



# Li-Rich Layered Oxides and Their Practical Challenges: Recent Progress and Perspectives

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## Abstract

Lithium-rich layered oxides (LLOs), also known as  $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$  or  $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$  ( $\text{M}=\text{Ni}, \text{Co}, \text{Mn}$ ), have been regarded as some of the highest capacity lithium cathodes and have attracted increasing attention from battery researchers and engineers in recent years. This is because LLOs possess maximum possible capacities of  $\sim 280$  to  $310 \text{ mAh g}^{-1}$  with a high working potential of  $\sim 3.7 \text{ V}$  (vs.  $\text{Li}^+/\text{Li}^0$ ) and an astounding energy density of  $\sim 900 \text{ Wh kg}^{-1}$ . Despite these promising properties, these technologically important cathodes have not yet been successfully commercialized due to low initial Coulombic efficiency, poor rate capabilities and gradual capacity/voltage fade during electrochemical cycling as well as further complications from continuous structural changes during cycling. Here, researchers have concluded that these issues mainly originate from the electrochemical activation of  $\text{Li}_2\text{MnO}_3$  components, which, although it provides anomalously high capacity performances, also causes associated complex anionic redox activities of O and irreversible structural and phase transformations during charging at potentials greater than  $4.5 \text{ V}$  (vs.  $\text{Li}^+/\text{Li}^0$ ). To provide perspectives, this review will summarize various attempts made towards addressing these issues and present the connections between electrochemical properties and structural change. In addition, this review will discuss redox chemistries and mechanistic behaviours during cycling and will provide future research directions to guide the commercialization of LLOs.

**Keywords** Li-rich layered oxide · Surface coating · Voltage fade · Oxygen activities · Lithium-ion battery

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## 1 Introduction

Lithium-ion batteries (LIBs) have experienced major breakthroughs in battery technology since being commercialized less than 3 decades ago. Since then, LIBs have been successfully applied in electrified vehicles (EVs) and are integral to daily life, with demand for higher energy density ever increasing. The International Energy Agency reported that the number of EVs (including battery electric vehicles (BEVs) and plug-in hybrid electric vehicles (PHEVs)) surpassed 3 million in 2017, which is a 56% increase from 2016 [1] and that this is a strong driving force for breakthroughs and evolution in battery technologies, in which aside from battery costs and safety [2], long-range BEVs require higher volumetric and gravimetric energy density (*i.e.*  $750 \text{ Wh L}^{-1}$  and  $350 \text{ Wh kg}^{-1}$ ) [3].

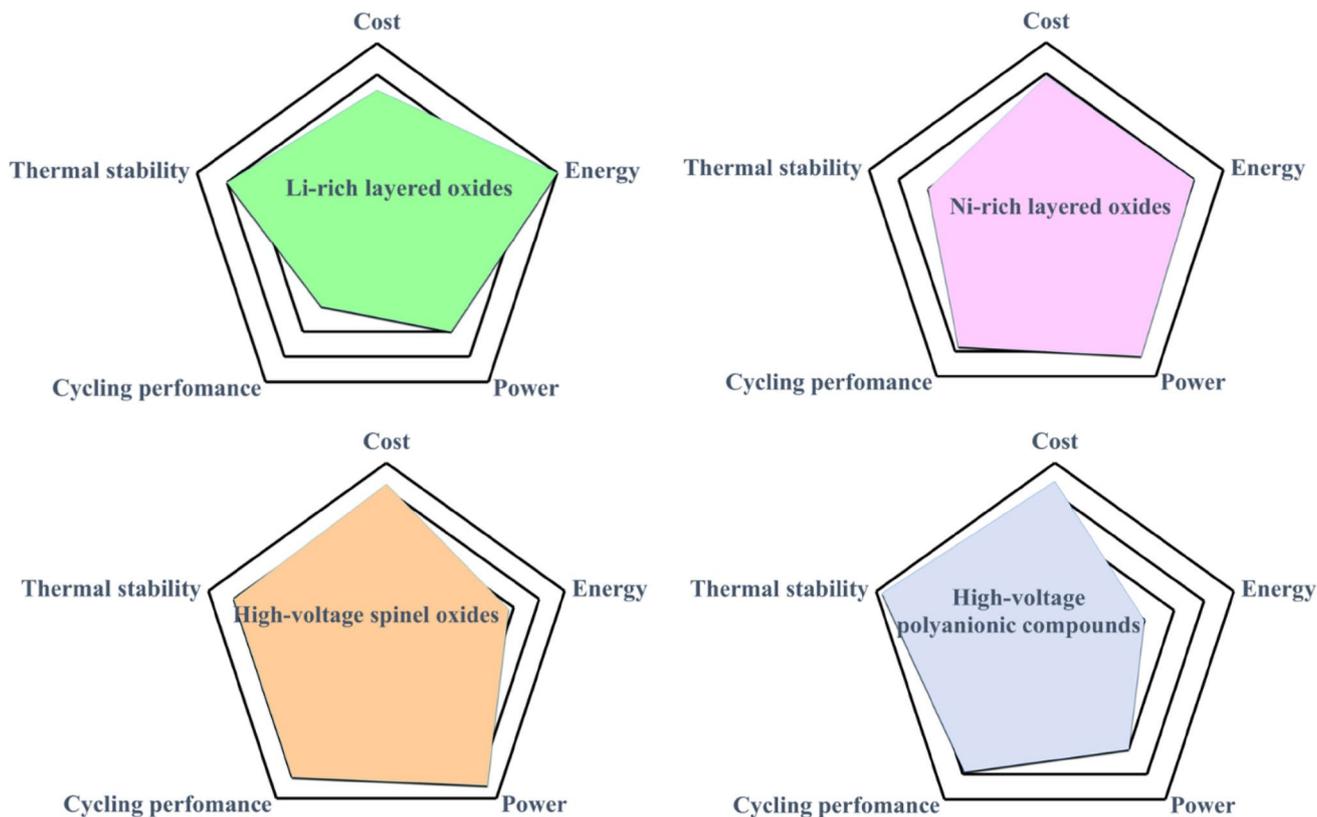
However, cathodes in LIBs are intrinsic bottlenecks that restrict LIBs capacities and energy performances and current commercial cathode materials for BEVs and PHEVs such as  $\text{LiFePO}_4$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) and the  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$  ( $x+y < 0.5$ ) (NCM) family

[e.g.  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  (NCM622),  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (NCM811)] exhibit gravimetric energy densities lower than  $800 \text{ Wh kg}^{-1}$  [4]. In addition, the overall energy density of LIBs is further reduced by battery packaging.

To address these issues, considerable research has been conducted on the optimization and design of new cathode materials with high capacities (e.g.  $> 200 \text{ mAh g}^{-1}$ ) or high voltage (e.g.  $\geq 4 \text{ V vs. Li}^+/\text{Li}^0$ ) [5–11] with prospective high-voltage candidates including high-voltage spinel oxides ( $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ), lithium-rich layered oxides (LLOs) ( $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ ,  $\text{M}=\text{Ni, Co, Mn, etc.}$ ), nickel-rich layered oxides ( $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ ,  $\text{M}=\text{Co, Mn and Al}$ ) and high-voltage sulphate-, phosphate- or silicate-based polyanionic compounds (Fig. 1). And in particular,  $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$  or  $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$  ( $\text{M}=\text{Ni, Co, Mn}$ ), known as LLOs, has attracted immense attention from researchers because they can deliver the highest energy density ( $\sim 900 \text{ Wh kg}^{-1}$ ) thus far as compared with other conventional cathode materials.

The concept of LLO cathode materials originated from Thackeray et al. who investigated rock-salt-phase  $\text{Li}_{1.09}\text{Mn}_{0.91}\text{O}_2$  and later introduced a strategy to design new cathode materials with high capacities ( $> 200 \text{ mAh g}^{-1}$ ) [13, 14]. Since then, the discharge capacity of LLOs has

improved substantially, reaching above  $300 \text{ mAh g}^{-1}$  [15]. However, several issues still need to be addressed for LLOs before commercialization, including low initial Coulombic efficiency (ICE), capacity and voltage fade and poor rate capability [16–18]. And although numerous strategies have been applied to overcome these challenges, such as surface modification [19], lattice doping [20, 21] and more recently the alteration of O activities [22], the fundamental origins of the crystal structural change related to these issues, especially the voltage fade, and the mechanisms of how these changes contribute to such fading during cycling have not been elucidated clearly. Until recently, however, few studies have achieved breakthroughs in the understanding of the fundamental origin of the crystal structural changes [23–28] and most reviews have mainly focused on the structure [29], electrochemical performance [30], synthesis methods [31] or characterization technique [32] of LLO materials. Therefore, this review will comprehensively present the structure-function relationship of LLO materials along with explanations of their modifying strategy-issue connection from a fundamental perspective. In addition, this review will provide suggestions for ongoing high-energy cathode research.



**Fig. 1** Radar plot comparing the volumetric energy density, power, cycling performance, thermal stability and costs of various high-voltage cathode materials. *Source:* Reproduced with permission from Ref. [12]

## 2 Crystal Structures and Mechanistic Reactions

### 2.1 Crystal Structure

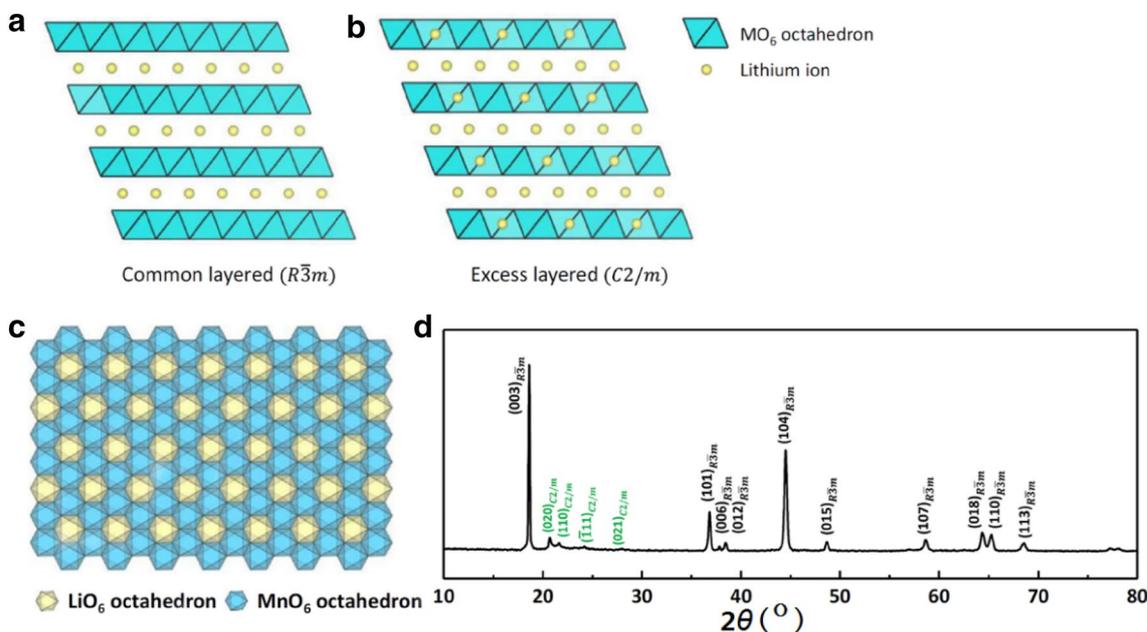
LLOs can be categorized into the  $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$  model (M stands for transition metals (TMs)) based on a two-phase model first proposed by Thackeray et al. [14, 33] and the  $\text{Li}(\text{Li}_x\text{M}_{1-x})\text{O}_2$  model based on a solid solution model with a homogeneous long-range order as proposed by Dahn et al. [34, 35]. Here, both models are widely used in the literatures, and currently, the optimal model is still a matter of debate with no agreement being reached on the definition of the original structure of LLOs [36].

For the two-phase ( $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ ) model, LLOs are regarded as composites in which a monoclinic symmetry  $\text{Li}_2\text{MnO}_3$  phase (space group  $C2/m$ ) is structurally integrated with a trigonal symmetry  $\text{LiMO}_2$  phase (space group  $R\bar{3}m$ ) at the atomic level [14] due to the similar O3-type layered structures of the two phases [37] with Li atom sites occupying octahedral sites in the structure with three  $\text{MO}_6$  octahedral layers (Fig. 2a, b). Here, Mn and excess Li atoms (at a Li/Mn ratio of 1:2) form the  $\text{MO}_6$  octahedral layers in the structure of the  $\text{Li}_2\text{MnO}_3$  phase [37], and therefore,  $\text{Li}_2\text{MnO}_3$  can be reformulated as  $\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$  [29]. Furthermore, the distances between the close-packed layers of the (001) plane in the  $\text{Li}_2\text{MnO}_3$  monoclinic phase and the (003) plane in the  $\text{LiMO}_2$  trigonal phase are

both  $\sim 4.7 \text{ \AA}$ , allowing for the compatible integration of the two phases at the atomic level [38].

And as a result of the high compatibility of these two phases, researchers have also proposed that the  $\text{MO}_6$  octahedral layers can contribute to a monoclinic superstructure with one  $\text{LiO}_6$  octahedron surrounded by six  $\text{MnO}_6$  octahedra to form a hexagonal  $\text{LiMn}_6$  honeycomb in the Mn-rich layer, allowing for a solid solution ( $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ ) model (Fig. 2c) [39] in which the cation ordering-derived superstructure can produce broad and weak peaks in the  $2\theta$  range of  $20^\circ$ – $30^\circ$  in the X-ray diffraction (XRD) patterns of LLOs (Fig. 2d).

Different synthetic methods have been suggested to be the cause of the discrepancy in the two LLO models. Based on this, Table 1 summarizes competing two-phase and single-phase models of LLOs through comparisons of experimental evidence and synthesis methods of various compounds reported in the literature in which 30% of the reported literature supports the two-phase composite model and 70% considers LLOs as a solid solution of either  $R\bar{3}m$  or  $C2/m$ . Here, much of the literature suggesting a phase composite model is solely based on selected characterization techniques and their conclusions do not appear to be reliable due to the structural complexity and similarity between the two phases of LLOs, and in their final analyses, a unique reference structure for the LLOs cannot be fully established because of the strong correlation to synthesis conditions and compositions.



**Fig. 2** Schematic of structure crystallography. **a**  $\text{LiMO}_2$  structure ( $R\bar{3}m$ ), **b** monoclinic  $\text{Li}_2\text{MnO}_3$  ( $C2/m$ ), **c** Li/Mn atom ordering in  $\text{LiM}_2$  layer in  $\text{Li}_2\text{MnO}_3$ , **d** XRD pattern of layered  $0.5\text{Li}_2\text{MnO}_3-0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  material. Source: Reproduced with permission from Ref. [37]

**Table 1** Summary of reported LLO materials with notations based on competing models

	Material composition; notation	Characterization techniques	Synthesis method/sintering conditions	Ref.
Two-phase ( $R\bar{3}m + C2/m$ ) composite	$\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.10}\text{O}_2$ ; $0.5\text{LiCo}_{0.25}\text{Mn}_{0.375}\text{Ni}_{0.375}\text{O}_2 - 0.5\text{Li}_2\text{MnO}_3$	NPD, magnetic susceptibility studies	Co-precipitation Commercial powder (Toda HE5050)	[40]
	$\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$	In situ XRD, HAADF-STEM	Co-precipitation, 600 °C-6 h and 900 °C-14 h	[41]
	$\text{Li}_{1.2}\text{Mn}_{0.61}\text{Ni}_{0.18}\text{Mg}_{0.01}\text{O}_2$ ; $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 - 0.4\text{LiNi}_{0.45}\text{Mn}_{0.525}\text{Mg}_{0.025}\text{O}_2$	SXRPD, HAADF-STEM, NBED, EELS	Solid-state reaction, 1000 °C for 24 h	[42]
	$0.5\text{Li}_2\text{MnO}_3 - 0.5\text{LiMn}_{0.42}\text{Ni}_{0.42}\text{Co}_{0.16}\text{O}_2$	SXRPD	Solid-state reaction 1000 °C for 20 h	[43]
	$\text{Li}_{1.19}\text{Ni}_{0.25}\text{Mn}_{0.56}\text{O}_2$ ; $\text{Li}_{1.25}\text{Ni}_{0.17}\text{Mn}_{0.61}\text{O}_2$ ; $\text{Li}_{0.85}\text{Ni}_{0.57}\text{Mn}_{0.55}\text{O}_2$ (74:26 wt%)	SXRPD, NPD	Single-step one-pot method, 850 °C for 6 h at 1 °C/min	[44]
	$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$	La-APT, STEM-EDS	–	[45]
	$\text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2$ ; $\sim 0.5\text{Li}_2\text{MnO}_3 - 0.5\text{LiCoO}_2$	HAADF-STEM, SAED, EELS, EXAFS	900 °C for 12 h	[46]
	$\text{Li}_{1.2}\text{Mn}_{0.567}\text{Ni}_{0.166}\text{Co}_{0.067}\text{O}_2$	ABF/HAADF-STEM	Solid-state reaction 1000 °C for 20 h	[38]
	$\text{Li}[\text{Li}_{(1-x)/3}\text{Co}_x\text{Mn}_{(2-2x)/3}]\text{O}_2$ ( $0 \leq x \leq 1$ )	Monte Carlo simulation	Combinatorial synthesis, 900 °C/800 °C cooling rate of 1 °C/min	[47]
	$\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$	HAADF-STEM, EELS	Co-precipitation, 900 °C-24 h	[48]
	$\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.10}\text{O}_2$ ;	AC-STEM, EELS	Commercial powder (Toda HE5050)	[49]
	$\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.51}\text{Al}_{0.05}\text{Co}_{0.08}\text{O}_2$	XRD, HRTEM, NBED, Raman Spectroscopy	Solution combustion reaction, 700 °C-1 h and 900 °C-20 h	[50]
	$\text{Li}_{1.2}\text{Ni}_{0.22}\text{Co}_{0.12}\text{Mn}_{0.5}\text{O}_2$	NPD, XRD	Co-precipitation, 900 °C-16 h	[51]
	$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ ; $0.5\text{Li}_2\text{MnO}_3 - 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$	ED, HAADF-STEM, EELS, XEDS	Co-precipitation, 900 °C-15 h	[52]
	$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$	XRD, HRTEM, HAADF-STEM, SAED, EELS, XEDS	Co-precipitation, 900 °C-6 h	[53]
	$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ ; $0.5\text{Li}_2\text{MnO}_3 - 0.5\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$	NPD	Co-precipitation, 900 °C-6 h	[54]
	$\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$	XRD	Co-precipitation, 900 °C-15 h	[55]
	$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ ; $(1-x)\text{Li}_2\text{MnO}_3 - x\text{LiFeO}_2$ ( $x=0.5$ )	STEM-EELS, NBED, HRTEM	Co-precipitation, mixed alkaline hydrothermal method (220 °C-8 h, 850 °C-1 h) and cooled by quenching	[56]
	$C/2m$ Single phase	NMC. $\text{Li}_2\text{MnO}_3$ composite and multilayer films	HAADF-STEM, SAED, HRTEM	Pulsed laser deposition(750 °C)
$0.5\text{Li}_2\text{MnO}_3 - 0.5\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$		ABF/HAADF-STEM, XRD, Raman Spectroscopy	Co-precipitation, 450 °C-6 h and 850 °C-12 h	[58]
$\text{Li}(\text{Li}_{0.19}\text{Ni}_{0.16}\text{Co}_{0.08}\text{Mn}_{0.57})\text{O}_2$		XRD, HRTEM, SAED	Co-precipitation, 900 °C-10 h	[59]
$\text{Li}_{(2x+2)/(2+x)}\text{Ni}_{(2-2x)/(6+3x)}\text{Co}_{(2-2x)/(6+3x)}\text{Mn}_{(2+4x)/(6+3x)}\text{O}_2$ ( $0 \leq x \leq 1$ )		XRD, HRTEM, Raman Spectroscopy	Spray pyrolysis, 900 °C-10 h	[60]
$\text{Li}(\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56})\text{O}_2$		XRD, HRTEM, SAED	Solid-state reaction, 800 °C-10 h and 900 °C-12 h	[61]
$\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ ; $\text{Li}(\text{Ni}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375})\text{O}_2 - \text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$		XRD, SAED, TEM, EXAFS, HAADF-STEM, STEM-EDS	–	[18]
$x\text{Li}_2\text{MnO}_3 - (1-x)\text{LiNi}_{2/3}\text{Co}_{1/6}\text{Mn}_{1/6}\text{O}_2$		XRD, Raman Spectroscopy, TEM	Sol-gel, 950 °C-12 h	[62]
$\text{Li}_{1.200}\text{Mn}_{0.540}\text{Ni}_{0.130}\text{Co}_{0.13}\text{O}_{2+\delta}$		XRD, HRTEM	Electrospinning, 800 °C-12 h	[63]
$\text{Li}_{1.16}\text{Mn}_{0.6}\text{Co}_{0.12}\text{Ni}_{0.12}\text{O}_2$		Raman Spectroscopy, XRD	Hydrothermal (180 °C-12 h, 450 °C-6 h, 650 °C-24 h)	[63]
$\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{X}_{0.03}\text{O}_2$ ( $\text{X} = \text{Si}$ and $\text{Sn}$ )		XRD, HAADF/ABF-STEM	Sol-gel, 450 °C-5 h and 900 °C-12 h	[64]

