Supporting Information

Highly reversible Li_2RuO_3 cathodes in sulfide-based all solid-state lithium batteries

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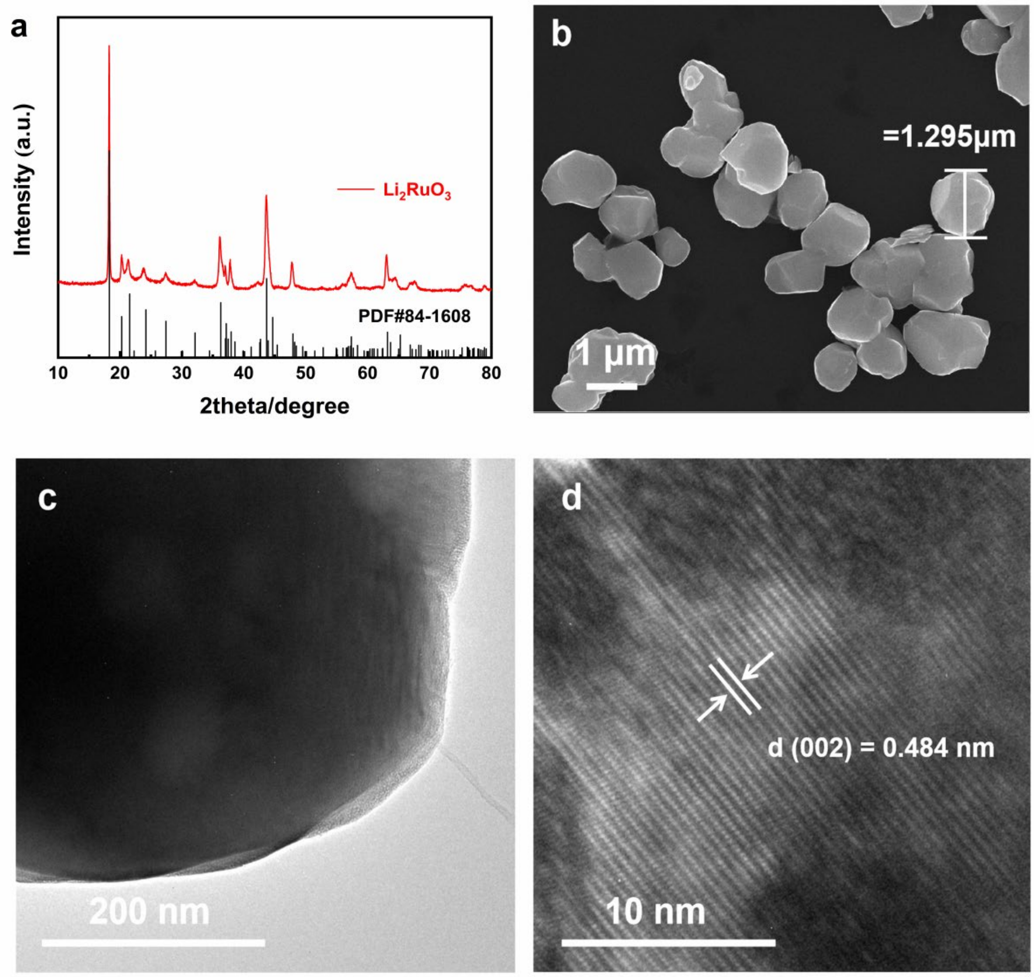

Fig. S1 The structure and morphology characterizations of the LRO. (a) XRD pattern; (b) Typical SEM image of LRO powders; (c, d) HRTEM images of LRO.

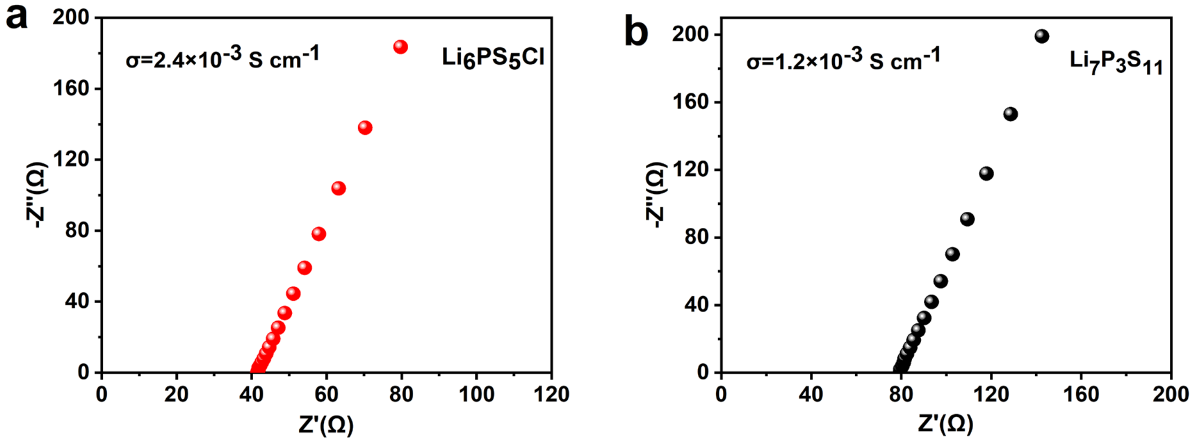

Fig. S2 EIS plots of LPSCl (a) and LPS (b) measured at room temperature.

