Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Origins and characterization of oxygen loss phenomenon in layered oxide cathodes of Li-ion batteries

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Table S1 A summary of different types of LLMO cathodes, with typical examples and their characteristics related to oxygen loss phenomenon. Notes: the value of capacity and voltage hysteresis were obtained from the voltage and discharge/charge profile of these cathode materials.

Categories	LLMO composition	Capacity ($mAhg^{-1}$)	voltage hysteresis (V *vs.* Li^+/Li)	Gas formed during cycling	CEI composition	Thermal instable temperature (°C)
Traditional LLMO	$LiCoO_2$[1–5]	274	~4.5	O_2, CO_2	LiF, Li_2CO_3, Li_2O, Li_xPF_y, $Li_xPF_yO_z$,	240
	$LiNiO_2$[5–8]	275	~4.6	O_2, CO_2	Li_2CO_3, LiOH	200
	$LiMnO_2$[9]	270	/	/	/	/
NMC-based LLMO	$Li(Ni_{0.85}Mn_{0.075}Co_{0.075})O_2$[10,11]	206	~4.2	O_2, CO_2	Li_2CO_3, LiF, Li_xPF_y, $Li_xPF_yO_z$	225
	$Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O_2$[11–14]	203	~4.2	O_2, CO_2	$Li_xPF_yO_z$, LiOH, Li_2O_3, Li_2O	232
	$Li(Ni_{0.7}Mn_{0.15}Co_{0.15})O_2$[11,12]	194	4.3	O_2, CO_2	/	242
	$Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$[11,12,15]	187	/	O_2, CO_2	Li_2O_3, Li_2O	264
	$Li(Ni_{0.5}Mn_{0.2}Co_{0.3})O_2$[11,12,16]	175	/	O_2, CO_2	Li_xPF_y, $Li_xPF_yO_z$, LiF	290
	$Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$[11,12,17,18]	163	/	O_2, CO_2	LiF, Li_2CO_3	306
Ni-rich LLMO (Exclude NMC)	$Li[Ni_{0.5}Mn_{0.5}]O_2$[19,20]	163	~4.3	/	$Li_xPF_yO_z$, Li_2CO_3, LiF	307.1
	$Li[Ni_{0.6}Mn_{0.5}]O_2$[19]	165	~4.3	/	/	298.1
	$Li[Ni_{0.7}Mn_{0.5}]O_2$[19]	171	~4.3	/	/	273.7
	$Li[Ni_{0.8}Mn_{0.5}]O_2$[19]	205	~4.3	//	/	249
	$Li[Ni_{0.9}Mn_{0.5}]O_2$[19]	212	~4.3	/	/	230.4
	$LiNi_{0.94}Co_{0.06}O_2$[21]	~230	~4.1	/	/	191
	$LiNi_{0.9}Co_{0.1}O_2$[22]	~190	~4.2	/	/	/
	$LiNi_{0.90}Co_{0.07}Mg_{0.03}O_2$[23]	228.3	~4.3	/	/	243.7
	$LiAl_{0.05}Ni_{0.95}O_2$[24]	~200	~4.5	O_2, CO_2	/	/
	$Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$[21]	~200	/	/	/	241
Li- and Mn-rich LLMO	xLi_2MnO_3 (1–x) $LiMO_2$[6,25,26]	~300	~4.4	O_2, CO_2	/	/
	$Li_{1.286}Ni_{0.071}Mn_{0.643}O_2$[27]	250	~4.25	O_2, CO_2	/	/
	$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$[28]	~300	~4.2	/	/	/
	$Li_{1.2}Co_{0.1}Mn_{0.55}Ni_{0.15}O_2$[10,29]	~200	/	/	LiF, $LiPO_yF_z$, Li_2CO_3	/

	$Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$[30]	~275	~4.5	O_2, CO_2	/	/
Other Li-rich LLMO	Li_2RuO_3[31–34]	~164	~4.1	O_2, CO_2	Li_2CO_3, LiF	/
	$Li_2Ru_{0.75}Ti_{0.25}O_3$[35]	~180	~4.0	O_2, CO_2	/	/
	$Li_2Ru_{0.75}Mn_{0.25}O_3$[35]	~177	~4.0	O_2, CO_2	/	/
	$Li_2Ru_{0.75}Fe_{0.25}O_3$[35]	~177	~3.9	O_2, CO_2	/	/
Other Mn-rich LLMO	$Li_{0.7}Mn_{0.78}Co_{0.22}O_2$[36]	~260	~4.5	O_2, CO_2	/	/
	$Li_{0.75}Mn_{0.78}Co_{0.11}Ni_{0.11}O_2$[36]	~245	~4.5	CO_2	/	/
	$Li_{0.74}Mn_{0.78}Ni_{0.22}O_2$[36]	~230	~4.3	CO_2	/	/

Table S2 The contribution of highlighted methods and the modification strategies based on the study

Characterization methods	Phenomenon detected/ degradation mechanism	Modification strategies	Examples	Improvement (Retention, cycles, Current)
DEMS/OMES Soft-XAS, RIXS	Gaseous products release at high voltage during cycles	Composition design& electrolyte additives	Al^{3+} substitution in $LiNiO_2$: $LiAl_{0.1}Ni_{0.9}O_2$[37]	$LiAl_{0.1}Ni_{0.9}O_2$:~100% , 50, 0.4 mA cm^{-2} $LiNiO_2$: 68%, 50, 0.4 mA cm^{-2}
			Addition of Lithium fluoromalonate(difluoro)borate (LiFMDFB)[38]	LiFMDFB added: 85%, 200, 0.5; Without LiFMDFB: 40%, 200, 0.5
EPR	Crystal structures changes during cycling and thermal treatment	Elemental doping	Yttrium surface gradient doping in $LiNi_{0.93}Co_{0.07}O_2$ (NC): $LiNi_{0.91}Co_{0.07}Y_{0.02}O_2$ (NCY)[39]	NC shows a structure transformation from layered to spinel that started at 200 °C, and to spinel at above 300 °C, while NCY shows a much better stability
			Nd/Al dual doped $Li_{1.2}Mn_{0.533}Ni_{0.267}O_2$[40]	Nd/Al dual doped $Li_{1.2}Mn_{0.533}Ni_{0.267}O_2$: 90.1, 200, 1C; $Li_{1.2}Mn_{0.533}Ni_{0.267}O_2$: 76.4, 200. 1C.
TEM, XAS, XPS, NMR	The formation of CEI during the cycles, enhancing the oxygen loss	Coating layer	Li_2TO_3 coating on $LiNi_{0.5}Mn_{0.5}O_2$[20]	Li_2TO_3 coated $LiNi_{0.5}Mn_{0.5}O_2$: 83, 100. 0.2; $LiNi_{0.5}Mn_{0.5}O_2$: 58, 100, 0.2.
CT, TXM, ND	Cracks formed during the cycles, under cell, electrode, particle level	Modification of synthesis condition	Synthesis of layered nanorod gradient (NRG) $Li[Ni_{0.81}Co_{0.06}Mn_{0.13}]O_2$ cathode particle[41]	NRG: 88.3%, 1000, 1C $Li[Ni_{0.82}Co_{0.14}Al_{0.04}]O$: 55.9%, 1000, 1C
TXM	Inhomogeneous lithiation across the whole electrode and even single particle	To be developed		
CDI	Nano scaled Stain stress arisen at particles under nano scales, inducing the following degradation			

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