**Table 1** (continued)

	Material composition; notation	Characterization techniques	Synthesis method/sintering conditions	Ref.
	$x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}(\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25})\text{O}_2$ ( $0 \leq x \leq 1$ )	XRD, HRTEM	Auto-combustion route, 800 °C-12 h	[65]
	$\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$	XRD	Mixed hydroxide method, 480 °C-3 h and 900 °C-3 h	[35]
	$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$	XRD	Co-precipitation 750 °C-12 h	[36]
	$x\text{Li}_2\text{MnO}_3-y\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2-(1-x-y)$ $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$	STEM-EELS, TEM, XRD	Co-precipitation, 900 °C-12 h	[66]
	$\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$	NMRS, XRD, DIFFaX simulation	Double mixed hydroxide method, 480 °C-12 h and 1000 °C-3 days	[67]
	$\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ ; $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$	HAADF-STEM, D-STEM, XRD, NBED	EDTA and citric acid compl- exation route, 850 °C-5 h	[68]
	$\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$	HAADF-STEM, EELS, XEDS	Co-precipitation, commercial powder (Toda HE5050)	[69]
	$\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$	HAADF-STEM, XEDS	Hydrothermal assisted, 900 °C-24 h	[70]
	$\text{Li}_{1.25}\text{Mn}_{0.56}\text{Ni}_{0.19}\text{O}_{1.93}$	XRD, HAADF-STEM, EELS	Solid-phase calcination method, 900 °C-12 h	[71]
	$\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$	SXRPD, HRTEM	Solid-state reaction	[28]
	$\text{Li}(\text{Li}_{0.20}\text{Ni}_{0.20}\text{Mn}_{0.60})\text{O}_2$	HAADF-STEM, EELS	Hydrothermal assisted, 900 °C and cooling by quenching	[72]
	$\text{Li}_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_3$	XRD, NPD	Co-precipitation, 900 °C-12 h	[73]
	$\text{Li}_{1.2}(\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13})\text{O}_2$ ; $\text{Li}_y\text{MO}_2$ , $y > 1$ , $M = \text{Mn, Co and Ni}$ and $\text{Mn} > \text{Ni} > \text{Co}$	HAADF-STEM, XEDS, EELS	Molten salt method	[69]
	$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$	XRD, HAADF-STEM, NMRS	–	[74]
	$\text{Li}(\text{Li}_{0.23}\text{Ni}_{0.15}\text{Mn}_{0.62})\text{O}_2$	XRD	Solid-state reaction, 900 °C-8 h	[75]
	$\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13})\text{O}_2$	XRD, ABF/HAADF-STEM	Co-precipitation, 500 °C-5 h and 850 °C-12 h	[76]
	$\text{Li}_{1.85}\text{Mn}_{0.7}\text{Co}_{0.45}\text{O}_3$ , $\text{Li}_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_3$ ; $\text{Li}_{2-\delta}(\text{Mn}_{1-x}\text{Co}_x)_{1+\delta}\text{O}_3$	XRD, HREM, TEM, ED	Co-precipitation, 950 °C-12 h	[77]
	$\text{Li}(\text{Li}_{0.20}\text{Mn}_{0.58}\text{Ni}_{0.18}\text{Co}_{0.04})\text{O}_2$	XRD, HAADF-STEM	Co-precipitation, 1000 °C-12 h, different cooling rates	[78]
$\bar{R}3m$ Single phase	$\text{Li}_{1.20}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$	XRD, NPD	Sol-gel, (800-1000) °C	[79]
	$\text{Li}(\text{Co}_{1-x}\text{Li}_{x/3}\text{Mn}_{2x/3})\text{O}_2$ ( $0 \leq x \leq 1$ )	XRD	Solid-state reaction, 900 and 1000 °C-20 h	[80]
	$\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/3}\text{Li}_{(1-2x)/3}]\text{O}_2$ ( $0 \leq x \leq 0.5$ )	XRD, NMRS, first-principles computations	Co-precipitation, 900 °C-24 h	[81]
	$\text{Li}(\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3})\text{O}_2$ ( $0 \leq x \leq 0.5$ )	SXRPD, TEM, ED	Co-precipitation 900 °C-24 h, cooled by quenching	[82]
	$\text{Li}[\text{Li}_{(1-x)/3}\text{Co}_x\text{Mn}_{(2-2x)/3}]\text{O}_2$ ( $0 \leq x \leq 1$ )	Monte Carlo simulation	Combinatorial synthesis, quenched from 900/800 °C	[47]
	$\text{Li}_{1.20}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$	HAADF-STEM, electron nanodif- fraction	Sol-gel, 900 °C	[83]
	$\text{Li}(\text{Li}_{x/3}\text{Co}_{1-x}\text{Mn}_{2x/3})\text{O}_2$ ( $0.5 \leq x \leq 1$ )	XRD	Spray drying, 750–950 °C-15 h	[84]
	$\text{Li}_{1.17}\text{Mn}_{0.56}\text{Ni}_{0.135}\text{Co}_{0.135}\text{O}_2$	XRD	Carbonate synthesis route, 500 °C-3 h and 900 °C-18 h, cooling by quenching	[85]
	$\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$ ( $x = 1/2, 2/7$ and $1/5$ )	XRD, FT-IR	Co-precipitation, 500 °C-12 h and 1000 °C-12 h	[86]

**Table 1** (continued)

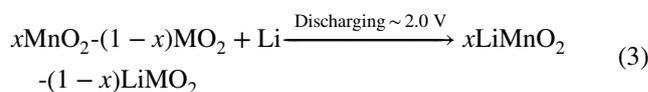
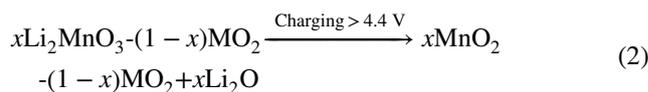
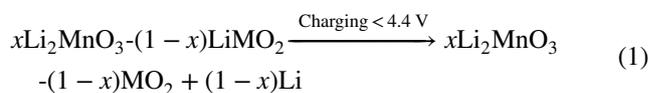
Material composition; notation	Characterization techniques	Synthesis method/sintering conditions	Ref.
$\text{Li}(\text{Li}_{0.144}\text{Ni}_{0.136}\text{Co}_{0.136}\text{Mn}_{0.544})\text{O}_2$	NPD, HRTEM, EELS	Co-precipitation, 500 °C-5 h and 800 °C-15 h	[15]
$\text{Li}_{1.7}\text{Mn}_{0.4}\text{Co}_{0.9}\text{O}_3$ ; $\text{Li}_{1.6}\text{Mn}_{0.2}\text{Co}_{1.2}\text{O}_3$ ; $\text{Li}_{2-6}(\text{Mn}_{1-x}\text{Co}_x)_{1+\delta}\text{O}_3$	XRD, HREM, TEM, ED	Co-precipitation, 950 °C-12 h	[77]
$\text{Li}_{1.2}\text{Ni}_{0.175}\text{Co}_{0.1}\text{Mn}_{0.52}\text{O}_2$	XRD, Raman Spectroscopy	Co-precipitation commercial powder (Toda)	[87]
$\text{Li}(\text{Ni}_{0.183}\text{Li}_{0.20}\text{Co}_{0.022}\text{Mn}_{0.583})\text{O}_2$	XRD, HAADF-STEM	Co-precipitation, 1000 °C	[88]
$x\text{Li}_2\text{MnO}_3-(1-x)\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ( $x=0.7$ and $0.3$ )	Raman Spectroscopy, XRD	Co-precipitation, 900 °C-12 h	[87]

XRD: X-ray powder diffraction, NPD: neutron powder diffraction, SXRPD: Synchrotron X-ray powder diffraction, HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy, ABF-STEM: annular bright-field scanning transmission electron microscopy, AC-STEM: aberration-corrected scanning transmission microscopy, ED: electron diffraction, FT-IR: fourier transform infrared microscopy, NMRS: nuclear magnetic resonance spectroscopy, HRTEM: high-resolution transmission electron microscopy, XEDS: X-ray energy-dispersive spectroscopy, NBED: nanobeam electron diffraction, EELS: electron energy loss spectroscopy, La-APT: laser-assisted atom probe tomography, HREM: high-resolution electron microscopy, SAED: selected area electron diffraction

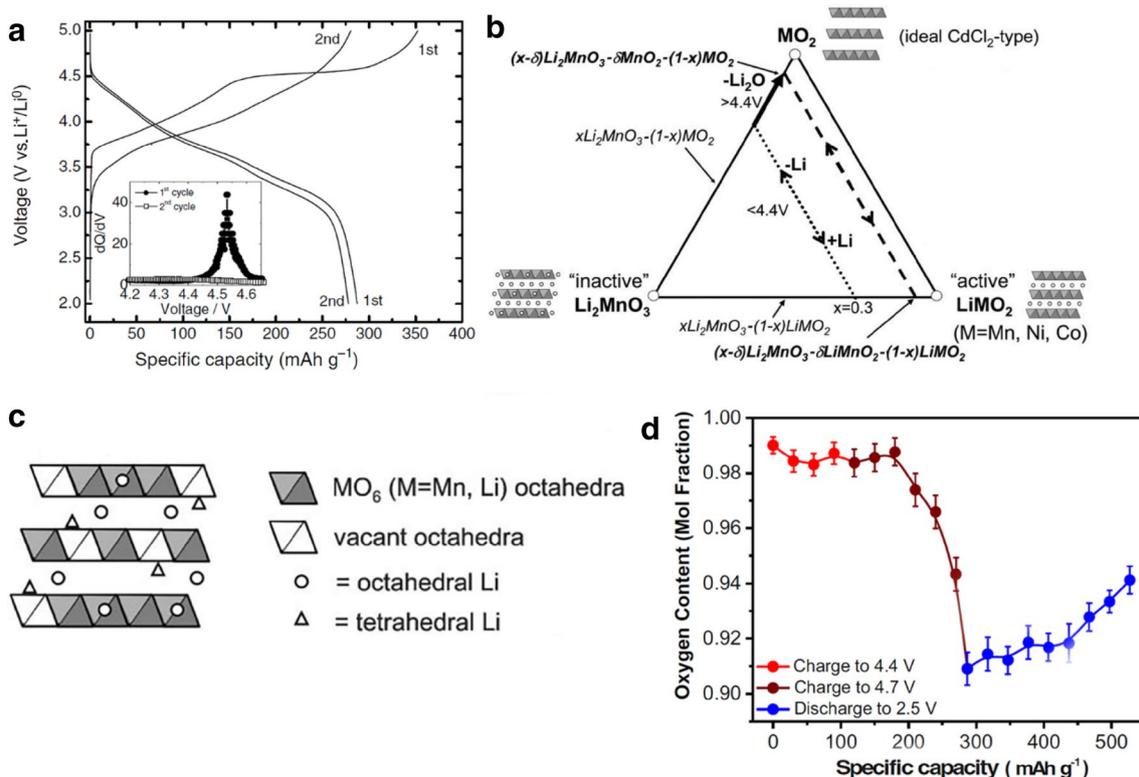
## 2.2 Mechanistic Reactions of LLOs

Although the structure of LLOs is still debated, Mn-containing LLOs do possess unique mechanistic behaviours based on highly compatible intergrown structures in which it is generally accepted that the mechanistic behaviours and corresponding structural and phase evolutions are similar for all LLOs [14]. Therefore, by using the two-phase notation as a model and the composition triangle originating from Thackeray et al. [14], the mechanistic reactions of layered  $0.3\text{Li}_2\text{MnO}_3-0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (as an example) can be clearly described by using its typical initial two cycles and corresponding incremental capacity ( $dQ/dV$ ) plots (Fig. 3a) [14, 89]. Here, upon charging to 4.4 V, Li extraction occurs with the redox couple of  $\text{Ni}^{2+}/\text{Ni}^{4+}$  in the electrochemically active  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  component based on a solid solution reaction mechanism to form  $0.3\text{Li}_2\text{MnO}_3-0.7\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  [14, 90]. During this stage, the  $\text{Li}_2\text{MnO}_3$  component is electrochemically inactive and can act as a Li reservoir to compensate for Li extraction from the active layer through Li migration from the octahedral sites in the  $\text{MO}_6$  octahedral layers to the tetrahedral sites in the Li-consuming layers, thus ensuring integrated structural stability (Fig. 3b) [14]. In addition, the existence of Li in both tetrahedral and octahedral sites in the Li-consuming layer can endow LLO materials with more interstitial Li spacing and enhance reaction kinetics. Furthermore, as charging voltage increases to above 4.4 V, a long flat plateau can be observed which can be associated with the activation process of the  $\text{Li}_2\text{MnO}_3$  phase involving Li loss and O release from the monoclinic structure [39]. Here, the product obtained at the end of the charging process is a metastable  $\text{MnO}_2$  phase, implying a two-phase reaction mechanism. And upon discharge, Li can intercalate into  $\text{MnO}_2$  and  $\text{MO}_2$  lattices to

form rock-salt-type  $\text{LiMnO}_2$  and  $\text{LiMO}_2$  phases, respectively [14, 22]. Overall, as described in the composition triangle (Fig. 3c) [14], the mechanistic reactions of LLO electrodes in the initial cycles can be illustrated as follows:



Here, the process of  $\text{Li}^+$  extraction (Eq. 2) along with O evolution during  $\text{Li}_2\text{MnO}_3$  activation in the first cycle [16, 25, 54, 91, 92] is a one-off reaction behaviour that is not only linked with initial irreversibility but also linked with the highly anomalous reversible capacity involving the anionic redox species, O, which can coordinate with metal ions (*i.e.* Mn, Ni or Li) or form peroxy-like  $\text{O}_2^{2-}$  species [39]. In their study, Koga et al. [93] proposed that all cations were in the oxidation state of +4 after charging and recovered to their normal state after discharging, implying that TM cation redox cannot fully explain the observed extra capacity. Here, the researchers concluded that lattice oxygen could undergo reversible redox reactions within the bulk and that irreversible O loss occurred at the surface [94]. Furthermore, researchers have conducted theoretical and experimental studies and have reported that the anionic redox reactions of O anions can not only lead to extra capacity, but also affect the mechanistic behaviour and electrochemical performance of LLOs [22, 95]. In addition,



**Fig. 3** **a** Typical voltage profiles and  $dQ/dV$  plots (inset) of  $0.3\text{Li}_2\text{MnO}_3\text{-}0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrode. **b** Compositional phase diagram illustrating the electrochemical reaction pathways at different voltages in LLO electrodes. **c** Schematic of diffusion from octa-

hedral sites to tetrahedral sites. **d** Oxygen content in  $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrode during the first cycle. *Source:* **a** Reproduced with permission from Ref. [89]. **b, c** Reproduced with permission from Ref. [14]. **d** Reproduced with permission from Ref. [96]

Armstrong et al. [54] were the first to track oxygen evolution using in situ differential electrochemical mass spectrometry (DEMS) and powder neutron diffraction (NPD). Here, the researchers demonstrated that  $\text{O}_2$  was released from LLOs during charging and suggested that this surface oxygen loss can lead to structural changes, with Li from octahedral sites migrating into Li layers and creating vacancies which were subsequently occupied by TM ions, simulating the formation of metastable rock-salt  $\text{MnO}_2$ . In later studies, Hy et al. [91] used in situ surface-enhanced Raman spectroscopy (SERS) to confirm the formation of a  $\text{Li}_2\text{O}$  phase and Muhammad et al. [96] reported significant drops in the O content in a  $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrode during the first charge (190–280  $\text{mAh g}^{-1}$ ) (e.g. 4.4–4.7 V) (Fig. 3d). Here, the decomposition of conventional electrolyte solutions can also occur, especially at high-voltage operations ( $> 4.4$  V).

