4 and $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ cathodes for high-performance lithium-ion batteries, a simple, economic, easy to control, and reliable synthesis technique still needs to be developed.

4. Summary and Perspectives

Mn-based materials have shown advantages in material cost and energy density among LIBs' cathode materials, due to their richness in the Earth's crust and wide range of valance states. This has led to the generation of series of potential cathode materials with low cost per Wh, such as spinel LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and Li-rich $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$, rock-salt $\text{Li}_{1.2}\text{Mn}_{0.625}\text{Nb}_{0.175}\text{O}_{1.95}\text{F}_{0.05}$, Olivine LiMnPO_4 and LiMnFePO_4 , etc. However, the Mn dissolution and Jahn–Teller effect of Mn-based materials are not negligible, which is detrimental to electrochemical performance. Element doping and surface coating are the major strategies to solve the above problems, which can efficaciously promote the stability and kinetics of Mn-based materials, then improve the cycling performance and rate capability. Some special problems need special improvement strategies; for example, the oxygen release of Li-rich materials can be eliminated by constructing oxygen vacancy and the stability of DRX compounds can be improved by F fluorination.

Among the materials mentioned in this review, spinel LiMn_2O_4 has been successfully commercialized, while layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, olivine-type LiMnPO_4 and LFMP, as well as LRM have the potential to be applied as cathode materials for LIBs in the near future. The applications of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and DRXs, however, are limited due to their high discharge potential and poor cycle performance, respectively. For the Mn-based cathode materials, some prospects are suggested: (1) achieving a uniform coating by simple methods, (2) introducing doping elements into the precursors, (3) producing high-voltage electrolytes with low cost, and (4) analyzing the synergistic effect of multi-element doping and the influences of different components on the cathode's electrochemical properties, via theoretical calculations.

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