Supporting Information for

Stabilizing the cationic/anionic redox of Li-rich layered cathodes by tuning upper cut-off voltage for high energy-density lithium-ion batteries

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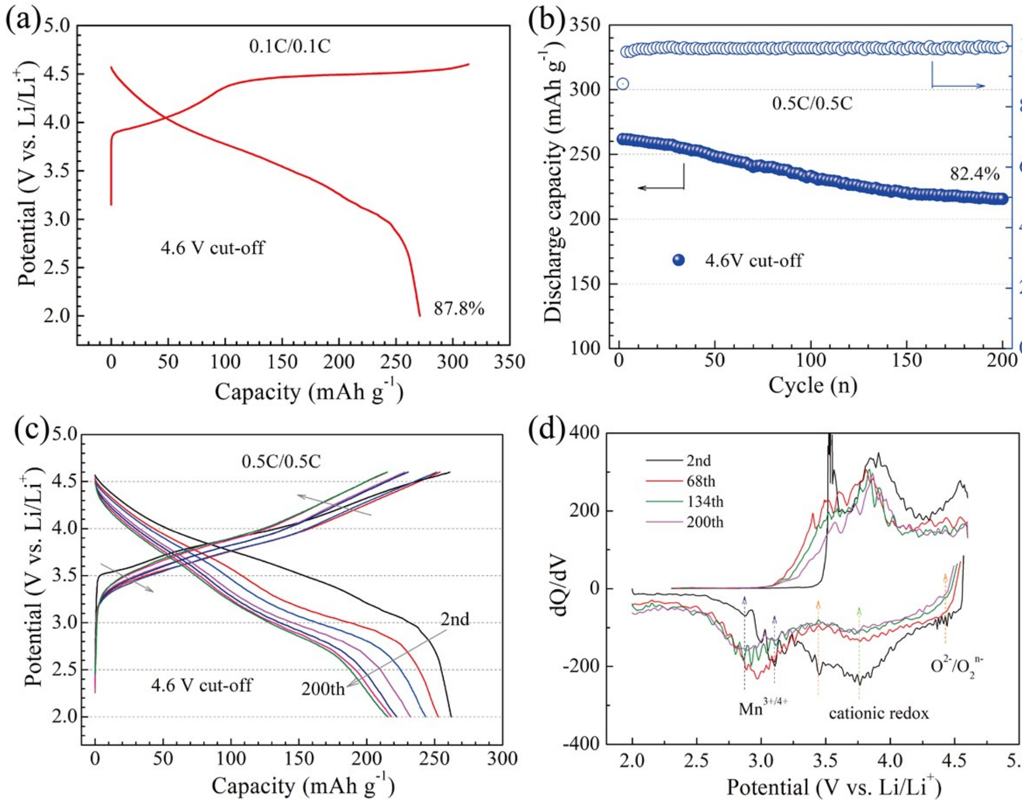


Figure S1 Electrochemical performance of LLOs cycled under the upper cut-off voltage of 4.6 V (vs. Li/Li^{+}): (a) the initial charge/discharge curve at 0.1C, (b) cyclic test at 0.5C, (c) charge/discharge profile under 0.5C at different cycles, and (d) dQ/dV curves at different cycles.

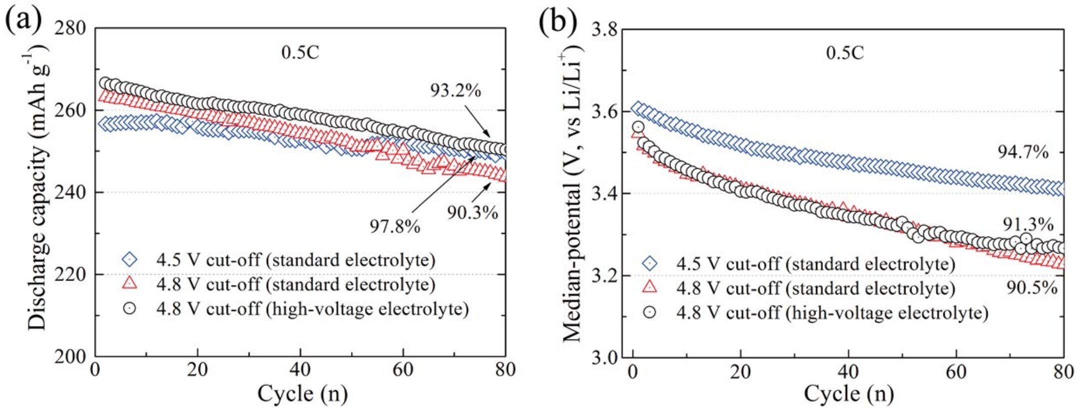


Figure S2 (a) Capacity and (b) voltage stability of LLOs employing the standard electrolyte and the high-voltage electrolyte in half cells.