In general, the mechanistic behaviours of LLOs are complex and are closely related to performance. However, significant research is required to elucidate these behaviours. In addition, although researchers have reported that anionic oxygen redox reactions and oxygen evolution give rise to the extra capacity in LLOs, the relationship between these

two oxygen activities is not fully understood. However, the phase evolution and electrochemical performance of LLOs are obviously linked to the activities associated with the  $\text{Li}_2\text{MnO}_3$  activation process. Overall, the precise understanding of high-voltage ( $> 4.4$  V) mechanisms and corresponding effects on electrochemical performance is attainable through a combination of advanced characterization tools to explain bulk and surface reactions of LLOs.

### 3 Challenges and Strategies

To address the challenging issues of LLOs (*i.e.* low ICE, capacity and voltage fade and poor rate capability), it is vital to understand the origin of such issues, which are closely connected to underlying mechanistic reactions and structural/chemical evolutions. Here, many methods have been attempted by researchers, and surface modifications and lattice doping have been reported to be useful. In this review, various surface modifications and lattice doping strategies for LLOs are summarized, along with corresponding effects on the issues of low ICE, capacity/voltage fade and poor rate capability (Tables 2, 3).

### 3.1 Low Initial Coulombic Efficiency (ICE)

#### 3.1.1 The Origins of Low ICE

All LLOs suffer from low ICE, which is unfavourable in real-world applications [16, 28, 54, 73, 97]. For example, Wu et al. [98] reported that LLOs generally suffered from an initial capacity loss in the range of 60–120 mAh g<sup>-1</sup>, implying an ICE of ~65% to 83%, based on a systematic investigation of surface modifications on LLOs. Similarly, Rozier et al. [29] reported an ICE of 25% for a Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> electrode (Fig. 4a), Thackeray et al. [89] reported an ICE of 81.3% for a 0.3Li<sub>2</sub>MnO<sub>3</sub>-0.7LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> electrode and West et al. [99] reported an ICE of 27% for a Li<sub>1.2</sub>Ni<sub>0.175</sub>Mn<sub>0.52</sub>O<sub>2</sub> electrode, indicating that ICEs vary with LLO composition.

Mechanistically, the mechanisms for these low ICEs or the initial irreversible capacity loss are typically a combination of irreversible Li and O loss from the LLO lattice in conjunction with possible electrolyte decomposition at high voltage (Eq. 2) [15, 28, 100, 101]. For example, Kang et al. [102] reported that acid treatment can be applied to 0.5Li<sub>2</sub>MnO<sub>3</sub>-0.5LiNi<sub>0.44</sub>Co<sub>0.25</sub>Mn<sub>0.31</sub>O<sub>2</sub> to remove Li<sub>2</sub>O from the Li<sub>2</sub>MnO<sub>3</sub> component before cycling and can greatly improve ICE. And although this approach is not considered to be fully successful because the acid-leached samples demonstrated worse cycling performances and rate capabilities as compared with pristine samples, this approach does confirm the origin of low ICE and can guide researchers. Furthermore, researchers also proposed a combination of LLOs with Li receptor oxides such as V<sub>2</sub>O<sub>5</sub> [103] and MnO<sub>2</sub> [104], which can act as intercalation hosts to “catch” isolated Li<sup>+</sup> for reinsertion back into the layered lattice after the initial charge, to improve ICE. Alternatively, Xu et al. [28] used in situ DEMS to characterize two LLOs (Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> and Mn-free Li<sub>1.2</sub>Ni<sub>0.2</sub>Ru<sub>0.6</sub>O<sub>2</sub>) by monitoring gas (O<sub>2</sub> and CO<sub>2</sub>) evolutions at 4.5 V during the first charge and suggested that O<sub>2</sub> evolution only contributed to less than half of the total capacity loss, whereas non-volatile electrolyte decomposition played a major role in this context (Fig. 4b). However, from the perspective of this review, low ICE mainly arises from the loss of Li and O because high ICE values (90%–95%) can be achieved through O activity (anionic redox) modifications and Li diffusion enhancements without targeting electrolyte decomposition/passivation [101, 105].

#### 3.1.2 Efforts to Improve ICE

**3.1.2.1 Particle Size Control** The use of nanocomposites and nanometre-thick coatings has proved to dramatically impact electronic and ionic conduction pathway optimizations [106, 107], which are closely related to the Coulombic efficiency (CE) of LIB electrode materials. And because nanoparti-

cles typically possess higher surface areas that are directly exposed to electrolytes, there are higher rates of side reactions. Therefore, it is important to keep primary particle sizes at an appropriate scale for LLOs [108, 109]. This was demonstrated by Li et al. [110] and Yabuuchi et al. [111], both of whom claimed that particle size can greatly affect LLO structural evolutions and electrochemical properties. In the study by Li et al. [110], the researchers compared the charge-discharge profiles of LLO electrodes with large and small particle sizes at different cycles and their corresponding structural evolutions during cycling using in situ XRD (Fig. 5a, b) and reported that the large-particle LLO exhibited a two-phase reaction mechanism, whereas the small-particle LLO exhibited no phase separation upon charging to above 4.5 V (Fig. 5a, b). Here, the researchers suggested that O loss occurred throughout the bulk of small-particle LLO, whereas O loss only occurred on the surface of large-particle LLO, resulting in smaller capacity loss and higher ICE for the large-particle LLO. Despite these results, this study sacrificed the completeness of the reactions and the deliverable capacity to increase the ICE and cycling performance of the LLOs and did not show a solid improvement to the ICE. Nevertheless, there is no doubt that particle size can affect LLOs through its effects on structural evolution during cycling [108–111].

**3.1.2.2 Surface Modification** Because O loss occurs at the electrode/electrolyte interface and is accompanied by various side reactions [110, 112–114], surface modification has become one of the most effective approaches to improve ICE, in which surface modifications can act as a protective layer or a source of surface structure modification to positively influence ICE. For example, Wu et al. [98] investigated ICE based on a series of protective coatings on LLOs (Fig. 6a, b) and reported that the coated samples, in particular those with Al<sub>2</sub>O<sub>3</sub> and AlPO<sub>4</sub> coatings, exhibited higher ICE and discharge capacities than pristine samples. In another study, Sun et al. [59] reported that a thin AlF<sub>3</sub> coating can effectively enhance the electrochemical performance of Li(Li<sub>0.19</sub>Ni<sub>0.16</sub>Co<sub>0.08</sub>Mn<sub>0.57</sub>)O<sub>2</sub> (Fig. 6c) and hypothesized that the improvement can be attributed to the transformation of the Li<sub>2</sub>MnO<sub>3</sub> component to a spinel phase resulting from the effects of Li chemical leaching by the AlF<sub>3</sub> layer. Here, the researchers suggested that the coating-induced changes to the original structure/composition can alter mechanistic behaviours and vary O activities during O evolution and Li<sub>2</sub>MnO<sub>3</sub> activation, thus reducing Li and O loss and improving ICE. Furthermore, the researchers also hypothesized that this improvement arose from the increased retention of oxide ion vacancies in the lattice after the initial charge, particularly in the Al<sub>2</sub>O<sub>3</sub>- and AlPO<sub>4</sub>-modified samples. Overall, a wide range of materials, including other oxides and electron and ion conductive materials, have been employed as coatings to improve the ICE of different LLOs.

**Table 2** Surface modification strategies to improve ICE

Type of coating	Surface coating	LLOs	First cycle (DC, CE at 0.1 C) (pristine)	First cycle (DC, CE at 0.1 C) (modified)	Capacity retention (modified)	Rate performance (DC <sub>pristine</sub> , DC <sub>modified</sub> , C rate)	Ref.
<i>Surface gradient doping</i>	Na <sup>+</sup>	0.5Li <sub>2</sub> MnO <sub>3</sub> -0.5LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub>	187, 63%	286, 87%	~88% after 100 cycles at 0.2 C	128, 182, 2 C	[116]
	PO <sub>4</sub> <sup>3-</sup>	Li <sub>1.17</sub> Mn <sub>0.5</sub> Ni <sub>0.17</sub> Co <sub>0.16</sub> O <sub>2</sub>	276, 72%	300, 86%	95% after 100 cycles at 0.1 C	17, 128, 6 C	[117]
	Nb <sup>5+</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	276, 81%	320, 87%	94.5% after 100 cycles at 0.1 C	175, 200, 2 C	[118]
	Si <sup>4+</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	283, 78.8%	286.5, 81.4%	70.4% after 100 cycles at 1 C	13.2, 50, 10 C	[64]
	Sn <sup>4+</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	283, 78.8%	279.3, 82.1%	86.2% after 100 cycles at 1 C	13.2, 127, 10 C	[64]
<i>Typical surface coating</i>	AlF <sub>3</sub>	Li(Li <sub>0.19</sub> Ni <sub>0.16</sub> Co <sub>0.08</sub> Mn <sub>0.57</sub> )	227.6, 82.8%	240.6, 96.3%	91.6% after 100 cycles at 0.5 C	164.2, 190, 2 C	[59]
	PrPO <sub>4</sub>	Li(Li <sub>0.19</sub> Ni <sub>0.16</sub> Co <sub>0.08</sub> Mn <sub>0.57</sub> )	282.8, 81.8%	286.9, 90%	89.3% after 100 cycles at 0.5 C	80.6, 124.2, 10 C	[64]
	Al <sub>2</sub> O <sub>3</sub>	Li <sub>1.2</sub> Ni <sub>0.13</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> O <sub>2</sub>	283, 84.5%	248, 84.1%	82% after 50 cycles at C/3	–	[119]
	TiO <sub>2</sub>	Li <sub>1.2</sub> Ni <sub>0.13</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> O <sub>2</sub>	283, 84.5%	287, 87.1%	78% after 50 cycles at C/3	–	[119]
	Zr phosphate	Li(Li <sub>0.2</sub> Ni <sub>0.17</sub> Co <sub>0.07</sub> Mn <sub>0.56</sub> )O <sub>2</sub>	202, 71%	216, 80%	91% after 100 cycles at 0.1 C	80, 125, 2 C	[120]
	LiFePO <sub>4</sub>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	243, 70.5%	267, 63%	88% after 20 cycles at 0.1 C	–	[121]
	Al <sub>2</sub> O <sub>3</sub>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	243, 70.5%	285, 51%	80% after 20 cycles at 0.1 C	–	[121]
	(rGO <sup>^</sup> )/AlPO <sub>4</sub>	Li(Li <sub>0.190</sub> Mn <sub>0.54</sub> Co <sub>0.143</sub> Ni <sub>0.127</sub> )O <sub>2</sub>	218, 75.69%	240, 83.6%	95% after 100 cycles at 0.1 C	50, 110, 5 C	[122]
	FePO <sub>4</sub>	Li <sub>1.2</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> Mn <sub>0.54</sub> O <sub>2</sub>	250.3, 78.3%	271.7, 85.1%	95% after 100 cycles at 0.5 C	150, 166, 2 C	[123]
	LiCoPO <sub>4</sub>	Li <sub>1.2</sub> Ni <sub>0.18</sub> Mn <sub>0.59</sub> Co <sub>0.03</sub> O <sub>2</sub>	251, 75.83%	250, 82.5%	98% after 40 cycles at 20 mA g <sup>-1</sup>	25, 90, 2 C	[124]
	CaF <sub>2</sub>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	275.8, 76%	277.3, 89.6%	91.2% after 80 cycles at 0.2 C	85, 141, 3 C	[125]
	AlPO <sub>4</sub>	Li <sub>1.2</sub> Ni <sub>0.13</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> O <sub>2</sub>	249, 76.2%	261.9, 85.2%	~97% after 40 cycles at 0.1 C	–	[126]
	MnO <sub>x</sub>	Li(Ni <sub>0.2</sub> Li <sub>0.2</sub> Mn <sub>0.6</sub> )O <sub>2</sub>	265.1, 71.6%	298.1, 90.2%	88.9% after 30 cycles at 0.1 C	205, 222, 2 C	[127]
	TiO <sub>2</sub>	Li(Li <sub>0.2</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> Ni <sub>0.13</sub> )O <sub>2</sub>	241.3, 76.5%	258.3, 86%	75% after 80 cycles at 0.1 C	–, 105, 5 C	[128]

**Table 2** (continued)

Type of coating	Surface coating	LLOs	First cycle (DC, CE at 0.1 C) (pristine)	First cycle (DC, CE at 0.1 C) (modified)	Capacity retention (modified)	Rate performance (DC <sup>pristine</sup> , DC <sup>modified</sup> , C rate)	Ref.
	MgO	Li(Li <sub>0.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> )O <sub>2</sub>	79.65%	282.2, 80.8%	96% after 100 cycles at 200 mA g <sup>-1</sup>	–	[129]
	Sm <sub>2</sub> O <sub>3</sub>	Li(Li <sub>0.2</sub> Mn <sub>0.56</sub> Ni <sub>0.16</sub> Co <sub>0.08</sub> )O <sub>2</sub>	298.1, 86%	287.7, 86%	92% after 80 cycles at 200 mA g <sup>-1</sup>	125, 153, 2000 mA g <sup>-1</sup>	[130]
	ZrO <sub>2</sub>	Li(Li <sub>0.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> )O <sub>2</sub>	254.7, –	253.1, –	94.9% after 50 cycles at 0.5 C	–	[130]
	FeF <sub>3</sub>	Li(Li <sub>0.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> )O <sub>2</sub>	260, 72%	280, 80%	95% after 100 cycles at 0.5 C	80, 110, 5 C	[131]
	La <sub>2</sub> O <sub>3</sub>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	242.2, –	276.9, –	71% after 100 cycles at 0.1 C	33, 90, 5 C	[132]
	CeF <sub>3</sub>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	229, 72%	222.8, 80%	91.7% after 50 cycles at 0.1 C	82.2, 103.1, 5 C	[133]
	Pr <sub>6</sub> O <sub>11</sub>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	290.1, 79.8%	283.7, 85.6%	97.9% after 50 cycles at 0.2 C	132.5, 162.2, 5 C	[134]
	MgF <sub>2</sub>	Li(Li <sub>0.2</sub> Ni <sub>0.17</sub> Co <sub>0.07</sub> Mn <sub>0.56</sub> )O <sub>2</sub>	211, 70.4%	220, 76%	86% after 50 cycles at 0.1 C	110, 130, 2 C	[135]
	BiOF	Li(Li <sub>0.18</sub> Ni <sub>0.15</sub> Co <sub>0.15</sub> Mn <sub>0.52</sub> )O <sub>2</sub>	248, 75%	292, 92%	92% after 100 cycles at 0.2 C	–, 78, 25 C	[136]
	MWCNT <sup>+</sup>	Li <sub>1.17</sub> Ni <sub>0.17</sub> Co <sub>0.1</sub> Mn <sub>0.56</sub> O <sub>2</sub>	234.8, ~84%	241.5, 87%	75.7% after 50 at 0.2 C	24, 103, 10 C	[137]
	C	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	253, 84.3%	263, 96.7%	92% after 100 cycles at 0.2 C	13, 54, 20 C	[138]
	C	0.33Li <sub>2</sub> MnO <sub>3</sub> ·0.67Li(Mn <sub>1/3</sub> Ni <sub>1/3</sub> Co <sub>1/3</sub> )O <sub>2</sub>	290.2, 78%	334.5, 92.2%	~90% after 50 cycles at 1 C	55.3, 122.3, 30 C	[139]
	ZnO	0.3Li <sub>2</sub> MnO <sub>3</sub> ·0.7LiNi <sub>5/21</sub> Co <sub>5/21</sub> Mn <sub>11/21</sub> O <sub>2</sub>	283, 81.7%	316, 89.1%	78.8% after 50 cycles at 1 C	112, 124, 5 C	[140]
	PEDOT:PSS*	Li <sub>1.17</sub> Mn <sub>0.56</sub> Co <sub>0.095</sub> Ni <sub>0.175</sub> O <sub>2</sub>	265, 89.8%	260, 89.7%	67.3% after 50 cycles at 1 C	20, 83, 9 C	[141]
	PEDOT:PSS*	Li <sub>1.2</sub> Ni <sub>0.2</sub> Mn <sub>0.6</sub> O <sub>2</sub>	265.6, 77.18%	286.5, 77.9%	~80% after 100 cycles at 1 C	62, 135, 2 C	[142]
	Graphene	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	256, 69%	~290, 74%	90% after 100 at 0.5 C	–, 50, 12 C	[143]
	Polyaniline	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	291.9, 81.31%	313.5, 89.0%	~100% at 0.1 C	60, 199, 10 C	[144]
	rGO <sup>^</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	284, 76.5%	313, >100%	94.5% after 70 cycles at 40 mA g <sup>-1</sup>	50, 125, 10 C	[145]
	Li <sub>3</sub> PO <sub>4</sub>	Li(Li <sub>0.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> )O <sub>2</sub>	241, –	215.6, –	87% after 200 cycles at 150 mA g <sup>-1</sup>	71, 121, 10 C	[146]
	Li <sub>3</sub> PO <sub>4</sub> /C	Li <sub>1.2</sub> Ni <sub>0.13</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> O <sub>2</sub>	266, 83.3%	–, 88.3%	100% after 50 cycles at 0.2 C	83, 124, 1000 mA g <sup>-1</sup>	[147]