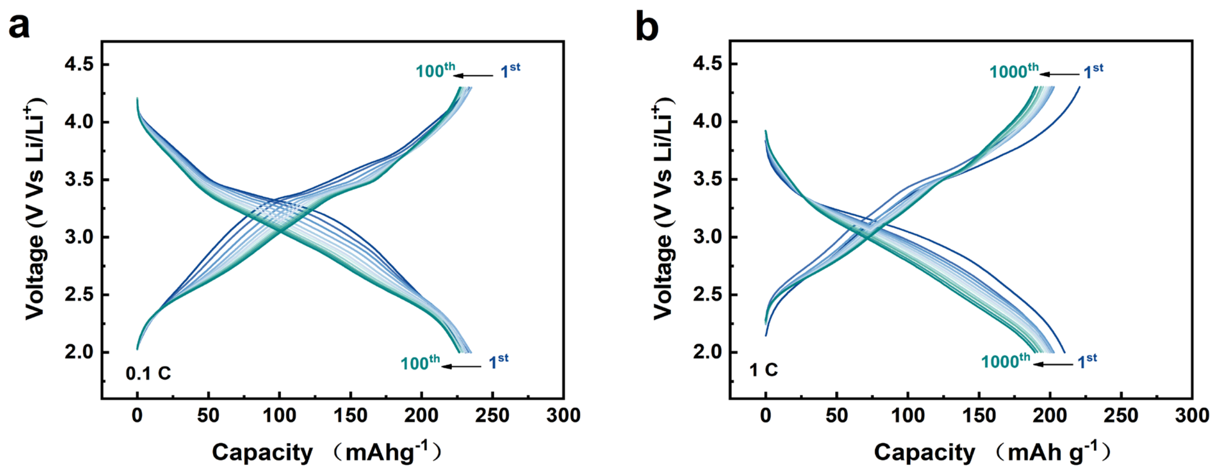

Fig. S3 The voltage profiles of LRO in ASSLBs cycled between 2.0 and 4.3 V with current 0.1C (a) and 1C (b).

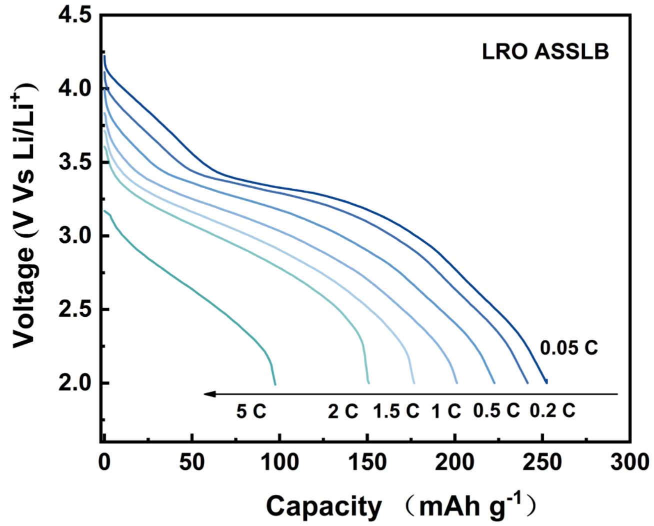

Fig. S4 Discharge voltage curves of LRO in ASSLBs at different current densities.