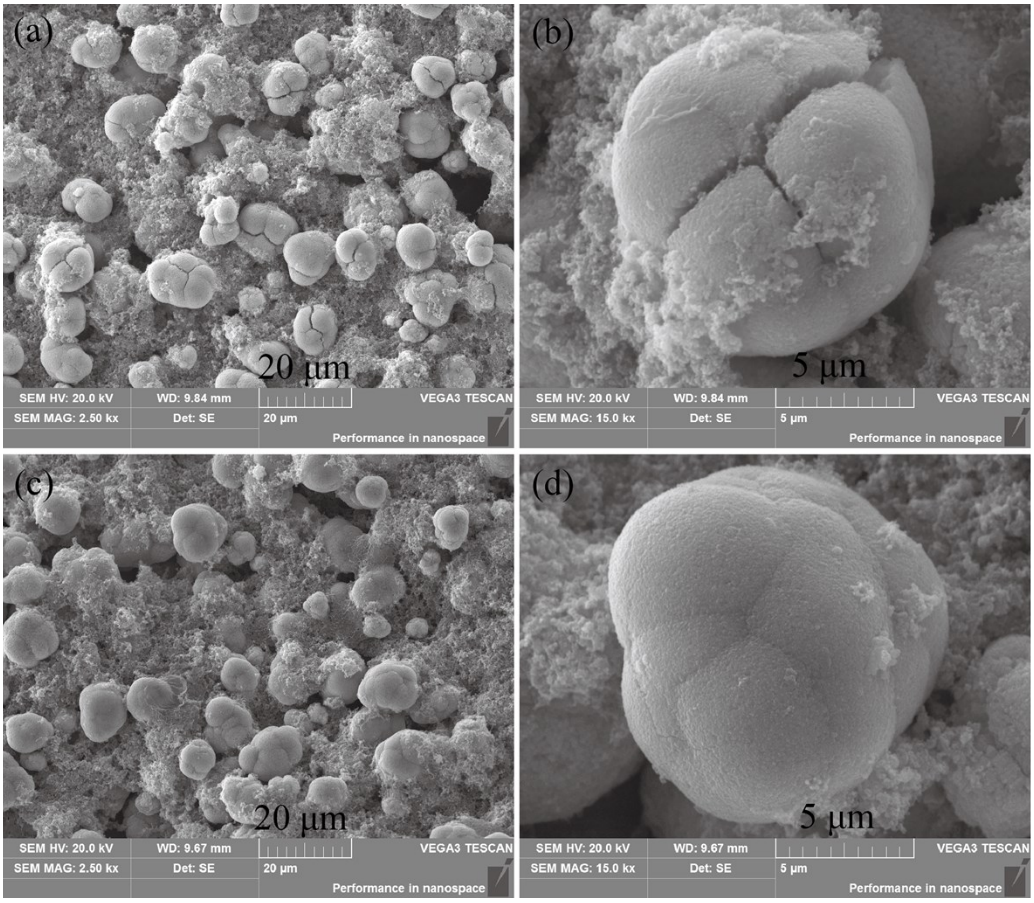


Figure S3 SEM images of the cycled LLO electrodes at fully discharged state after 200 cycles under the upper cut-off voltages of (a,b) 4.8 V and (c,d) 4.5 V.