**Table 2** (continued)

Type of coating	Surface coating	LLOs	First cycle (DC, CE at 0.1 C) (pristine)	First cycle (DC, CE at 0.1 C) (modified)	Capacity retention (modified)	Rate performance (DC <sup>pristine</sup> , DC <sup>modified</sup> , C rate)	Ref.
	(NH <sub>4</sub> ) <sub>3</sub> AlF <sub>6</sub>	0.5Li <sub>2</sub> MnO <sub>3</sub> -0.5LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub>	269.1, 69.62%	277.9, 76.4%	85% after 50 cycles at 0.2 C	109, 143, 5 C	[148]
	Li-Ni-PO <sub>4</sub>	0.5Li <sub>2</sub> MnO <sub>3</sub> -0.5LiNi <sub>0.44</sub> Co <sub>0.25</sub> Mn <sub>0.31</sub> O <sub>2</sub>	240, 81%	260, 87%	74.4% after 50 cycles at 0.1 C	175, 200, 1 C	[149]
	AlPO <sub>4</sub>	Li(Li <sub>0.2</sub> Fe <sub>0.1</sub> Ni <sub>0.15</sub> Mn <sub>0.55</sub> )O <sub>2</sub>	246.2, 66.5%	267.2, 78.9%	88.95% after 100 cycles at 1 C	56, 136, 10 C	[150]
	LiAlSiO <sub>4</sub>	Li(Li <sub>0.17</sub> Ni <sub>0.2</sub> Co <sub>0.05</sub> Mn <sub>0.58</sub> )O <sub>2</sub>	262.5, 78.3%	273, 84.1%	Improved	124, 163, 5 C	[151]
	Li <sub>2</sub> TiF <sub>6</sub>	Li <sub>1.17</sub> Ni <sub>0.17</sub> Co <sub>0.1</sub> Mn <sub>0.56</sub> O <sub>2</sub>	263.9, 87.3%	260.2, 89%	94.3% after 100 cycles at 0.05 C	20, 93, 10 C	[152]
	LiV <sub>3</sub> O <sub>8</sub>	Li(Li <sub>0.17</sub> Ni <sub>0.17</sub> Co <sub>0.10</sub> Mn <sub>0.56</sub> )O <sub>2</sub>	253.9, 85.81%	250.1, 98.3%	92% after 100 cycles at 1 C	99, 158, 2 C	[153]
	Li <sub>3</sub> VO <sub>4</sub>	Li <sub>1.18</sub> Co <sub>0.15</sub> Ni <sub>0.15</sub> Mn <sub>0.52</sub> O <sub>2</sub>	253, 77.5%	276.4, 87.7%	78% after 100 cycles at 5 C	74, 124, 5 C	[154]
	Zr-abundant	Li <sub>1.2</sub> Ni <sub>0.13</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> O <sub>2</sub>	245, 70.3%	245, 70.9%	85% after 300 cycles at 6 A g <sup>-1</sup>	105, 130, 10 C	[155]
	LiMnPO <sub>4</sub>	Li(Li <sub>0.17</sub> Ni <sub>0.25</sub> Mn <sub>0.58</sub> )O <sub>2</sub>	260.8, 80.7%	293.3, 85.5%	~88.9% after 80 cycles at 30 A g <sup>-1</sup>	98, 141, 5 C	[156]
	Li <sub>2</sub> ZrO <sub>3</sub>	Li <sub>1.2</sub> Ni <sub>0.13</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> O <sub>2</sub>	235, 71%	225, 74%	85% after 100 cycles at 0.2 C	30, 55, 3 C	[157]
	MnO <sub>2</sub>	Li <sub>1.2</sub> Mn <sub>0.567</sub> Ni <sub>0.167</sub> Co <sub>0.066</sub> O <sub>2</sub>	280, 77%	299, 88%	93% after 50 cycles at 0.5 C	115, 157, 5 C	[158]
	LiAlO <sub>2</sub>	Li <sub>1.5</sub> Ni <sub>0.25</sub> Mn <sub>0.75</sub> O <sub>2.5</sub>	221.3, 66.8%	257.6, 82.9%	96.5% after 50 cycles at 1 C	23, 88, 10 C	[159]
	MoO <sub>3</sub>	Li[Li <sub>0.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> ]O <sub>2</sub>	271.9, 76.9%	272.7, 99.6%	88.5% after 50 cycles at 0.1 C	–	[160]
	MoS <sub>2</sub>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	236.9, 76.1%	228.5, 83.9%	92.7% after 100 cycles at 0.5 C	91, 129, 5 C	[161]
	P(VDF-TrFE) <sup>#</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	240.2, 70.3%	275.5, 79.1%	87.8% after 100 cycles at 0.5 C	91, 117, 5 C	[162]

CE: coulombic efficiency (%), DC: discharge capacity (mAh g<sup>-1</sup>)

<sup>^</sup>Reduced graphene oxide

<sup>+</sup>Multi-walled carbon nanotube

<sup>\*</sup>Poly(3, 4-ethylenedioxythiophene)-poly(styrene sulphonate)

<sup>#</sup>Poly(vinylidene fluoride-trifluoroethylene)

**Table 3** Doping strategies to improve ICE

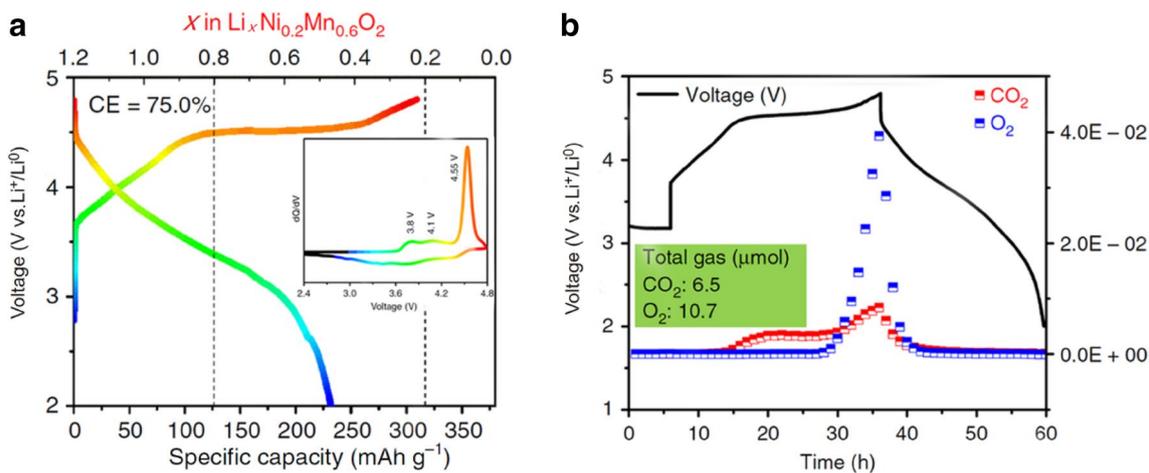
Dopant	LLOs	First CE (pristine) <sup>^</sup>	First CE (modified) <sup>^</sup>	First DC (pristine) <sup>^^</sup>	First DC (modified) <sup>^^</sup>	Capacity retention (modified)	Rate performance (DC <sub>pristine</sub> , DC <sub>modified</sub> , C rate)	Ref.
Na <sup>+</sup>	Li(Li <sub>0.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> )O <sub>2</sub>	–	–	241.9	215.6	–	66, 136, 5 C	[163]
K <sup>+</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> Ni <sub>0.13</sub> O <sub>2</sub>	74	77	302	315	85% after 110 cycles at 20 mA g <sup>-1</sup>	142, 197, 1000 mA g <sup>-1</sup>	[164]
K <sup>+</sup>	Li <sub>1.232</sub> Mn <sub>0.615</sub> Ni <sub>0.154</sub> O <sub>2</sub>	76	87	266	299	94% after 100 cycles at 0.5 C	90, 133, 10 C	[165]
Mg <sup>2+</sup>	Li <sub>1.5</sub> (Mn <sub>0.75</sub> Ni <sub>0.25</sub> )O <sub>2+δ</sub>	77.5	87.9	–	248.6	94.2% after 200 cycles at 0.5 C	65, 130, 10 C	[166]
Al <sup>3+</sup>	Li <sub>1.5</sub> Mn <sub>0.675</sub> Ni <sub>0.1675</sub> Co <sub>0.1675</sub> O <sub>2</sub>	72.9	81.2	278.7	323.7	~78% after 100 cycles at 0.5 C	60, 120, 20 C	[167]
Fe <sup>3+</sup>	Li <sub>1.2</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> Mn <sub>0.54</sub> O <sub>2</sub>	77.4	87.8	237	230	90.4% after 50 cycles at 0.1 C	–	[168]
Cr <sup>3+</sup>	Li <sub>1.2</sub> Mn <sub>0.567</sub> Ni <sub>0.167</sub> Co <sub>0.066</sub> O <sub>2</sub>	~77	~77	~262	~258	~90% after 200 cycles at 0.1 C	–	[51]
Y <sup>3+</sup>	Li <sub>1.2</sub> Mn <sub>0.6</sub> Ni <sub>0.2</sub> O <sub>2</sub>	~73	79	272.3	281	95.6% after 40 cycles at 1 C	50, 98, 5 C	[169]
Sn <sup>4+</sup>	Li(Li <sub>0.17</sub> Ni <sub>0.25</sub> Mn <sub>0.58</sub> )O <sub>2</sub>	78.1	77	257.3	232.2	86% after 400 cycles at 30 mA g <sup>-1</sup>	98, 112, 5 C	[170]
Ti <sup>4+</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> Ni <sub>0.13</sub> O <sub>2</sub>	–	~73	–	> 320	71% after 300 cycles at 0.2 C	81, 136, 5 C	[171]
Zr <sup>4+</sup>	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	70.3	70.9	233	242	~95% after 100 cycles at 25 mA g <sup>-1</sup>	145, 159, 250 mA g <sup>-1</sup>	[172]
Ru <sup>4+</sup>	Li <sub>1.2</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> Mn <sub>0.54</sub> O <sub>2</sub>	–	–	268	268	98.1% after 100 cycles at 0.1 C	80, 150, 5 C	[173]
Ru <sup>4+</sup>	0.55Li <sub>2</sub> MnO <sub>3</sub> -0.45LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub>	77.5	87.7	253	276.4	~92.5% after 50 cycles at 2 C	152, 181, 2 C	[174]
Nb <sup>5+</sup>	Li(Li <sub>0.2</sub> Ni <sub>0.2</sub> Mn <sub>0.6</sub> )O <sub>2</sub>	61	77	220	254	92.3% after 100 cycles at 0.1 C	80, 106, 5 C	[175]
W <sup>6+</sup>	Li <sub>1.13</sub> Ni <sub>0.3</sub> Mn <sub>0.57</sub> O <sub>2</sub>	69	81	251	284	~78% after 100 cycles at 1 C	30, 90, 40 C	[176]
SO <sub>4</sub> <sup>2-</sup>	Li(Li <sub>0.17</sub> Ni <sub>0.20</sub> Co <sub>0.05</sub> Mn <sub>0.58</sub> )O <sub>2</sub>	81.1	83.2	288.3	282.2	~80% after 400 cycles at 30 mA g <sup>-1</sup>	130, 160, 1500 mA g <sup>-1</sup>	[175]
SiO <sub>4</sub> <sup>4-</sup>	Li(Li <sub>0.17</sub> Ni <sub>0.20</sub> Co <sub>0.05</sub> Mn <sub>0.58</sub> )O <sub>2</sub>	81.1	83.5	288.3	261.2	~83% after 400 cycles at 30 mA g <sup>-1</sup>	130, 150, 1500 mA g <sup>-1</sup>	[175]
F <sup>-</sup>	Li <sub>1.2</sub> Mn <sub>0.567</sub> Ni <sub>0.167</sub> Co <sub>0.066</sub> O <sub>2</sub>	~77	~86	~262	~274	70% after 200 cycles at 0.5 C	–	[51]

CE: Coulombic Efficiency (%) at 0.1 C<sup>^</sup>, DC: Discharge capacity (mAh g<sup>-1</sup>) at 0.1 C<sup>^^</sup>

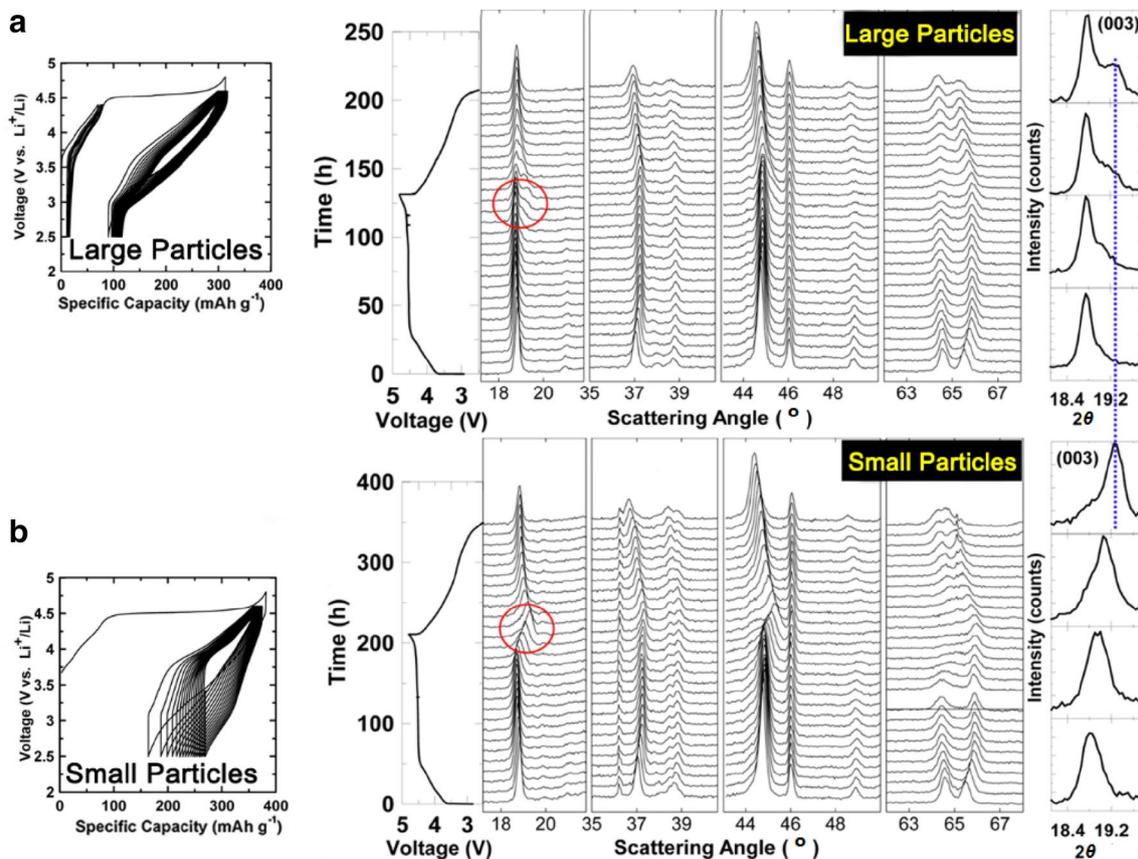
**3.1.2.3 Lattice Doping** In addition to surface modification, lattice doping with cationic and anionic ions has also been introduced to improve ICE for LLOs [21, 115]. For example, Qing et al. [116] employed gradient Na<sup>+</sup> doping to boost the kinetics of LLOs using a molten salt method (Fig. 7a) and reported the Na-doped LLO not only exhibited a higher ICE (87 vs. 63%), but also a higher discharge capacity (286 vs. 228 mAh g<sup>-1</sup>) during testing at 25 mA g<sup>-1</sup> in the range of 2.0–4.7 V (Fig. 7b, c). Here, the researchers attributed the noticeably better electrochemical performance of the doped LLO to the pinning effect of Na ions towards the stabilization of the LLO structure and the consequent improvements in electronic and ionic conductivities. In another study, Zhao et al. [117] employed gradient PO<sub>4</sub><sup>3-</sup> doping

and developed a spinel-like hierarchical structure on LLOs composed of a PO<sub>4</sub><sup>3-</sup>-enriched spinel-like surface and a PO<sub>4</sub><sup>3-</sup>-doped LLO core (Fig. 7d). Here, the optimal modified sample showed an enhanced ICE of 86% as compared with 72% for the pristine sample, indicating faster Li<sup>+</sup> diffusion and reduced irreversible Li<sub>2</sub>O due to the increased PO<sub>4</sub><sup>3-</sup> poly-anions (Fig. 7e).

Researchers have also reported the use of cationic and anionic ions as dopants in LLO lattices and reported that the performance effects were varied. For example, Pang et al. [51] reported that anionic doping with F<sup>-</sup> can promote larger lattice sizes and stimulate faster Li diffusions, whereas cationic doping with Cr<sup>3+</sup> can enhance structural stabilities but sacrifice capacity through reduced redox centres and



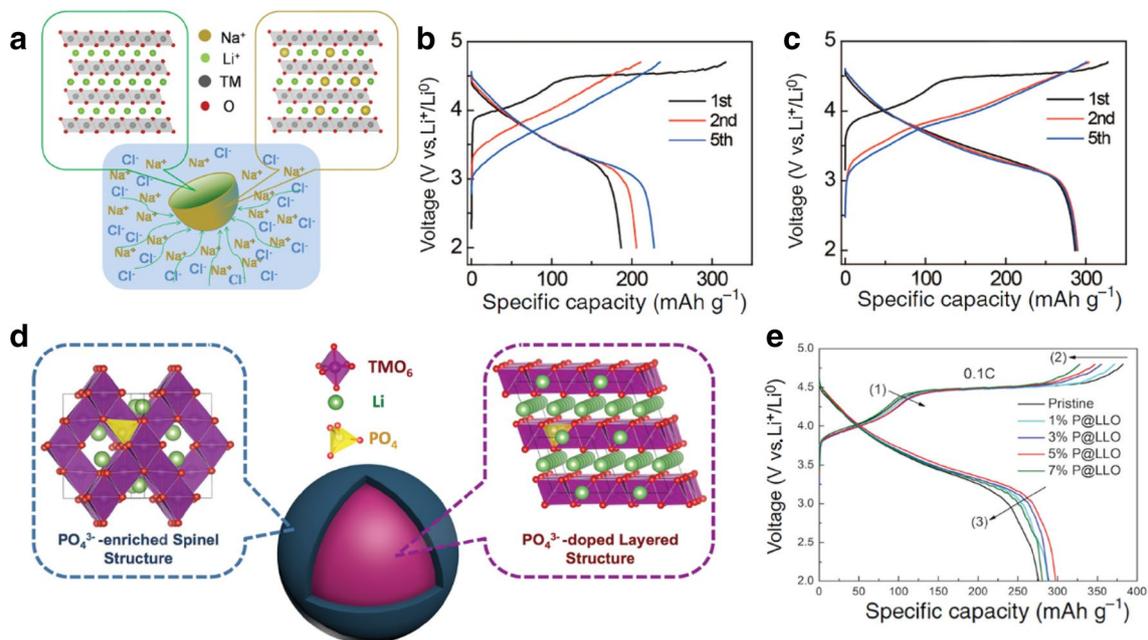
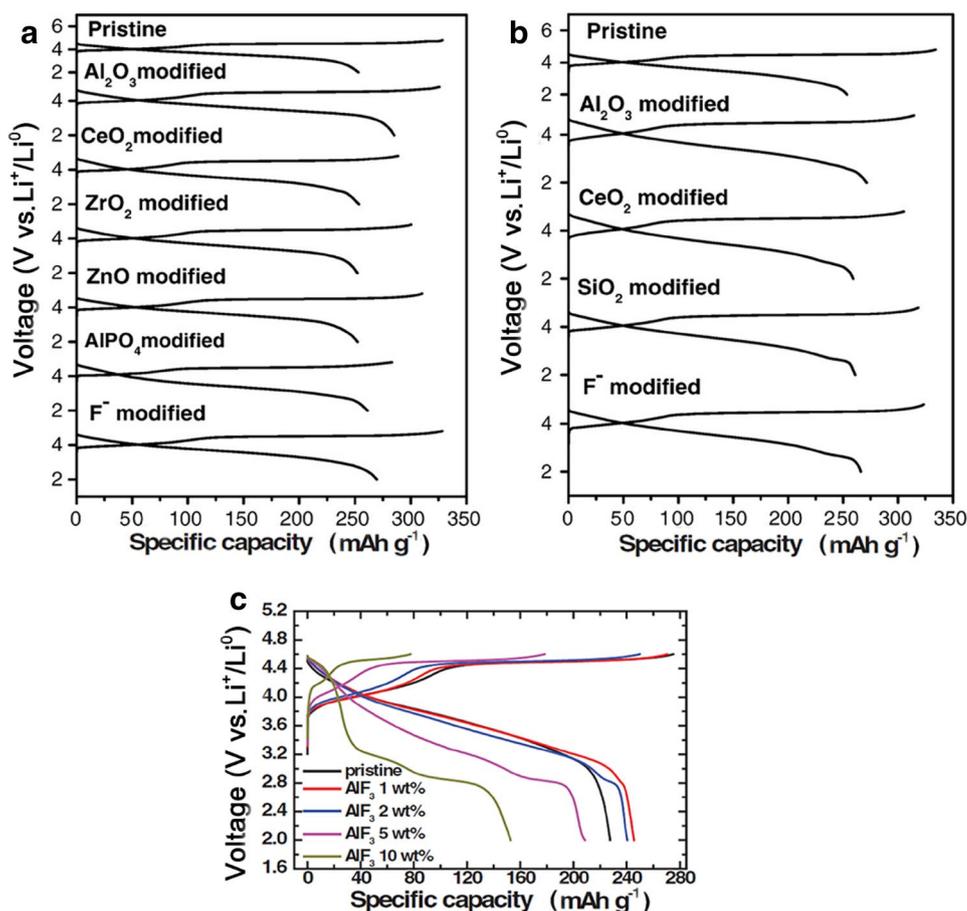
**Fig. 4** **a** First charge-discharge characteristics and  $dQ/dV$  plots. **b** Gas evolution rates of  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  electrode. *Source:* **a, b** Reproduced with permission from Ref. [28]