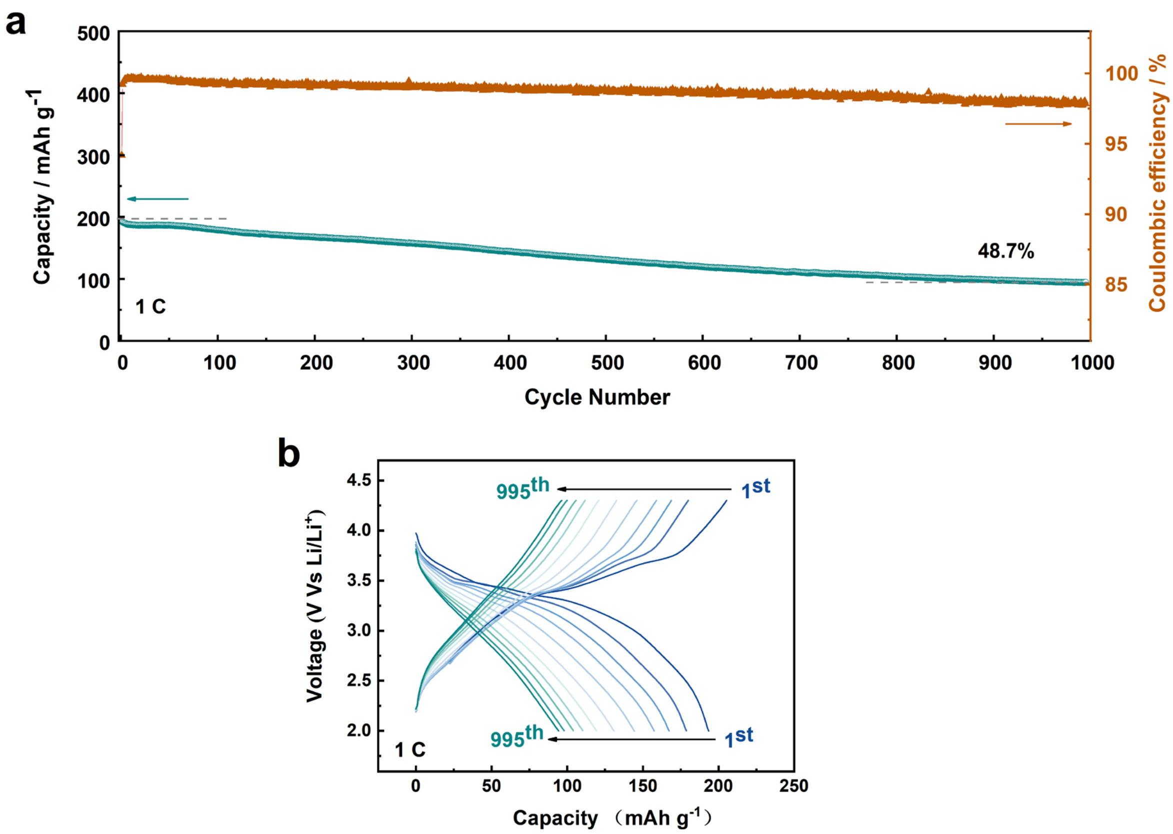

Fig. S5 (a) Cycling stability curves of LRO cathodes in LIBs at 1C with 1000 cycles between 2.0-4.3V. Before official cycling, the cells first precycled at low current density of 0.05C at 30°C for 5 cycles. (b) The corresponding voltage profiles of LRO in LIBs cycled between 2.0 and 4.3 V at 1C.

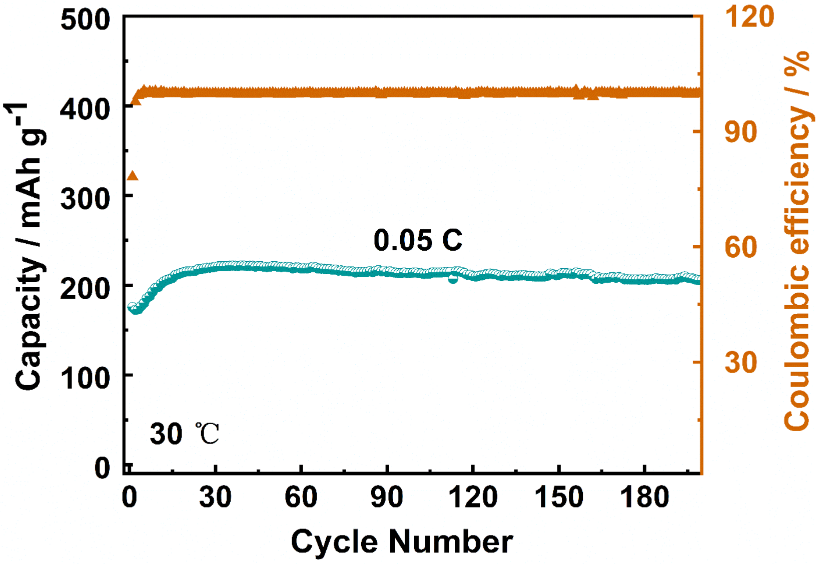

Fig. S6 Cycling performance of LRO in ASSLBs at 30 °C.

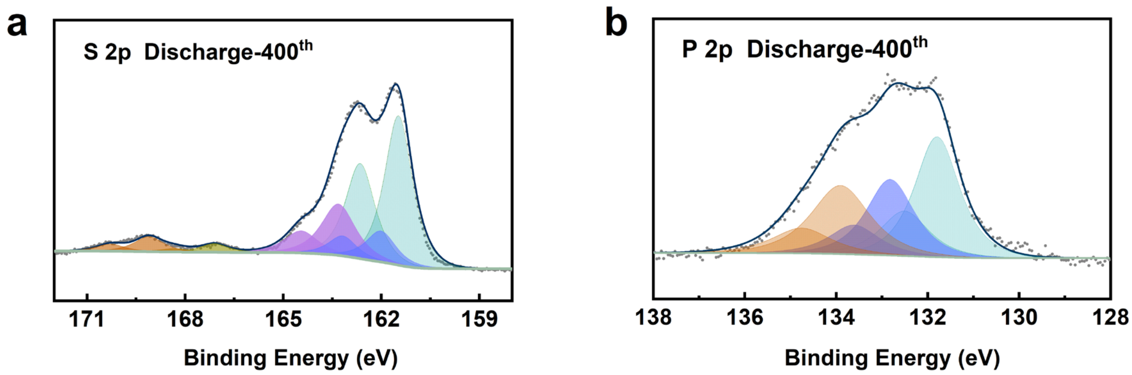

Fig. S7 S 2p (a) and P 2p (b) XPS spectra of LRO cathodes after 400 cycles.