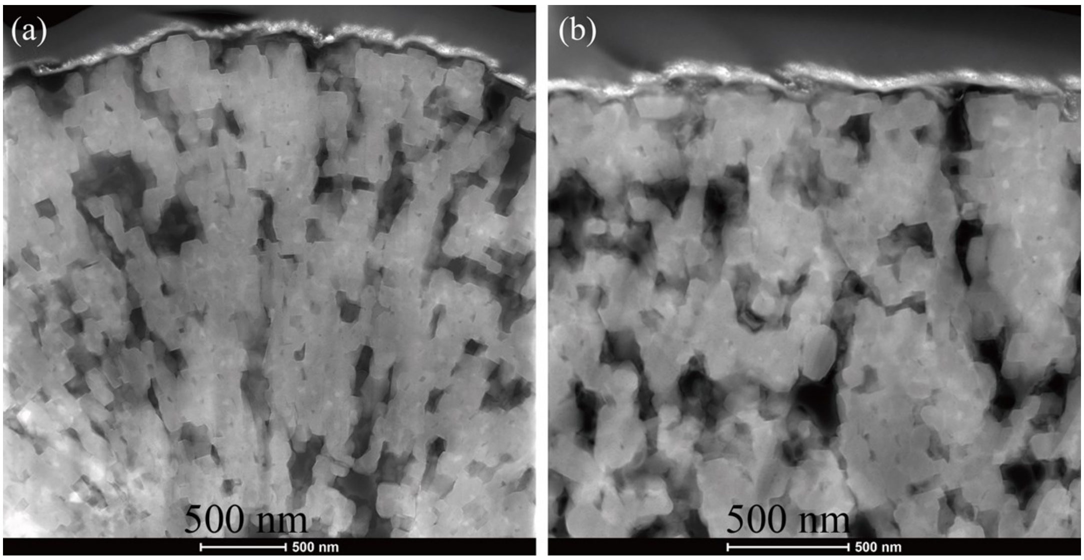


Figure S4 Cross-section of LLOs after 200 cycles under the upper cut-off voltages of (a) 4.8 V and (b) 4.5 V.

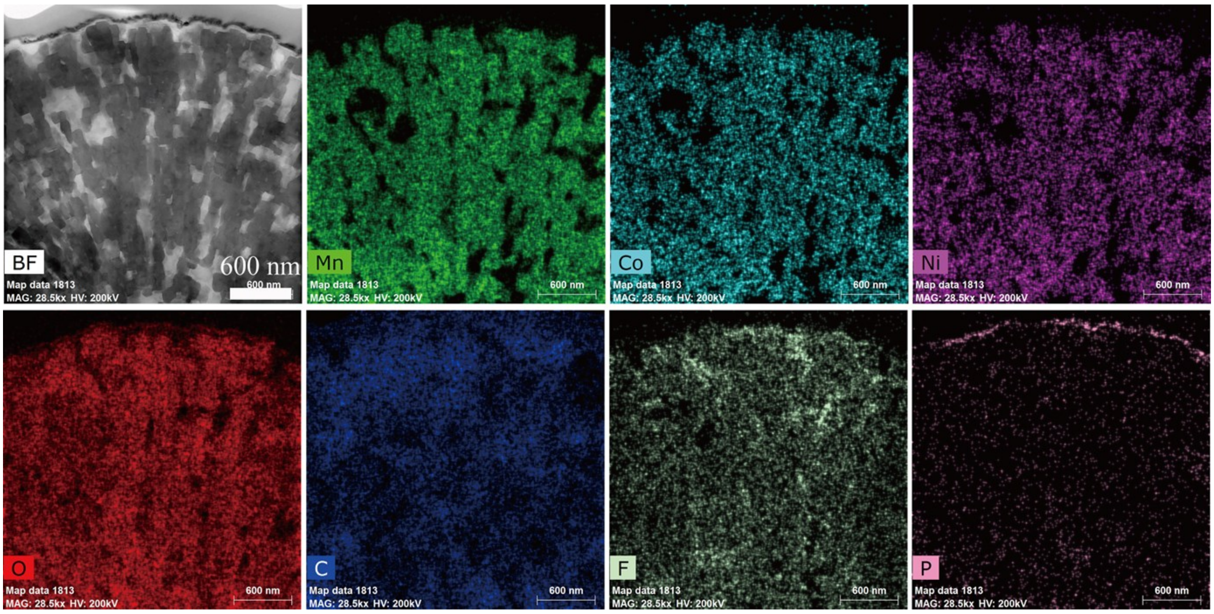


Figure S5 EDS elemental mapping of the cross-section of LLOs after 200 cycles under the upper cut-off voltage of 4.8 V.