**Fig. 5** Cell voltage as a function of capacity and selected in situ individual diffraction patterns during the first cycle of **a** large-particle and **b** small-particle LLOs. The cells were tested in a potential window of

2.0–4.8 V versus  $\text{Li}/\text{Li}^+$  at a current of  $C/100$ . *Source:* Reproduced with permission from Ref. [110]

**Fig. 6** Initial charge-discharge profiles of **a**  $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$ - $0.4\text{Li}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})\text{O}_2$  and **b**  $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$ - $0.4\text{Li}(\text{Mn}_{1/6}\text{Ni}_{1/6}\text{Co}_{2/3})\text{O}_2$  with various coatings and F doping. **c** Initial charge-discharge curves of pristine and  $\text{AlF}_3$ -modified  $\text{Li}(\text{Li}_{0.19}\text{Ni}_{0.16}\text{Co}_{0.08}\text{Mn}_{0.57})\text{O}_2$  electrodes. **d** Initial charge-discharge profiles of  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13})\text{O}_2$ ,  $\text{V}_2\text{O}_5$ -modified samples and  $\text{V}_2\text{O}_5$ . *Source: a, b* Reproduced with permission from Ref. [98], *c* Reproduced with permission from Ref. [59]



**Fig. 7** **a** Schematic of gradient surface  $\text{Na}^+$  doping in LLOs and the initial charge-discharge profiles of **b** pristine and **c** Na-doped LLOs. **d**, **e** Schematic of gradient polyanion doping in LLOs and the first

charge-discharge curves of pristine and  $\text{PO}_4^{3-}$ -doped LLOs. *Source: a–c* Reproduced with permission from Ref. [116]. *d, e* Reproduced with permission from Ref. [117]

therefore suggested that co-doping can be a viable strategy to combine the benefits of various dopants to achieve optimal electrochemical performances. Overall, by regulating the loss of Li and O in LLOs, ICE can be improved, in which particle size control, surface coating and lattice doping prove to be useful in the reconstruction of surface structures, leading to possible stabilization of bulk structures, and are therefore feasible strategies.

## 3.2 Capacity and Voltage Fade

The capacity and voltage fade in LLOs, especially sustained average voltage, decreases during electrochemical cycling, significantly lowers energy efficiency and complicates corresponding battery management systems. Therefore, capacity and voltage fade has been thoroughly studied to achieve a better fundamental understanding. And because capacity fade is often coupled with voltage fade in LLOs, they will be reviewed simultaneously.

### 3.2.1 The Origins of Capacity and Voltage Fade

Capacity and voltage fade is a key issue in the practical application of LLOs and has been extensively investigated. Here, fading is believed to be caused by (1) TM/Li migration/layered-spinel transition/O redox, (2) the valence drop of TM ions and (3) porogenic behaviours or cracking, and all of these are closely linked to each other [48, 52, 97, 177].

#### 3.2.1.1 TM/Li Migration/Layered-Spinel Transition/O Redox

TM migration is an intrinsic feature of the electrochemical process in LLOs which causes an increase in trapped TM ions in interstitial tetrahedral sites, and cation migration from a TM slab to a Li slab is closely associated with the layered-spinel transition and the formation of spinel-like structures and is known to be associated with voltage fade [178–183]. In one study, Dogan et al. [184] used  $^6\text{Li}$  magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy to confirm that TM migration in LLOs was a limited reversible process that could cause gradual decay of LLO capacity and voltage during cycling. Moreover, recent studies have also shown that there is a close coupling between TM migration and the anion redox reactions of O [27, 97, 181, 185, 186] and this was further supported by first-principles calculations (Fig. 8) [23]. In a further study, Kleiner et al. [177] experimentally demonstrated that the host structure of  $\text{Li}_{1.17}\text{Ni}_{0.19}\text{Co}_{0.10}\text{Mn}_{0.54}\text{O}_2$  could undergo an irreversible transition metal-ion migration during long-term cycling (Fig. 9a), resulting in a high capacity drop ( $50 \text{ mAh g}^{-1}$ ) between the initial two cycles and  $\sim 0.4 \text{ mAh g}^{-1}$  drop per cycle in the following cycles (Fig. 9b). In another study, Zheng et al. [72] combined aberration-corrected scanning transmission electron microscopy (AC-STEM) with electron energy loss spectroscopy (EELS) to probe the structural

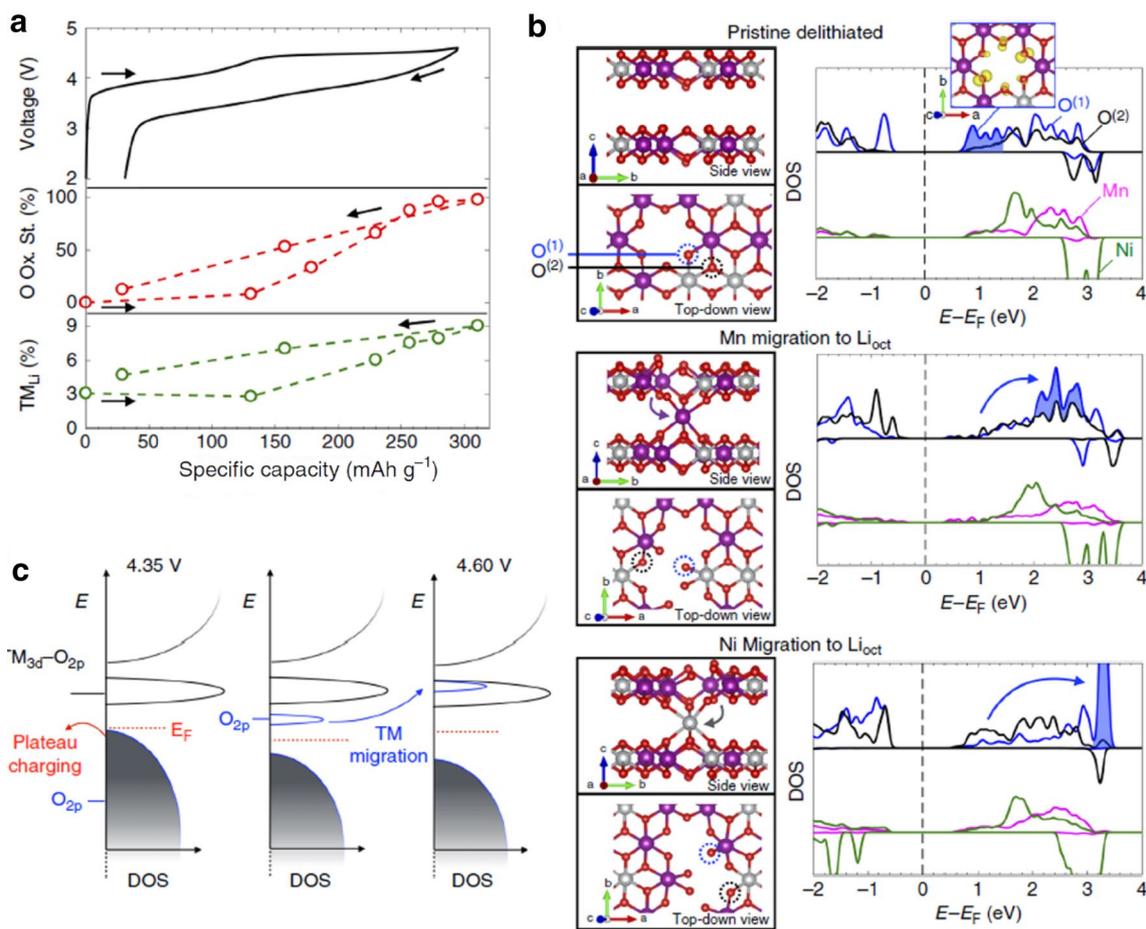
changes in  $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$  during cycling (Fig. 9c) and revealed that the layered structure experienced phase transformations, including a defect spinel-like structure and a disordered rock-salt structure. Finally, Yan et al. [187] combined STEM with density functional theory (DFT) calculations to investigate the structural evolution of  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  during cycling and concluded that the successive phase transitions of  $C2/m$ ,  $I41$  and spinel occurred after extended cycling (Fig. 9d, e). And based on these results, it is clear that TM migration, layered-spinel transition and O redox are closely connected to each other and contribute to the capacity and voltage decay of LLOs.

#### 3.2.1.2 Valence Drops of TM Ions During Cycling

Alternatively, Hu et al. [25] achieved better fundamental understandings of voltage fade and suggested that the origin of voltage fade may arise not only from changes in TM migration and O redox activity, but also from the valence drop process of TM ions as induced by O release based on structural changes in  $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ . Here, the researchers noticed that lower-voltage  $\text{Mn}^{3+}/\text{Mn}^{4+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$  redox couples became major contributors to capacity in extended cycling, which was directly linked to voltage fade (Fig. 10a), and that the shift of redox couples from O and Ni to Mn and Co had dramatic influences on voltage profiles (Fig. 10b, c). This finding was also supported by other researchers. For example, Zheng et al. [48] examined the structural changes of  $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$  electrodes and ascribed the capacity fading to the irreversible formation of  $\text{Mn}^{2+}$  species from the disproportionate reaction of  $\text{Mn}^{3+}$  (Fig. 11), in which  $\text{Mn}^{2+}$  species dissolved in the electrolyte and the number of redox centres in the LLOs was permanently reduced.

#### 3.2.1.3 Porogenic Behaviours and Cracking Issues

In addition to  $\text{Mn}^{2+}$  dissolution, particle fragmentation of LLO particles can be induced by spinel grain formations (Fig. 11). In addition, the formation of cracks or porogenic behaviours on the surface or in the bulk of LLO materials has also been proposed and is directly related to high strain and high-voltage cycling [185, 188]. For example, Chen et al. [97] used *operando* neutron powder diffraction and transmission X-ray microscopy methods to reveal that generated cracks, possibly occurring alongside the two-phase and  $\text{Li}_2\text{MnO}_3$  reactions during the charge process (Fig. 12a), accounted for capacity fade, and suggested that controlling phase separation and O evolution can prevent capacity fade in LLOs. Similarly, Liu et al. [74] found that layered-spinel transition was an irreversible behaviour that occurred not only on the surface, but also in the internal bulk structure of  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$  during cycling (Fig. 12b) and can induce surface cracking and bulk fragmentation. Here, the researchers suggested that surface degradation and drastic bulk evolution were the main degradation mechanisms and



**Fig. 8** Electronic structure related to cation migration. **a** Plot of the O fractional oxidation state and the migrated TM fraction as a function of capacity. **b** Projected density of states (pDOS) for TMs and two-coordinate (O<sup>(1)</sup>) and three-coordinate (O<sup>(2)</sup>) oxygen environments in

the pristine delithiated state (top) and after Mn (middle) and Ni (bottom) migration into octahedral sites in the Li layer. **c** Schematic of the reorganization of the electronic structure resulting from TM migration. *Source: a–c* Reproduced with permission from Ref. [23]

were the sources of the rapid failure of their LLO electrodes. In addition, by using in situ Bragg coherent diffractive imaging (BCDI) techniques, Singer et al. [26] directly captured structural evolution during cycling in primary particles and observed large quantities of dislocations and grain boundary movements, inducing strains between the grains and causing particle cracking in LLO electrodes (Fig. 12c). Overall, all these results suggest that porogenic behaviours and cracking issues are intrinsic properties of typical LLOs.

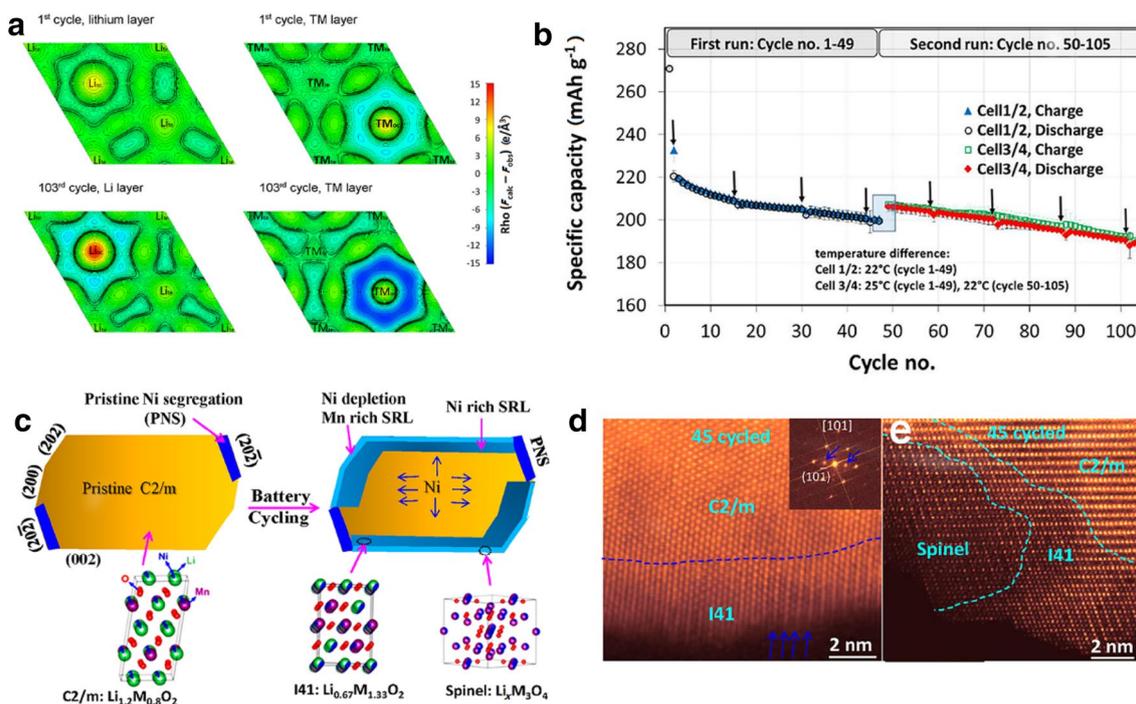
Alternatively, researchers have also reported that the release of O in the irreversible process of O redox activity can result in bulk/surface cracking [61, 97, 189] and can contribute to LLO capacity/voltage fade. In addition, researchers have also reported that pores can form within bulk structures through nucleating vacancies which can worsen LLO cracking issues in which nucleating vacancies are thought to be formed through the release of O during charging and exposed through the pathways of O diffusion [25]. Overall, deeper fundamental understandings of

the capacity and voltage fade of LLOs need to be achieved with direct detection and quantification of TM and oxygen activities through *operando* techniques such as in situ neutron powder diffraction, X-ray absorption spectroscopy and Raman spectroscopy. And in particular, correlations between fundamental reaction mechanisms and structure-property relationships are needed for further improvement.