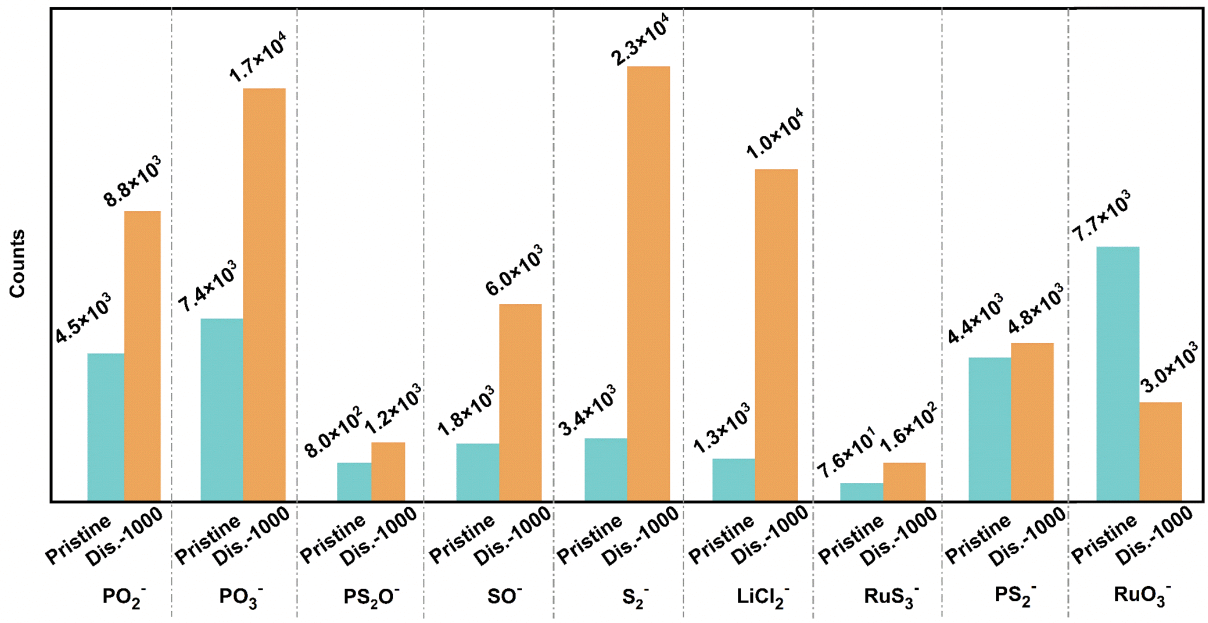

Fig. S8 Comparison of Tof-SIMs results of LRO electrodes at pristine and after 1000 cycles. “Dis.-1000” represents 1000th discharged state.