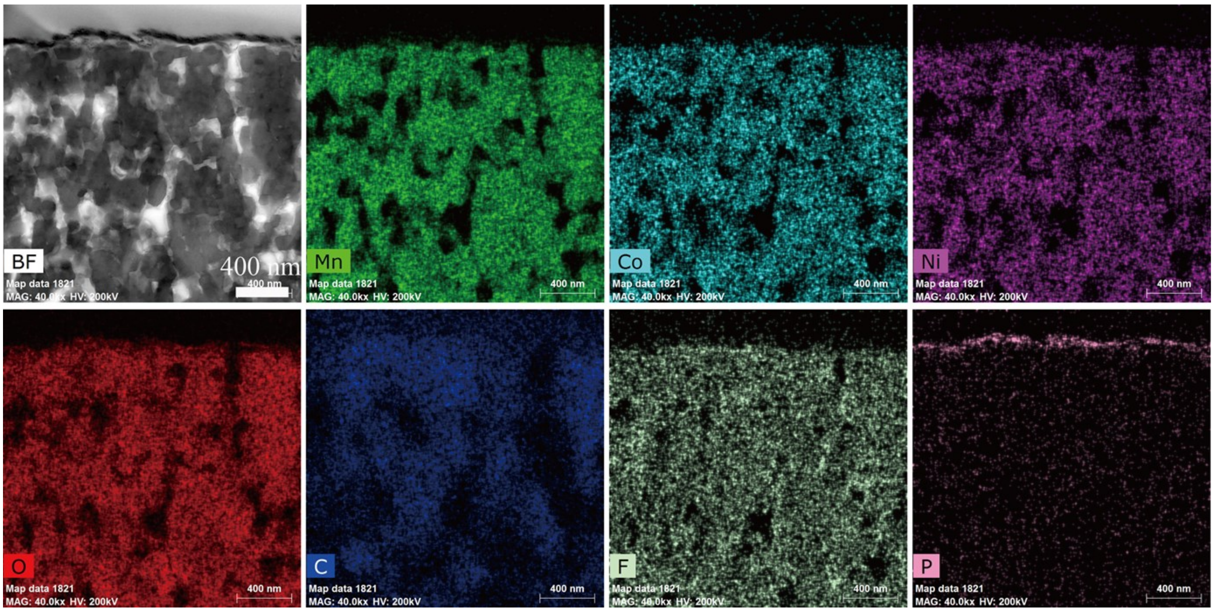


Figure S6 EDS elemental mapping of the cross-section of LLOs after 200 cycles under the upper cut-off voltage of 4.5 V.

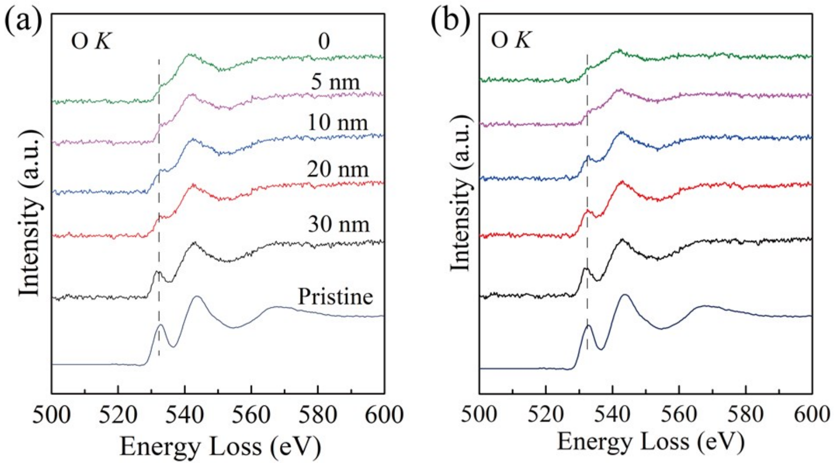


Figure S7 Enlarged O-K edges, integrated from surface to bulk of cycled particle under the upper cut-off voltages of (a) 4.8 V and (b) 4.5 V.

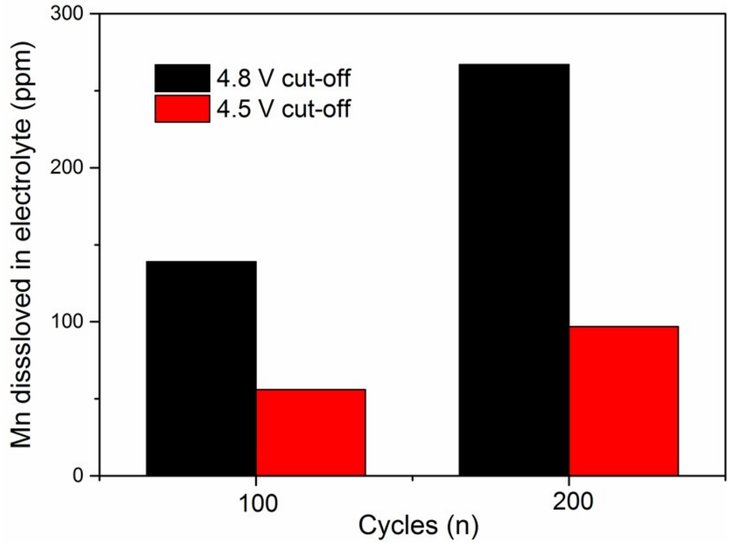


Figure S8 The Mn concentration dissolved in electrolyte under the upper cut-off voltages of 4.8 V and 4.5 V after 100 and 200 cycles.