### 3.2.2 Strategies to Suppress Voltage Fade

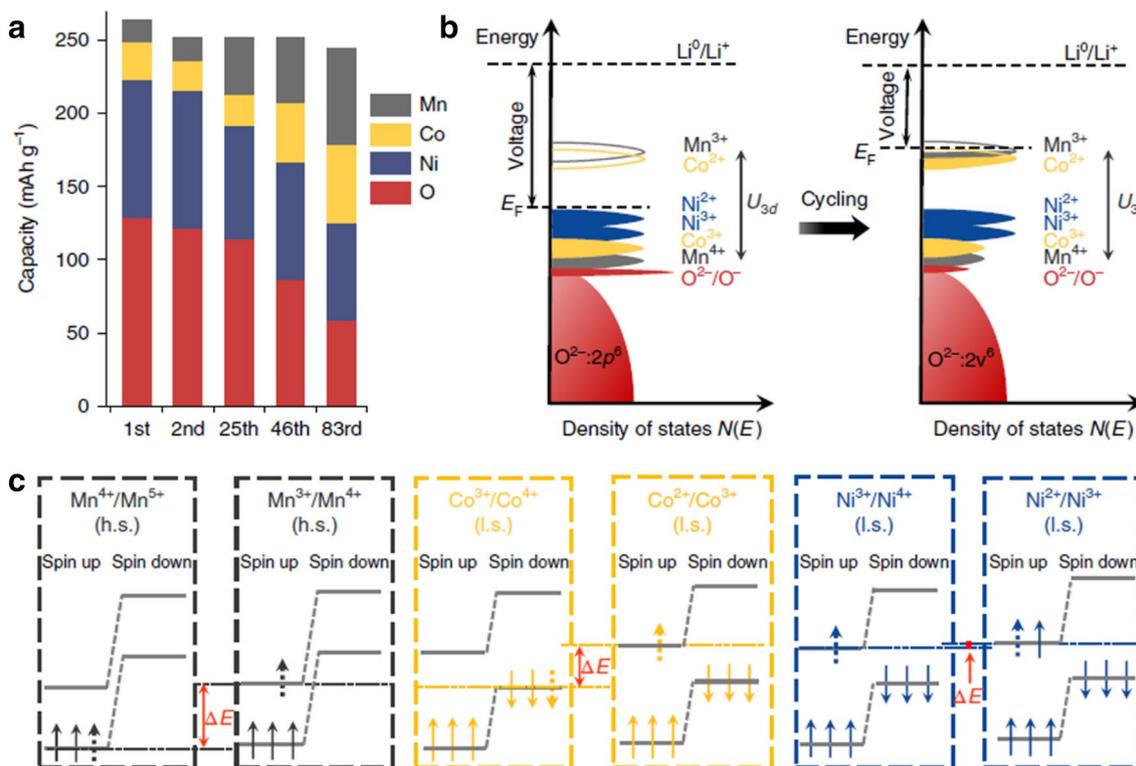
To mitigate capacity and voltage fade, electrolyte and binder modulation, surface modification and lattice doping are the most commonly used strategies.

**3.2.2.1 Electrolyte and Binder Modulation** Aside from intrinsic mechanistic issues, the instability and possible decomposition of conventional electrolytes can also affect the capacity and voltage fade of LLOs due to the need for high-voltage charging (>4.7 V). Because of this, conven-



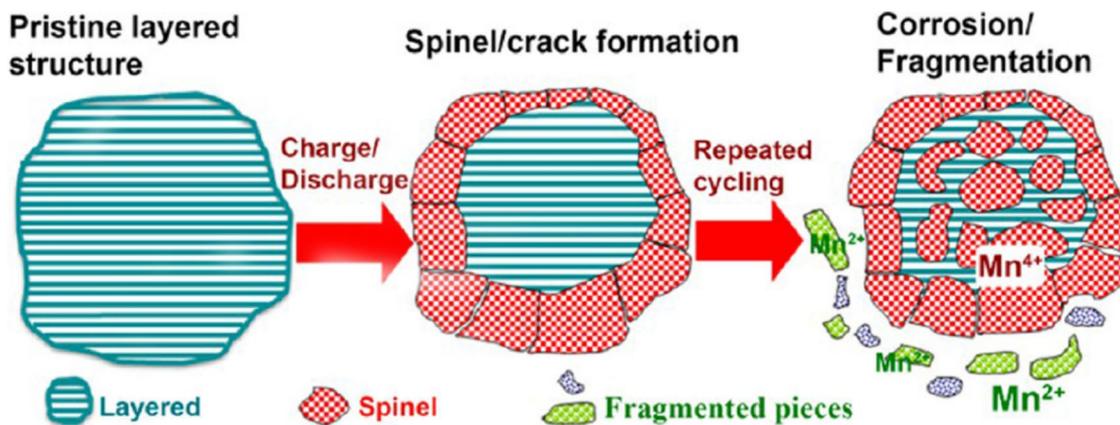
**Fig. 9** **a** Difference Fourier maps of the *ab* plane of discharged LLOs after the first cycle. **b** Mean specific capacity of LLOs in pouch cells upon cycling. **c** Schematic of cycling-induced surface layer evolution. **d, e** [101] and [010] zone axis STEM-HAADF images and

fast Fourier transformation (FFT) image of LLO electrodes after 45 cycles. *Source:* **a, b** Reproduced with permission from Ref. [177]. **c–e** Reproduced with permission from Ref. [187]



**Fig. 10** Evolution of redox couples in  $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$  upon cycling. **a** Contribution towards the discharge capacity of Ni, Co, Mn and O redox at various cycles. **b** Effects of electronic structure change

on the Fermi level. **c** Diagram of the correlation between redox couple and energy level of each element. *Source:* **a–c** Reproduced with permission from Ref. [25]



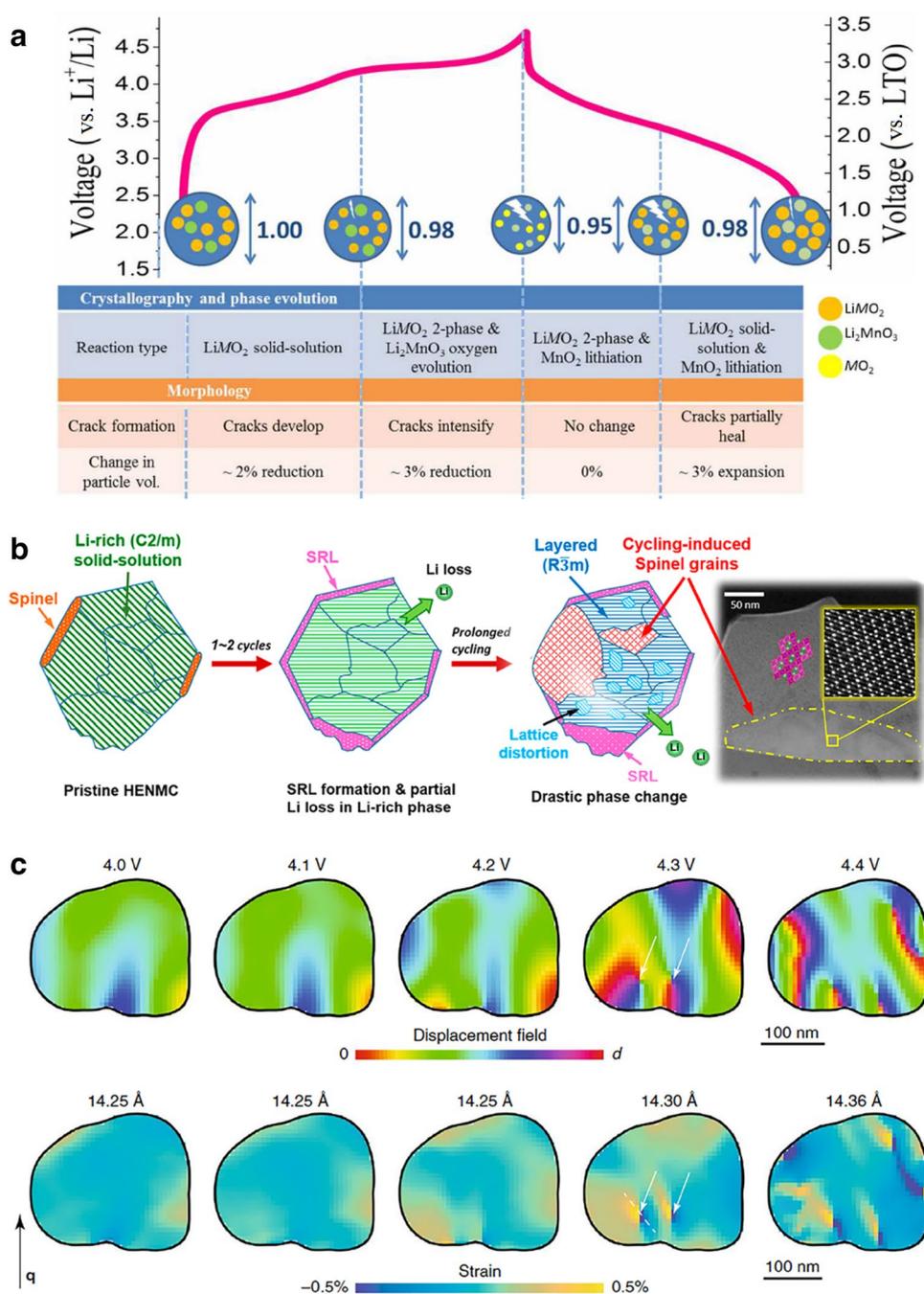
**Fig. 11** Schematic of corrosion/fragmentation-related capacity/voltage fade upon electrochemical cycling in  $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ . Source: Reproduced with permission from Ref. [48]

tional electrolytes and binders cannot meet the demands of high-voltage operations for LLOs; therefore, optional solvents (e.g. ionic liquids [190], suberonitrile [191]) and additives (e.g. tris(pentafluorophenyl) borane (TPFPB) [192], lithium bis(oxalate) borate (LiBOB) [193], dimethyl phenylphosphonite (DMPP) [194], lithium difluoro(oxalate) borate (LiDFOB) [195, 196], triethyl phosphite (TEP) [197], tris(trimethylsilyl)borate (TMSB) [198, 199], (trimethylsilyl)methanesulphonate (TMSOMs) [199], 1,3,6-hexanetricarbonitrile [200], tripropylborate (TPB) [201], phenyl vinyl sulphone (PVS) [200], tris(2,2,2-trifluoroethyl) phosphite (TTFP) [202], tri(hexafluoro-iso-propyl)phosphate (HFIP) [203]) have been frequently applied to achieve better electrolyte stability at such high working voltages. Here, most additives can improve capacity retention and even discharge voltage fade by forming protective solid electrolyte interphase (SEI) films on cathode surfaces to prevent direct contact between cathode surfaces and electrolytes. For example, Zheng et al. [192] reported that TPFPB as an anion receptor can be used as an electrolyte additive in  $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$  to effectively improve capacity retention and reduce voltage fade through the capture of oxygen species generated during  $\text{Li}_2\text{MnO}_3$  activation. In another example, Nayak et al. [193] reported that LiBOB as an electrolyte additive could slow down  $\text{Li}_2\text{MnO}_3$  activation and that the subsequent structural stabilization could restrict layered-spinel transition in  $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ . In addition, various binders other than the commonly used polyvinylidene fluoride (PVDF) have been found to be able to enhance LLO electrochemical performances [63, 204]. For example, Zhang et al. [205] used sodium carboxymethyl cellulose (CMC) as a binder in  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$  and reported excellent suppression of voltage fade (Fig. 13), revealing that the CMC binder could not only prevent the detachment of electrode materials from the current collector, but also possibly

introduce  $\text{Na}^+$  doping through an ion exchange process during discharge.

**3.2.2.2 Surface Modification** As for surface modifications, they can not only protect, but also enhance electronic/ionic conductivities and alter mechanistic behaviours of LLOs in terms of capacity and voltage fade. For example, Liu et al. [206] modified  $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.5}\text{O}_2$  with a hybrid surface coating layer composed of  $\text{Mg}^{2+}$  pillars and  $\text{Li-Mg-PO}_4$  (Fig. 14a) and reported significantly enhanced cycling performances (capacity of  $180 \text{ mAh g}^{-1}$  after 250 cycles at  $60^\circ\text{C}$ ) and average discharge voltage retention of 88.7% after extended cycling (Fig. 14b-c). In another example, Prakasha et al. [157] used  $\text{Li}_2\text{ZrO}_3$ , a well-known ion conductor, as a coating layer for LLOs to promote the migration of  $\text{Li}^+$  and resist the diffusion of  $\text{Mn}^{2+}$  and reported greatly suppressed layered-spinel transitions and voltage fade during cycling. Similarly, Wu et al. [150] modified  $\text{Li}(\text{Li}_{0.2}\text{Fe}_{0.1}\text{Ni}_{0.15}\text{Mn}_{0.55})\text{O}_2$  with an  $\text{AlPO}_4$  coating and reported that the coating reduced side reactions between the electrolyte and the electrode surface, decreased O vacancy mobility and promoted Li diffusion, leading to improved LLO electrochemical performances. In a further example, Kim et al. [207] modified the surface structure of LLOs to form a  $\text{Li}_2\text{MnO}_3$ -like coating on the surface and reported that the  $\text{Li}_2\text{MnO}_3$ -like layer possessed high atomic-level structural compatibility and exhibited a seamless surface-bulk connection with the core LLO structure. In addition, the researchers reported that compared with other coating materials, their  $\text{Li}_2\text{MnO}_3$ -like coating not only provided facile Li diffusion, but also suppressed layered-spinel transition, hence ameliorating the voltage fade problem of LLOs (Fig. 15a-c), in which the suppression of the layered-spinel transition was attributed to the unique atomic coordination of Li/Ni mitigating TM mixing (Fig. 15d).

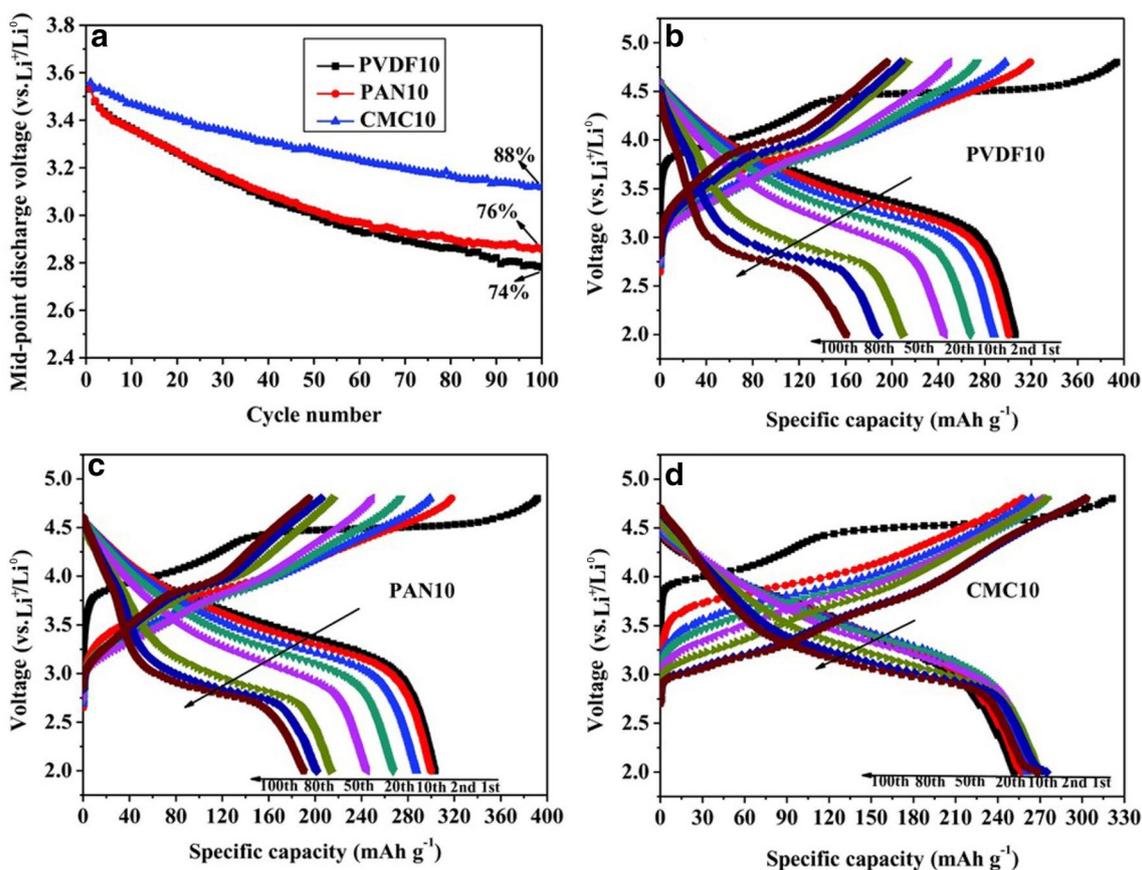
**Fig. 12** **a** Summary of the changes related to electrochemistry and morphology in  $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$  electrodes during cycling based on a combination of *operando* NPD and TXM results. **b** Schematic of the structural evolution of  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$  electrodes during electrochemical cycling. **c** Changes in the displacement field along  $q$  in a plane in LLO nanoparticles during charge and the strain along the (001) direction (perpendicular to the layers) inside the LLO nanoparticles calculated from 3D displacement fields. *Sources:* **a** Reproduced with permission from Ref. [97], **b** Reproduced with permission from Ref. [74], **c** Reproduced with permission from Ref. [26]



**3.2.2.3 Lattice Doping** Lattice doping is the most common approach used by researchers to reduce voltage fading through the blocking of TM migration and the stabilization of LLO structures [208, 209]. For example, Nayak et al. [50] replaced Mn ions with  $\text{Al}^{3+}$  ions in  $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}\text{O}_2$  and reported that the doped sample demonstrated noticeably reduced capacities and voltage fade and that this effect increased with Al doping amounts (Fig. 16). Here, Raman spectroscopy results suggested that Al doping can stabilize the layered structure during the charge-discharge process in LLOs. In another example, Yu et al. [210] introduced

$\text{Ti}^{4+}$  doping into an LLO structure to investigate its effects towards LLO voltage fade suppression and reported that  $\text{Ti}^{4+}$  doping can prevent the migration of Mn ions and therefore stabilize the layer structure. Furthermore, in addition to TM site doping, Li site doping with alkali cations (such as  $\text{Na}^+$  and  $\text{K}^+$ ) [116, 164] and O site doping with  $\text{F}^-$  [115, 211] have also been investigated by researchers with promising results.

Overall, it is generally accepted that oxygen activities play an important role in the suppression of capacity and voltage fade in LLOs. And although lattice doping and the



**Fig. 13** **a** Mid-point discharge voltage fade curves of LLOs and **b–d** voltage profiles of LLOs with 10 wt% PVDF, PAN and CMC binders. Source: **a–d** Reproduced with permission from Ref. [205]

control of synthesis conditions have been shown to affect oxygen activities, more precise control has yet to achieve and a deep understanding into this control is lacking. More importantly, more cost-effective methods for the large-scale synthesis of optimal LLOs in full cells are required for real-world applications.

### 3.3 Poor Rate Capability

The rate capability of an electrode is an important parameter in application for high-power applications such as EVs. In LLOs, rate performance is linked to Li diffusion kinetics within crystal structures and interfacial charge transfer reactions [55].