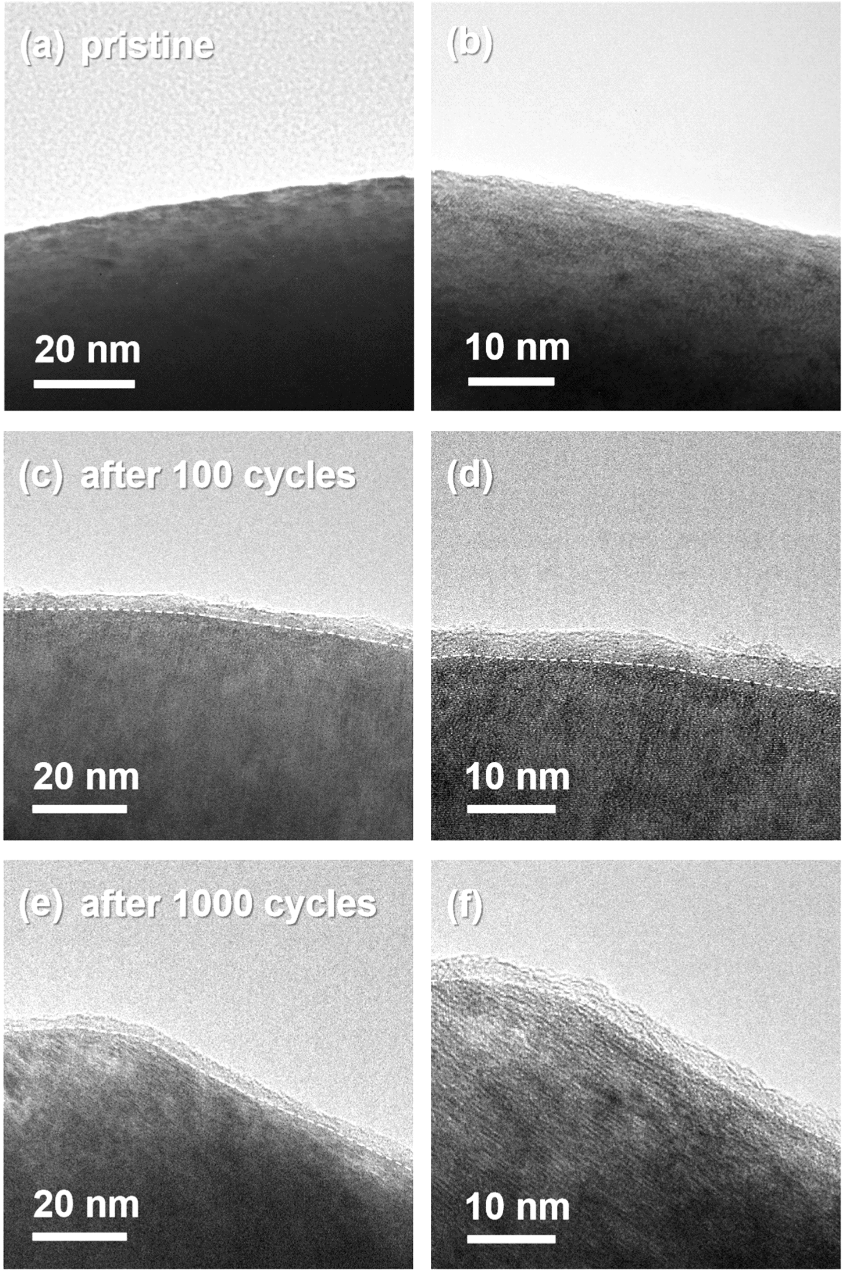

Fig.S9 TEM images of LRO particle and electrodes after cycles in ASSLBs. (a, b) at pristine, (c, d) after 100 cycles, (e, f) after 1000 cycles.

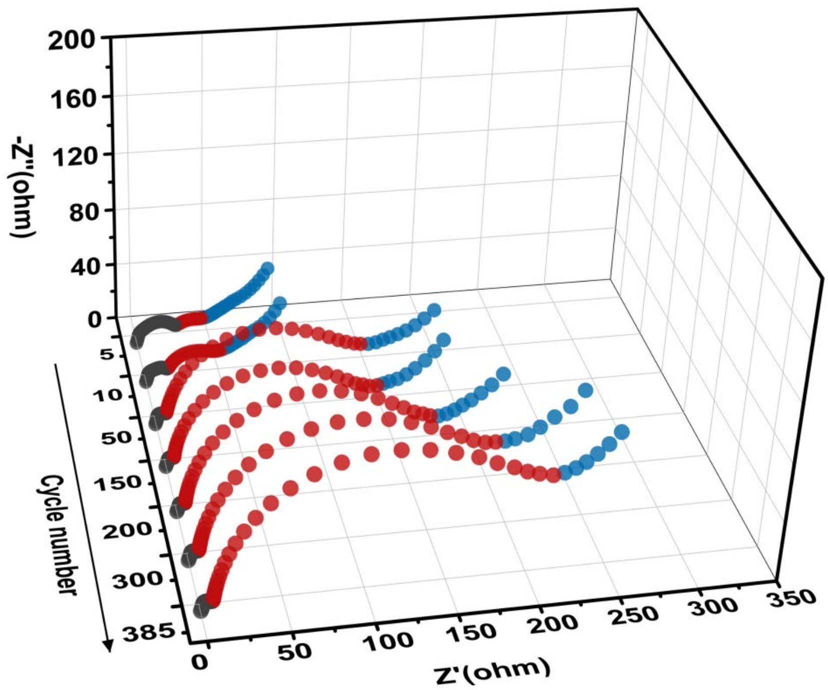

Fig. S10 Nyquist plot of the impedance spectrum during the LRO LIBs cycling.