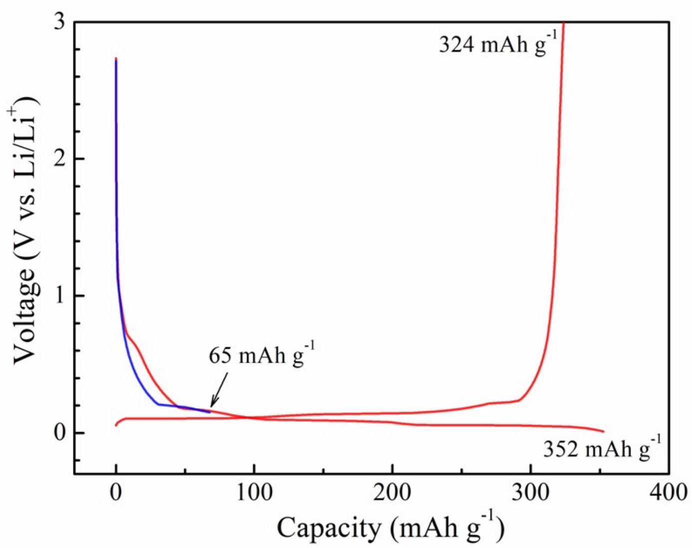


Figure S9 The pre-lithiation curves of the MCMB anode between 0.01 V and 3.0 V.

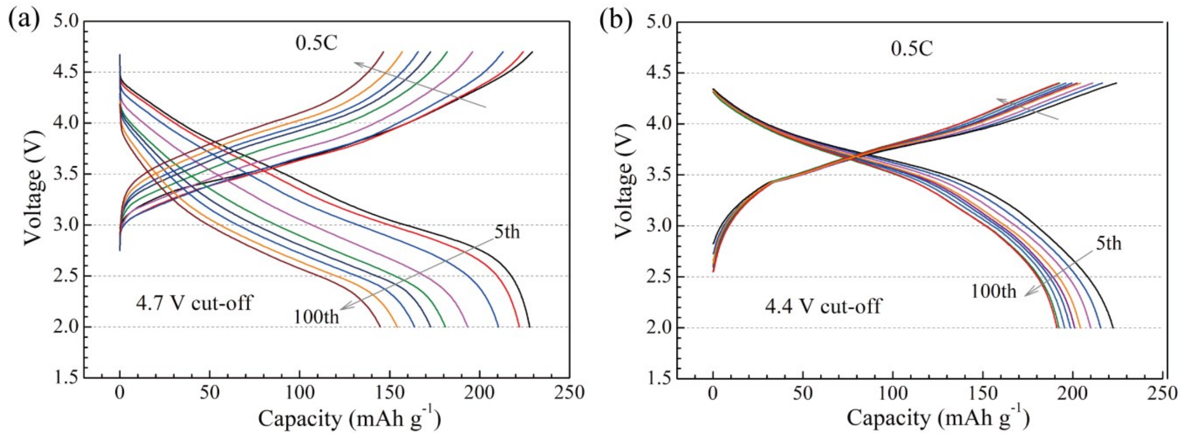
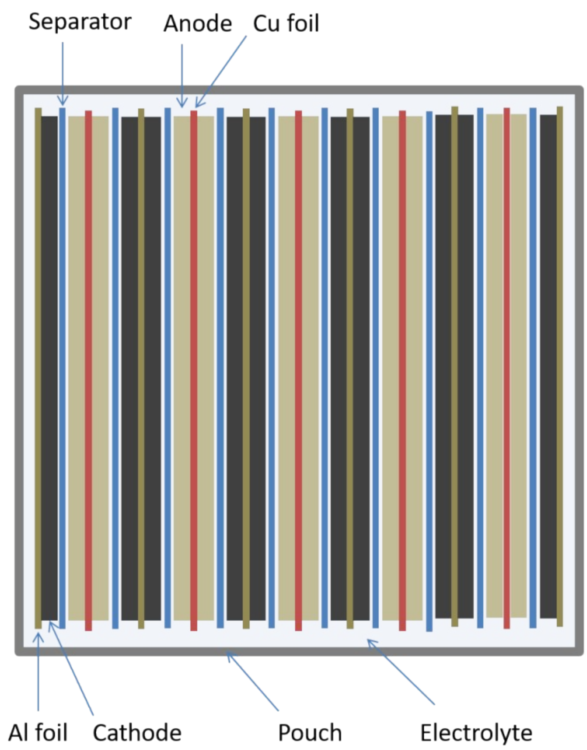