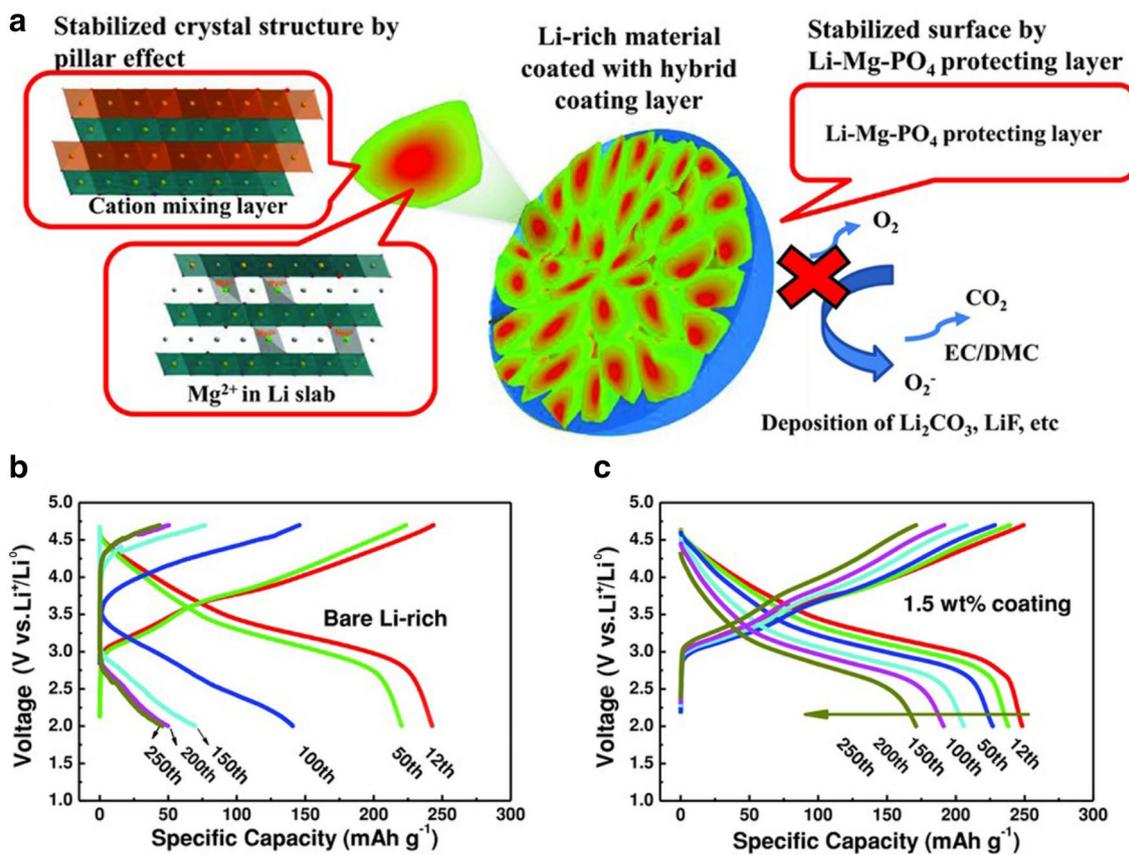
#### 3.3.1 The Origins of Poor Rate Capability

LLOs suffer from structural instabilities (TM migration and lattice dislocation) and complex O activities during cycling and therefore hinder Li diffusion, resulting in poor rate capabilities. Here, rate capability is determined by the Li mobility within cells, and for LLOs, the  $\text{Li}_2\text{MnO}_3$  component with

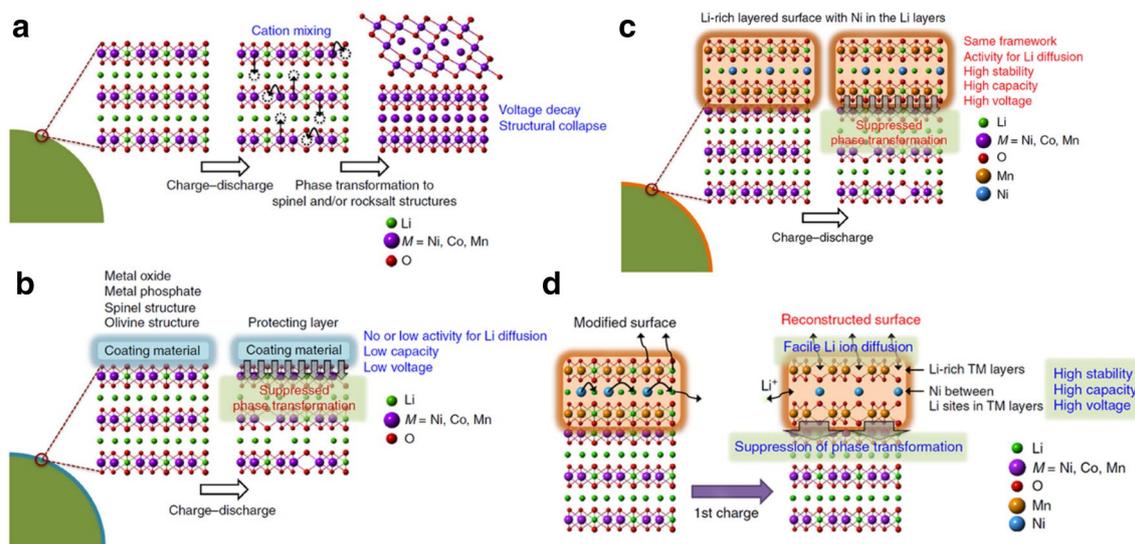
the  $C2/m$  monoclinic structure possesses relatively low Li diffusion kinetics as compared with other layered oxides [55, 212]. In a study, Zheng et al. [55] used galvanostatic intermittent titration technique (GITT) to confirm that the sluggish Li diffusion kinetics in  $\text{Li}_2\text{MnO}_3$  and  $\text{MnO}_2$  components was the rate-determining factor of  $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$  and limited the discharge capacity of LLOs at high rates. Similar results have also been reported in literature [31, 213, 214]. Furthermore, although the activation of  $\text{Li}_2\text{MnO}_3$  in LLOs is the origin of their anomalously high capacities and energy densities, it also causes surface structure transformations, which can increase interfacial resistances, impede Li diffusion kinetics and induce poor rate capabilities [18, 215, 216]. In addition, the oxidation of organic electrolytes at high voltage can induce the formation of undesirable surface passivation layers, which block Li diffusion and contribute to poor rate capabilities.

#### 3.3.2 Strategies for Improving Rate Performance

Various successful methods have been reported in the enhancement of LLO rate performances, and in this review,

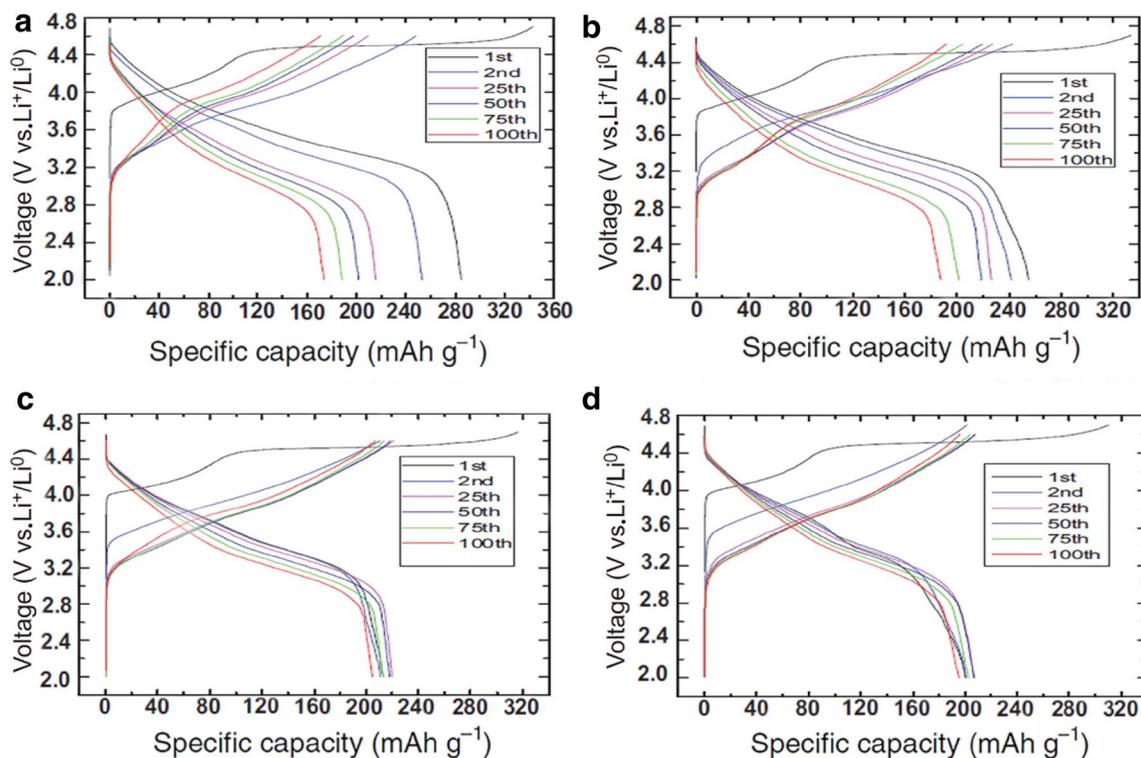


**Fig. 14** **a** Schematic of  $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.17}\text{Mn}_{0.5}\text{O}_2$  particles with surface modification. **b, c** Charge-discharge curves of bare and surface-modified LLOs at various cycles. *Source:* **a-c** Reproduced with permission from Ref. [206]



**Fig. 15** Surface crystal structure of LLOs and the effects of surface modification: **a** pristine sample, **b** with conventional surface coating and **c** with unique surface modifications in which Ni is located

between Mn layers. **d** Schematic of the effects of surface modification. *Source:* **a-d** Reproduced with permission from Ref. [207]



**Fig. 16** Charge-discharge curves of LLOs: **a**  $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}\text{O}_2$ , **b**  $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.54}\text{Al}_{0.02}\text{Co}_{0.08}\text{O}_2$ , **c**  $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.51}\text{Al}_{0.05}\text{Co}_{0.08}\text{O}_2$  and **d**  $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.48}\text{Al}_{0.08}\text{Co}_{0.08}\text{O}_2$ . Source: **a–d** Reproduced with permission from Ref. [50]

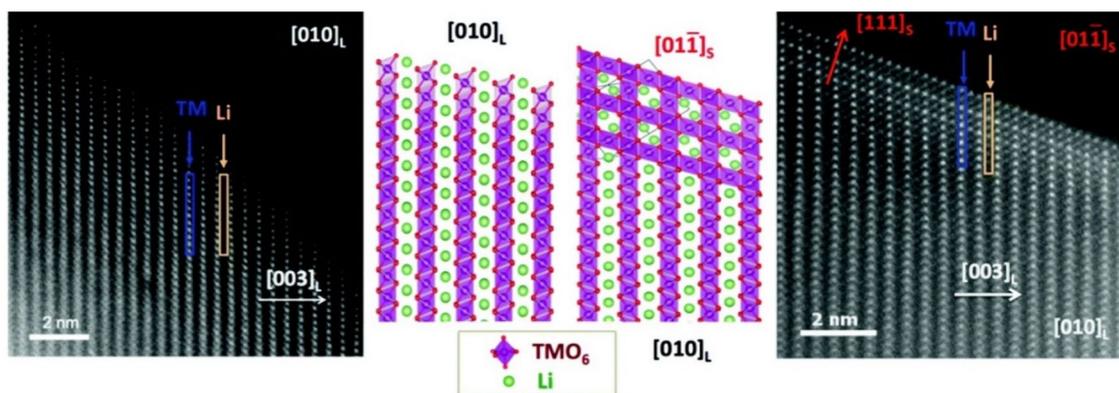
various enhancement strategies will be presented to assist with understanding and discussion.

**3.3.2.1 Surface Modification** Surface modification is still one of the most effective approaches to improve rate capability, and many studies have shown that solid electrolytes and ion conductive coating materials can improve the interfacial stability and rate capability of LLOs as compared with other surface coating materials that possess low Li conductivity and electronic conductivity and can block Li transport channels. Researchers have reported that carbon and other electronic conductive coating materials on LLOs can exhibit superior rate performance, mainly due to their high electronic conductivities and reduced charge transfer resistances [137–145, 217] and that surface coating with ionic conductive  $\text{AlPO}_4$  can retain O vacancies and stabilize electrode/electrolyte interface side reactions due to the high stability of  $\text{AlPO}_4$  (stemming from the high electronegativity of polyanions with Al ions) [150]. For example, Ahn et al. [155] reported that nanoscaled Zr-abundant nanolayers grown along the  $(20\bar{2})_m$  plane which are along the Li diffusion facets can exhibit a capacity of  $\sim 110 \text{ mAh g}^{-1}$  even at a high rate of 30 C in which Zr can prevent the segregation of TM ions along the  $(20\bar{2})_m$  plane and was believed to influence the electrochemical performance. In addition, the researchers also suggested that this surface modification can

induce O vacancies in the surface regions. Normally, cation-disordered structures impede Li diffusion [4, 206]; however, this study suggests the unexpected formation of percolation networks with facile Li transport in Li-disordered rock-salt structures [218, 219]. Based on this, surface modification can not only refer to coatings for protection and higher conductivity, but also refer to the pre-activation of  $\text{Li}_2\text{MnO}_3$ , surface structure tuning and surface gradient doping through pre-cycling treatments.

Pre-cycling treatments on LLO surfaces have been shown to improve rate performance, and surface treatments with  $\text{H}_2\text{SO}_4$  [220],  $\text{AlF}_3$  [221, 222],  $\text{NH}_4\text{H}_2\text{PO}_4$  [117],  $(\text{NH}_4)_2\text{HPO}_4$  [223],  $\text{Na}_2\text{S}_2\text{O}_8$  [224, 225],  $(\text{NH}_4)_2\text{SO}_4$  [226] and  $\text{NH}_4\text{HF}_2$  [227] have been used to activate  $\text{Li}_2\text{MnO}_3$  components and induce the formation of the spinel-like phase on the surface, which enhance Li diffusion (Fig. 17). For example, Wu et al. [228] pre-treated LLOs with  $\text{Mn}(\text{Ac})_2$  to achieve an encapsulating layer and annealed the samples to achieve a heterostructured spinel layer with three-dimensional (3D) Li diffusion channels that facilitated rapid Li diffusion and reported that the treated cathode exhibited improved cycling stability and rate capability (Fig. 18).

Aside from activating  $\text{Li}_2\text{MnO}_3$  with acidic species and facilitating fast Li diffusion channels, surface treatments with polyaniline [229], Super P [230], hydrazine [231] and reduced graphene oxide (rGO) [180] have all been shown to



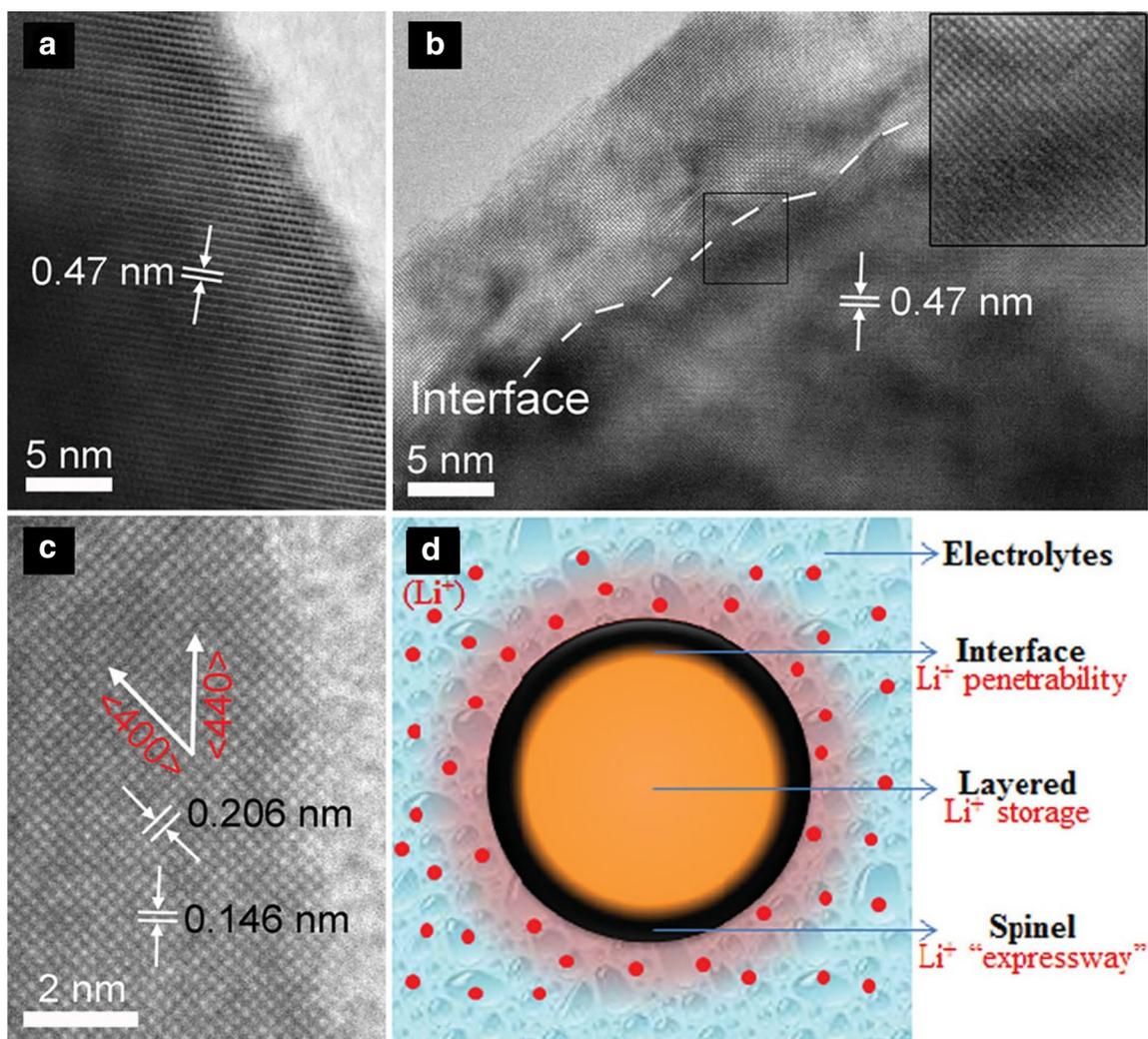
**Fig. 17** Spinel-like formations after surface treatment in LLOs. *Source:* Reproduced with permission from Ref. [117]

be able to prevent layered-spinel transitions in LLOs through limiting the formation of Li and O vacancies at the surface and thereby preventing induced structural instability in these materials. For example, Zhang et al. [232] introduced surface nitridation to  $\text{Li}(\text{Li}_{0.17}\text{Ni}_{0.25}\text{Mn}_{0.58})\text{O}_2$  through sintering in  $\text{NH}_4\text{OH}$  atmosphere at  $400^\circ\text{C}$  and reported that the nitrogen introduction improved interfacial stability and Li diffusion. Here, the researchers reported that the improved rate capability ( $164.7\text{ mAh g}^{-1}$  discharge capacity at 5 C rate) can be associated with the presence of surface nitrogen; however, explanations and findings related to the effects of surface nitridation are obscure. Furthermore, surface morphology tuning is also a possible approach to enhance the rate capability of LLOs. For example, Qing et al. [116] adopted a surface doping strategy to achieve surface gradient  $\text{Na}^+$  doping by soaking LLOs in molten  $\text{NaCl}$  before heat treatment. Here, the researchers reported that some of the  $\text{Li}^+$  layers were occupied by  $\text{Na}^+$ , resulting in a pinning effect that stabilized the structure and improved  $\text{Li}^+$  diffusion kinetics.