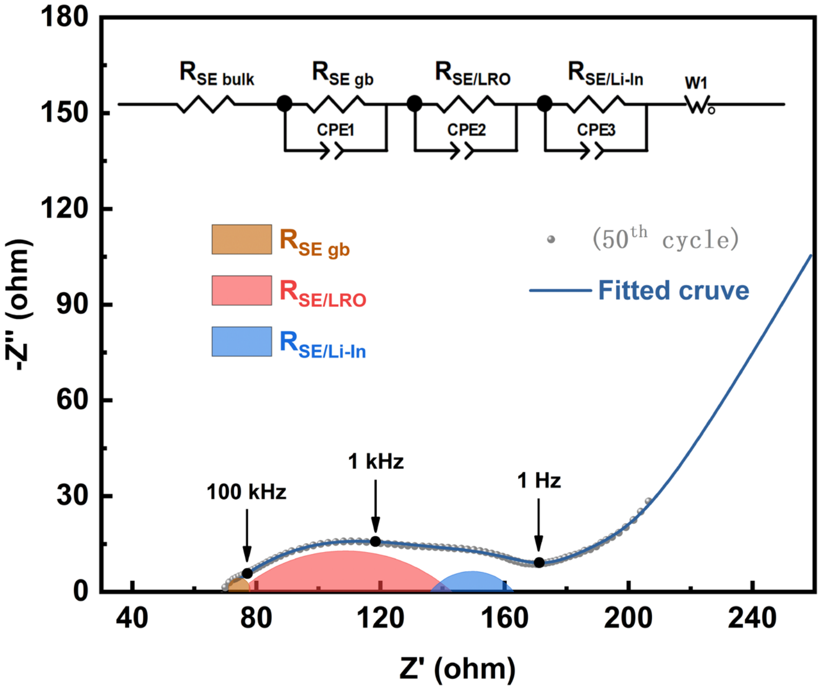

Fig. S11 A typical impedance spectra model (Nyquist plot) of the ASSLBs during cycling.

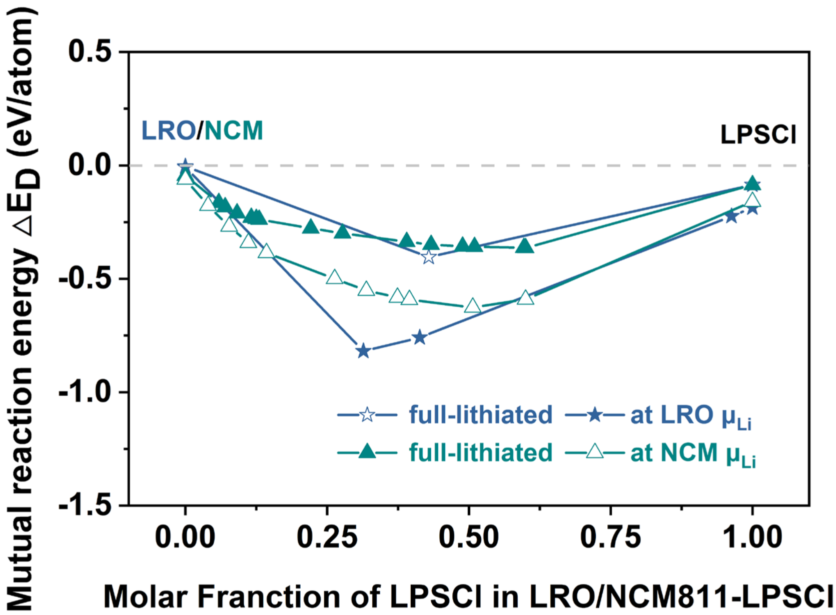

Fig. S12 The mutual reaction energy of the interface between LPSCl and LRO/NCM.

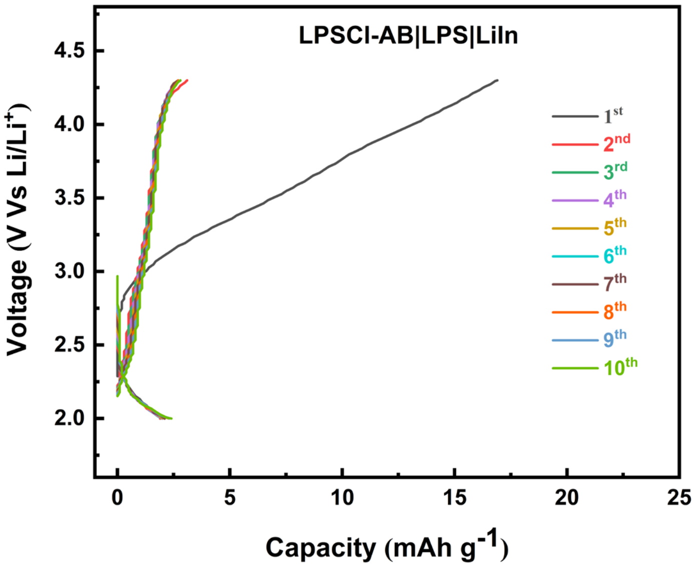

Fig. S13 Voltage profiles of the LPSCl-AB composite electrodes under the same test conditions as LRO ASSLBs.