Figure S10 Continuous charge/discharge curves of the MCMB|LLOs full cells cycled under the cut-off voltages of (a) 4.7 V and (b) 4.4 V.



Calculation Component	
Stack	5
Electrode Area (3cm x 5cm)	15 cm^2
Cathode	20 mg cm^{-2}
Anode	17 mg cm^{-2}
Al Foil (12 μm)	6 ea
Cu Foil (8 μm)	5 ea
Electrolyte	0.9 g
Separator	0.183 g
Pouch	0.86 g

Component	Cathode	Al Foil	Anode	Cu Foil	Separator	Electrolyte	Pouch	Total
Weight (g)	2.85	0.29	2.55	0.58	0.18	0.90	0.86	8.21
Mass fraction (%)	34.71	3.53	31.06	7.06	2.19	10.96	10.49	100

Figure S11 The main components of the pouch full cells using LLOs as cathode and MCMB as anode. The areal density of 20 mg cm^{-2} is commonly used for the active cathode materials in full cells. [1-3]

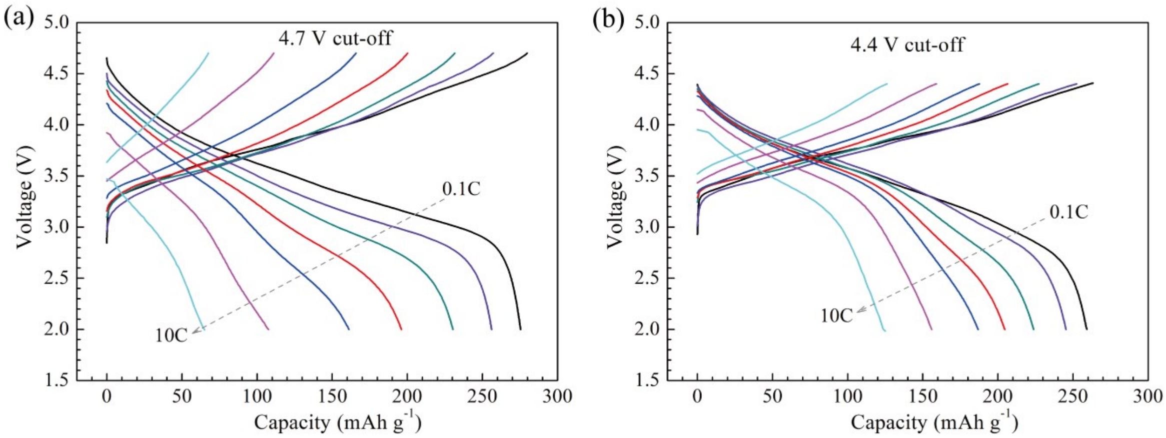


Figure S12 Charge/discharge curves of the MCMB|LLOs full cells at varied rates.

Table S1 A comparison of electrochemical performance of LLO cathodes between this work and recent related reports.

Method	Capacity retention % (cycles)	Ref.
stepped pre-cycling treatment from 4.5, 4.6 to 4.7 V	92.5 (55)	4
pre-cycling treatment from4.5 to 4.8V	92 (50)	5
4.8 V on two cycles and then 4.6 V on the subsequent cycles	84(100)	6
4.8 V on two cycles and then 4.6 V on the subsequent cycles	60 (290)	7
constant 4.6 V	70 (290)	7
pre-cycling treatment from 4.45, 4.55, 4.6 to 4.7 V	84(100)	8
4.8 V on first cycle and then 4.6 V on the subsequent cycles	83 (200)	9
4.8 V on first cycle and then 4.4 V on the subsequent cycles	86 (200)	9
4.6 V on first cycle and then 4.5 V on the subsequent cycles	95.2 (200)	This work

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