In addition, Ding et al. [64] investigated gradient surface doping using Si/Sn in which the interplanar spacings of the TM ions were expanded as Sn/Si atoms were doped into the lattice of LLO near the crystal surface and reported that such doping can result in structural stabilization and enhanced cycling performances in which the rate capability of their LLO was improved by improving  $\text{Li}^+$  diffusion through the enlargement of the interslab spacing of the TM layer. A similar gradient doping approach was conducted by Zhao et al. [117] in which polyanion doping resulted in a surface spinel transformation similar to that in acid treatments, which enhanced ionic and electronic conductivities through electrode surfaces and improved rate kinetics. Here, the researchers reported that a Mn-depleted surface layer can limit HF acid attacks and Mn dissolution and improve the stability of the electrode/electrolyte interface. In addition, these researchers also reported that  $\text{PO}_4^{3-}$  doping can

restrain TM-ion migration because the smaller  $\text{V}^{5+}$  cations tend to occupy tetrahedral interstitial sites. In another study, Liu et al. [118] also reported that surface doping with  $\text{Nb}^{5+}$  and other heavy element ions such as  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  can improve LLO capacity retention rates and rate capability. Here, the researchers suggested that these elements possess stronger bonds to oxygen as compared with Mn–O bonds and can limit oxygen evolution through surface oxygen deactivation and that doped  $\text{Nb}^{5+}$ ,  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  ions can enter the surface Li layers to inactivate  $\text{Mn}^{4+}$  ions and retain them in the TM layers, thus retarding migration and phase transformation. Surface gradient doping strategies have also been reported to improve LLO cycling stability and rate capabilities through the stabilization of LLO structures during electrochemical cycling. For example, Hu et al. [25] recently had suggested that  $\text{AlF}_3$  coatings can thermally stabilize LLO surface structures and restrict O release, thereby limiting structural instability and impedance build-up at the interface caused by electrolyte decomposition.

The surface coating of LLO cathode materials is an effective method to enhance rate performances through the passivation of electrode surfaces during cycling, the enhancement of LLO surface electronic and ionic conductivities and the ability to act as a protective barrier. Here, surface coating layers can act as protective layers to suppress side reactions, reduce interfacial resistances and stabilize interfaces, and some surface coatings can stabilize structural stability of LLO by partially removing  $\text{Li}_2\text{O}$  or enhance structural stability by limiting O release. Researchers also reported that the effectiveness of the surface coating approach depends on the thickness, uniformity, stability (thermal and mechanical), electronic and ionic conductivity of the coating layer and that these parameters are linked to the type of coating materials and methods adopted. For example, Qiu et al. [15] introduced O vacancies into the surface of LLOs through the interfacial modification of LLO surfaces using gas-solid interface reactions (GSIR) between LLOs and  $\text{CO}_2$  gas.

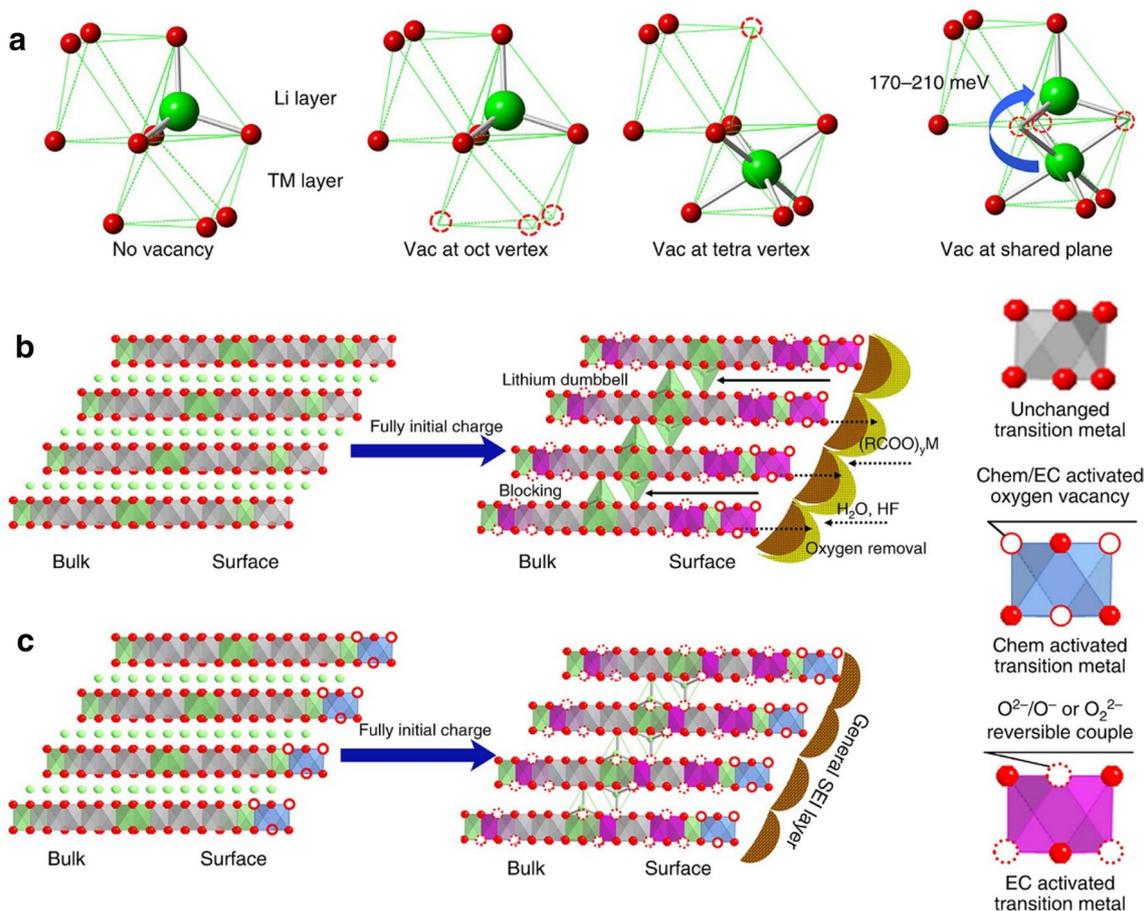


**Fig. 18** HRTEM images of treated and untreated samples with spinel heterostructure surfaces. *Source:* **a–d** Reproduced with permission from Ref. [228]

Here, the researchers reported that the induced O vacancies at the LLO surface suppressed O evolution and limited electrolyte decomposition due to the highly reactive O species (Fig. 19a–e). In addition, the researchers also reported that the presence of O vacancies destabilized the tetrahedral sites, which reduced the chance of Li atoms becoming trapped in the tetrahedral sites, impeding Li diffusion and affecting rate performances and capacity.

The surface of electrode materials can also influence the electrode/electrolyte contact, the reactivity of particles and the surface reactions and reactivity, and researchers suggest that hierarchical nanostructures with exposed (110), (100) and (010) planes with better Li intercalation kinetics can demonstrate improved rate capabilities [233, 234]. For example, Xia et al. [139] fabricated a layered-spinel carbon heterostructure using the carbothermal reduction method

and reported significantly enhanced rate performances. Here, the researchers suggested that the high-capacity Li-rich core with the spinel interlayer and the outside carbon-coated shell took advantage of the 3D Li<sup>+</sup> diffusion channels favoured by the spinel interlayer and demonstrated improved electrical conductivity due to the nanocarbon coating layer, in which a capacity of > 120 mAh g<sup>-1</sup> even at 20 C was obtained. In another example, Li et al. [235] synthesized a core-shell structure with a Ni-rich material as the core and a Mn-rich material as the shell and reported that the Ni-rich core contributed to high energy densities and the Mn-rich shell hindered electrolyte oxidation. A similar heterogeneous design was also adopted to enhance the rate capability of LLOs in other studies and was reported to also possess high capacity inner cores and structurally stable outer shells [236, 237]. Overall, all these presented strategies aim at limiting voltage fade and



**Fig. 19** **a** Schematic of the site stability and Li migration barrier under conditions of no oxygen vacancy and oxygen vacancies at different site vertices. Schematic of LLOs **b** without induced oxygen

vacancies and **c** with surface oxygen vacancies before and after initial charging. *Source:* **a–c** Reproduced with permission from Ref. [15]

have achieved improved rate performances as well because the origin of both issues is related to O activities in LLOs.

**3.3.2.2 Lattice Doping** Lattice doping with alkali metals such as  $\text{Na}^+$  [163, 208],  $\text{K}^+$  [164, 165] and  $\text{Mg}^{2+}$  [166] with large ionic radii has proved to enhance LLO rate performances. For example, Zheng et al. [165] synthesized K-doped  $\text{Li}_{1.212}\text{K}_{0.02}\text{Mn}_{0.615}\text{Ni}_{0.154}\text{O}_2$  which exhibited enhanced rate performances and suggested that  $\text{K}^+$  can restrict TM-ion migration and accompanying spinel formation in subsequent cycles. In another example, Yu et al. [166] doped  $\text{Mg}^{2+}$  ions into  $\text{Li}_{1.5}(\text{Mn}_{0.75}\text{Ni}_{0.25})\text{O}_{2+\delta}$  and reported stronger Mg–O bonds as compared with Li–O bonds, allowing for the suppression of irreversible Li extraction and subsequent oxygen loss. As a result, this Mg-doped cathode exhibited good capacity retention of 94% even after 200 cycles at 0.5 C and 92% after 100 cycles if cycled at 5 C. Overall, improvements in rate performance through lattice doping can be mainly attributed to the stabilization of LLO crystal structures through the suppression of O evo-

lution and accompanying phase transitions in subsequent cycles. Here, large dopant elements can hinder TM-ion migration and promote lattice expansion, favouring Li diffusion kinetics. In addition, researchers reported that the partial substitution of  $\text{Ti}^{4+}$  ions into Li sites of the  $\text{Li}_2\text{MnO}_3$  component can create Li vacancies and increase interlayer spacing, allowing for better Li diffusion kinetics [171] and that doping with anions such as  $\text{F}^-$  can improve rate kinetics in which  $\text{F}^-$  doping into O sites can result in larger crystal lattices and improved Li diffusion [51] along with restricted spinel-phase transformation [238]. Furthermore, 4d TMs such as Sn [170], Ru [174], Nb [175], Y [169], Zr [172] and Sb [63], and 5d metals such as W [176] have also been used as dopants in LLOs and have shown improved cycling stability and rate capabilities. Here, the observed enhanced electrochemical performances can mainly be attributed to reduced O loss due to strong 4d–O and 5d–O bonds as compared with 3d–O bonds. Moreover, researchers suggest that the strengthening of M–O covalent bonds can promote

reversible anionic redox instead of irreversible O loss that results from the breaking of M–O bonds [239].

### 3.3.2.3 Particle Morphology Control and Other Strategies for LLO Rate Enhancements

Architectures of nanosized LLOs that provide shorter Li diffusion pathways and more exposed surface sites for lithium intercalation/deintercalation can also enhance LLO rate capabilities [63, 240]. Here, the morphology of LLO plays a critical role in electrochemical performance in which hierarchical nanostructures with exposed (110), (100) and (010) planes favour Li intercalation kinetics, and LLOs possessing hierarchical porous structures can exhibit enhanced rate performances [233, 241–244]. Researchers also report that the formation of undesirable surface passivation layers due to organic electrolyte oxidation at higher voltage can cause poor rate capabilities due to increased Li diffusion resistances at the electrode/electrolyte interface [229, 245, 246]. In one study, Ming et al. [243] synthesized LLO nanoplates with built-in spinel/rock-salt tunnels (OAN-ST) that exhibited highly exposed (010) planes and reported that the resulting cathode exhibited enhanced capacity retention rates (92% after 100 cycles at 1 C), delivering high discharge capacities and ICE. Here the researchers attributed the performance enhancements to enhanced Li diffusion and intercalation kinetics as well as structural reinforcements through the accommodation of volume change during electrochemical cycling due to the peculiar structural design. In another study, Lin et al. [245] reported that other than the formation of surface passivation layers, progressive structural transitions can occur at the LLO surface depending on the crystal orientation and can result in impedance build-up and affect Li diffusion kinetics.

One reason for poor rate capability and irreversible capacity fading in LLOs is the formation of undesirable SEI layers (e.g.  $\text{Li}_2\text{CO}_3$ , LiF) on cathode surfaces, which can generate resistance to Li diffusion, and O species extracted during the  $\text{Li}_2\text{MnO}_3$  activation process can oxidize organic solvents and result in the formation of this surface passivation layer at the cathode/electrolyte interphase [247]. In addition, at higher voltages above 4.6 V, carbonate-based electrolytes can decompose and contribute to SEI layer formations as well. Based on this, researchers have reported that electrolyte additives such as TFPFB [192], tris(2,2,2-trifluoroethyl)phosphite [202] and LiBOB [193] can be useful to improve LLO rate capability by forming protective films at the cathode surface without impeding Li diffusion or by preventing undesirable parasitic reactions at the cathode/electrolyte interphase and therefore avoid the formation of undesirable surface passivating layers. For example, TFPFB with B atoms located at the centre has been found to be effective in the capture of active oxygen species and thus can limit side reactions at the interphase and assist in the

dissolution of by-products of these parasitic reactions [192]. Alternatively, LiBOB is an electrolyte additive that can slow down  $\text{Li}_2\text{MnO}_3$  activation and although studies report poor performances and an initial discharge capacity of only 215 mAh  $\text{g}^{-1}$ , cycling stability and rate performances can be enhanced with less discharge voltage fade [193]. However, the mechanisms behind the stabilization achieved by this additive have not yet been elucidated. Furthermore, with its stable chemical structure, PVS as an electrolyte additive can form a stable and ion conductive film on cathode surfaces to improve the capacity and rate performance of  $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13})\text{O}_2$  [248]. Lastly, lithium difluoro(oxalato) borate (LiODFB) can also be employed as an electrolyte additive in full cells with  $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Mn}_{0.5}\text{Co}_{0.17}\text{O}_2$  cathodes and graphite anodes to achieve better rate capabilities due to the improved electronic and ionic conductivities of the SEI layer at the anode surface and the alleviated metal-ion dissolution of the cathode surface [249].

Overall, lattice changes and phase transformations originating from the activation process of  $\text{Li}_2\text{MnO}_3$  are the major causes of poor rate capability; therefore, the optimization of the TM content and stabilization of TM lattices, especially Mn, are potential strategies to improve LLO rate capabilities.

## 4 Summary and Future Perspectives

Lithium-rich layered oxides (LLOs) possess high energy densities and are ideal for large-scale energy storage applications such as EVs and PHEVs. However, intrinsic weaknesses such as low initial Coulombic efficiency (ICE), severe capacity/voltage fade and poor rate capabilities impede further application. Therefore, in this review, fundamental origins of these issues and corresponding solutions are summarized along with opinions and perspectives.

Since the introduction of LLOs by Thackeray et al. in 1993, their electrochemical performances have continuously improved. And although the practical capacity of LLOs has reached  $\sim 330$  mAh  $\text{g}^{-1}$  and many breakthroughs have been achieved, challenging issues remain and are closely connected with  $\text{Li}_2\text{MnO}_3$  activation as well as the subsequent O release and evolution and the corresponding atomic (transition metal/cation migrations, mechanistic evolutions and valence drop cation redox reactions) and macroscopic (porogenic behaviours, surface cracking and pulverization) responses. To address these, commonly used strategies that have proved to be useful include particle size control, electrolyte and binder formulations, surface modifications and lattice doping. Although these strategies can partially mitigate some issues posed by LLOs, intrinsic issues that limit practical application have not been fully resolved. Here, many recent studies on LLOs have been able to find the root causes of these issues with the aid of advanced

characterization techniques, but more efforts are needed to obtain reliable conclusions and solutions. This is because none of these studies have been able to deliver clear and conclusive results regarding the fundamental origins of the challenges, especially the voltage fade, as well as the fact that many of the proposed solutions, such as surface modification, involve additional costs. Overall, an ICE greater than 90% for LLOs is required for communalization, and to achieve this, more intensive full-cell studies need to be conducted. In addition, volumetric energy densities of LLOs need to be improved through the improvement of LLO tap densities through the exploration of facile routes for low-cost large-scale synthesis.

Overall, an in-depth understanding of the correlation between O redox reactions and O release with respect to how it is affected by local structures is required and a promising and challenging approach is to create more triggering anionic redox reactions while lowering O release in which a noteworthy example is the use of electroactive cations such as Ru while maintaining strong d-sp hybridization to harvest additional capacity from  $O^{2-} \rightarrow O_2^{2-}$  redox. In addition, new cutting-edge probing techniques need to be developed to investigate redox origins such as the direct measurement of O activities in LLOs during lithiation/delithiation to provide clearer and more precise pictures of mechanistic behaviours along with currently available characterization tools and approaches. And from a material design perspective, achieving coupled cationic and anionic redox processes can be a good solution, in which the fast kinetics of cationic redox reactions can act as redox mediators for sluggish anionic processes. Overall, there has been clear progress in the commercialization of LLOs; however, intrinsic challenges remain for practical application. To address these challenges, this review has presented many promising strategies in the hope that LLOs will eventually become optimized enough to meet the demands of commercial and industrial applications.

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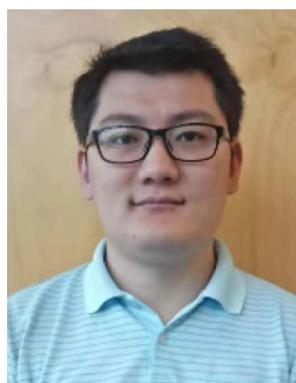


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