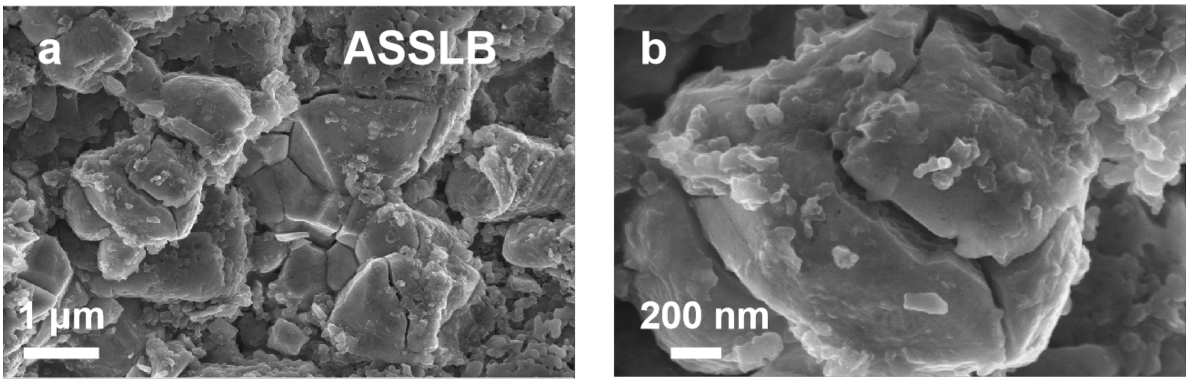

Fig. S14 The SEM images of LRO electrodes after 300 cycles in ASSLB.

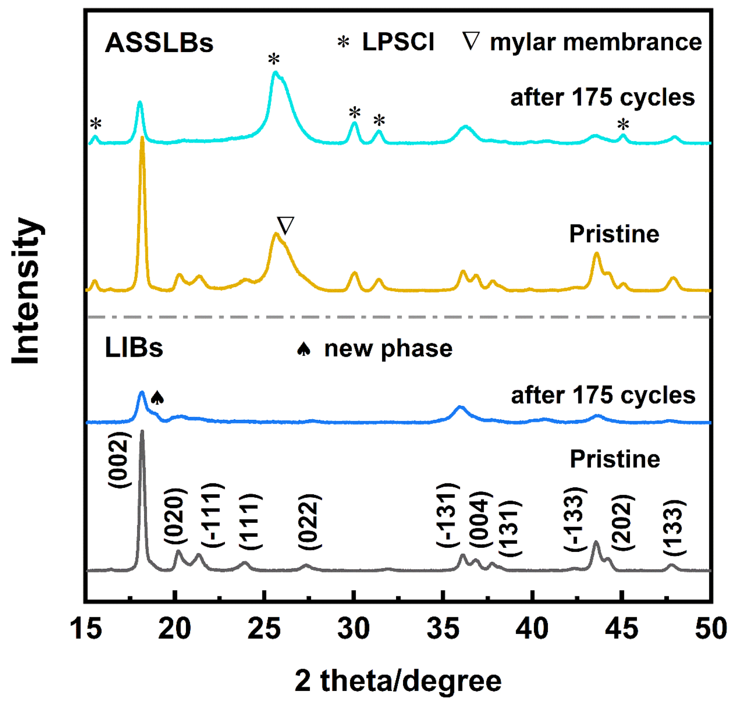

Fig. S15 Ex-situ XRD patterns of LRO in ASSLBs and LIBs.

Table S1. A detailed comparison of the electrochemical performance of the LRO with currently commercialized layered oxide cathode at the state-of-the-art ASSLBs reported in the literatures, including battery designs and operating conditions.

Ref.	Coating/cathode	Electrolyte	Voltage range (V vs Li/Li$^+$)	Current density (mA g^{-1})	Initial capacity (mAh g^{-1})	cycle number	Retention rate
[1]	$Li_2WO_4/LiCoO_2$	Li_6PS_5Cl	2.8-4.2	16	142	100	93%
[2]	$LiZr_2(PO_4)_3/LiCoO_2$	Li_6PS_5Cl	2.6-4.5	28	143.3	100	95.5%
[3]	$Li_2CoTi_3O_8/LiCoO_2$	$Li_{10}GeP_2S_{12}$	2.1-4.5	30	180	100	73.3%
[4]	bare/ SC-NCA811	Li_6PS_5Cl	3.0-4.3	20	191	200	63.1%
[4]	bare/ PC-NCA811	Li_6PS_5Cl	3.0-4.3	20	164	200	20.6%
[5]	bare/ rod-shaped-NCM75	Li_6PS_5Cl	3.0-4.3	100	194	200	79.1%
[6]	bare/ SC-NCM811	$Li_{10}SnP_2S_{12}$	2.85-4.35	18	187	100	64.5%
[7]	bare/ SC-NCM83	$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$	2.5–4.4	100	175.5	500	85.1%
[8]	$LiNbO_3$/Core-shell NCA	$Li_{10}GeP_2S_{12}$	2.72-4.32	60	184.1	400	89.4%
[9]	H-Li_3PO_4/NCM 811	$Li_{10}GeP_2S_{12}$	2.7-4.5	0.2 C	163.2	300	58.9%
[10]	Al/Core-shell NCM90	$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$	2.7-4.3	200	156.8	500	96.3%
[11]	$LiNbO_3$-$LiCoO_2$/NCM 811	$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$	2.7-4.38	60	182.4	585	80%
[12]	Li_2SiO_x/S-NMC	Li_6PS_5Cl	2.4-4.2	67	145	1000	62.9%
[13]	$LiNbO_3$/ NCM	Li_6PS_5Cl	2.8-4.2	32.3	168	2000	93%
[14]	$LiNbO_3$/NCA	$Li_{2.96}P_{0.98}S_{3.92}O_{0.06}$	2.8-4.2	13.3	165.7	50	93.45%
This work	bare/Li_2RuO_3	Li_6PS_5Cl	2.0-4.3 V	20	230	100	98%
This work	bare/Li_2RuO_3	Li_6PS_5Cl	2.0-4.3 V	200	203	1000	90%

Table S2. Phase equilibria and decomposition energies of the LPSCl-LRO, LPSCl-LCO and LPSCl-NCM interfaces. x is the Molar Fraction of LPSCl in [x·LPSCl + (1-x) ·LRO/LCO/NCM]

Celectrode	State	x	Phase equilibria	△H_D (eV/atom)
LRO	Chemical reaction			
	Full-lithiated	0.429	Li_3PO_4 Li_2S RuS_2 LiCl	-0.404
	Electrochemical reaction			
	At LRO μ_{Li}	0.314	Li_2SO_4 Li_3PO_4 RuS_2 LiCl	-0.819
		0.413	S_8O Li_3PO_4 RuS_2 LiCl	-0.759
		0.963	S_8O Li_3PS_4 RuS_2 LiCl	-0.224
LCO	Chemical reaction			
	Full-lithiated	0.024	$Li_{10}Co_4O_9$ Li_3PO_4 Li_2SO_4 CoO LiCl	-0.125
		0.15	Li_6CoO_4 Li_3PO_4 Co_9S_8 Li_2SO_4 LiCl	-0.298
		0.172	Li_2O Li_3PO_4 Co_9S_8 Li_2SO_4 LiCl	-0.317
		0.258	Li_3PO_4 Li_2S Co_9S_8 Li_2SO_4 LiCl	-0.363
		0.314	Li_3PO_4 Li_2S Li_2SO_4 Co_3S_4 LiCl	-0.361
		0.333	Li_3PO_4 Li_2S Co_2S_3 LiCl	-0.356
	Electrochemical reaction			
	At LCO μLi	0.04	CoO Li_2SO_4 Li_3PO_4 LiCl	-0.271
		0.188	Co_9S_8 Li_2SO_4 Li_3PO_4 LiCl	-0.585
		0.234	Co_3S_4 Li_2SO_4 Li_3PO_4 LiCl	-0.599
		0.25	Co_2S_3 Li_2SO_4 Li_3PO_4 LiCl	-0.597
		0.333	Co_2S_3 Li_2S Li_3PO_4 LiCl	-0.576
NCM	Chemical reaction			
	Full-lithiated	0.277	$LiMnO_2$ Co_9S_8 Li_2SO_4 Ni_3S_2 Li_2O LiCl Li_3PO_4	-0.299
		0.39	$LiMnO_2$ Co_9S_8 Li_2SO_4 Ni_3S_2 Li_2S LiCl Li_3PO_4	-0.337
		0.433	Co_9S_8 Li_2SO_4 MnO Ni_3S_2 Li_2S LiCl Li_3PO_4	-0.349
		0.489	Li_2SO_4 Co_2NiS_4 MnO Ni_3S_2 Li_2S LiCl Li_3PO_4	-0.357

		0.51	Li_2SO_4 $Co(NiS_2)_2$ Co_2NiS_4 MnO Li_2S LiCl Li_3PO_4	-0.359
		0.597	$Li(MnS_2)_2$ Li_2SO_4 $Co(NiS_2)_2$ Co_2NiS_4 Li_2S LiCl Li_3PO_4	-0.363
		0.6	$Li(MnS_2)_2$ MnS_2 $Co(NiS_2)_2$ Co_2NiS_4 Li_2S LiCl Li_3PO_4	-0.364
	Electrochemical reaction			
	At NCM μLi	0.319	MnO Ni_3S_2 Co_9S_8 Li_2SO_4 Li_3PO_4 LiCl	-0.552
		0.374	MnO Co_2NiS_4 Ni_3S_2 Li_2SO_4 Li_3PO_4 LiCl	-0.582
		0.395	MnO Co_2NiS_4 $Co(NiS_2)_2$ Li_2SO_4 Li_3PO_4 LiCl	-0.592
		0.507	Co_2NiS_4 $Co(NiS_2)_2$ Li_2SO_4 MnS_2 Li_3PO_4 LiCl	-0.626
		0.6	Co_2NiS_4 $Co(NiS_2)_2$ MnS_2 Li_3PO_4 LiCl Li_2S	-0.591

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