Supplementary Information

Refining Grain and Optimizing Grain Boundary by Al_2Yb to Enable the Dendrite-free Lithium Anode

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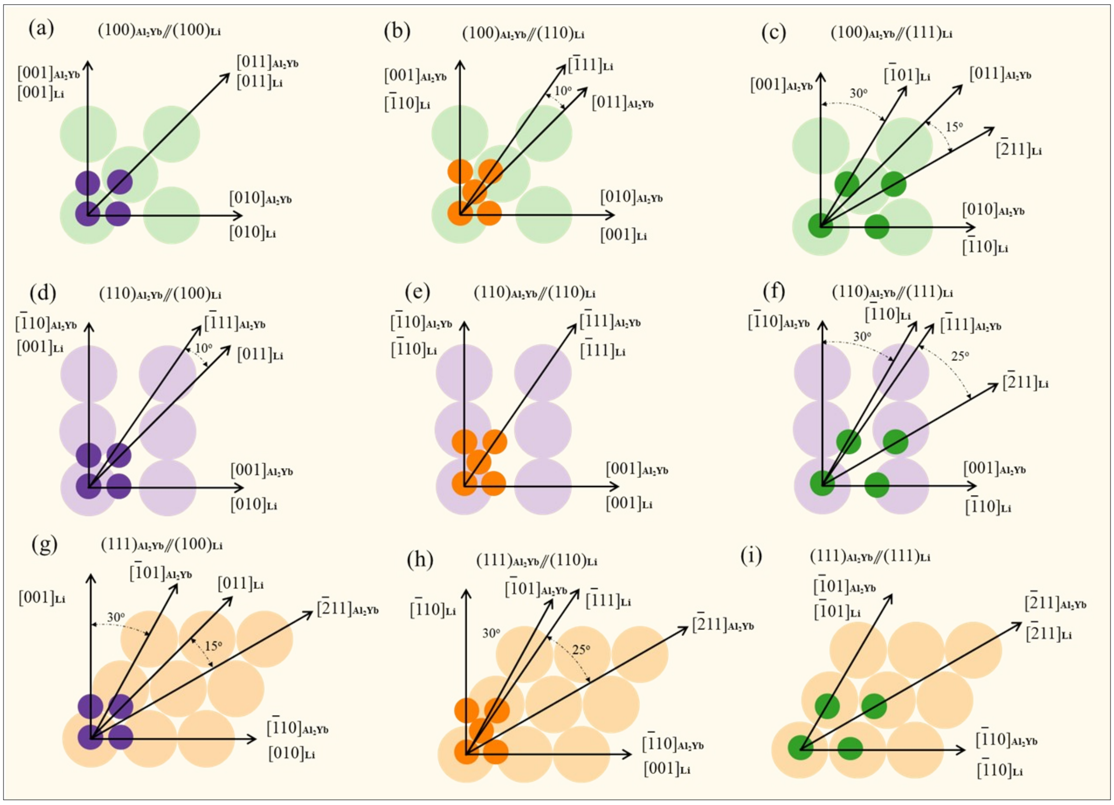
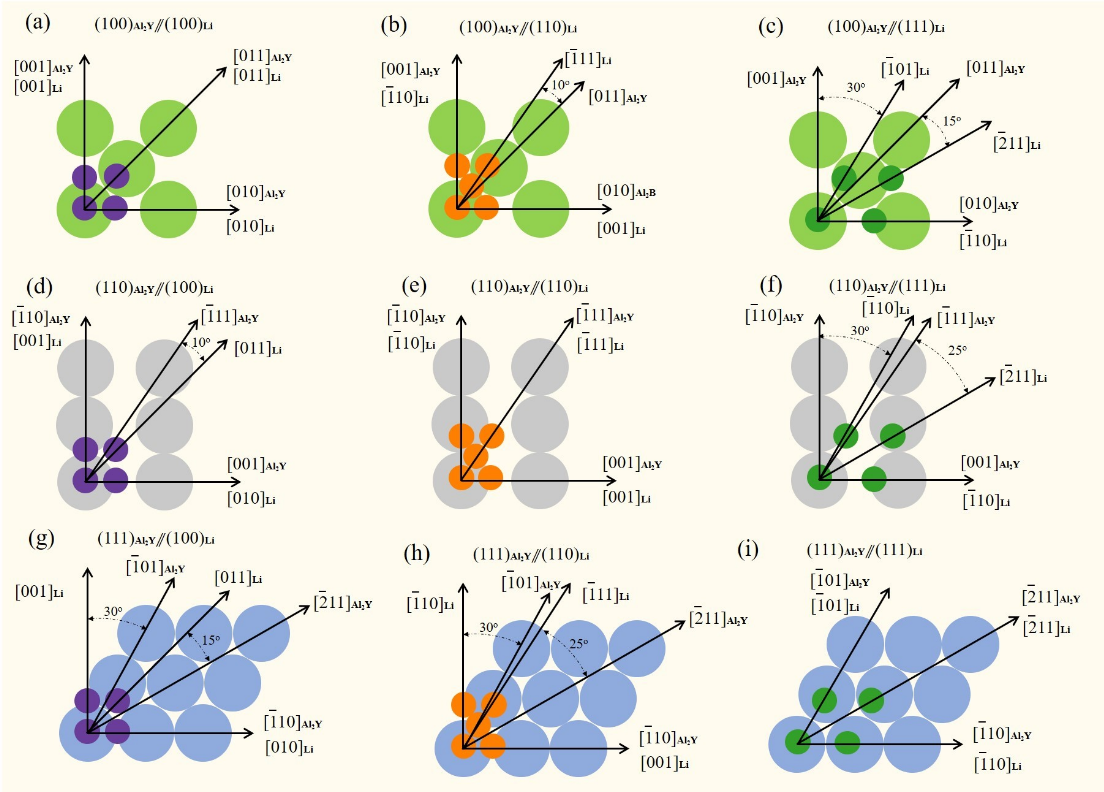
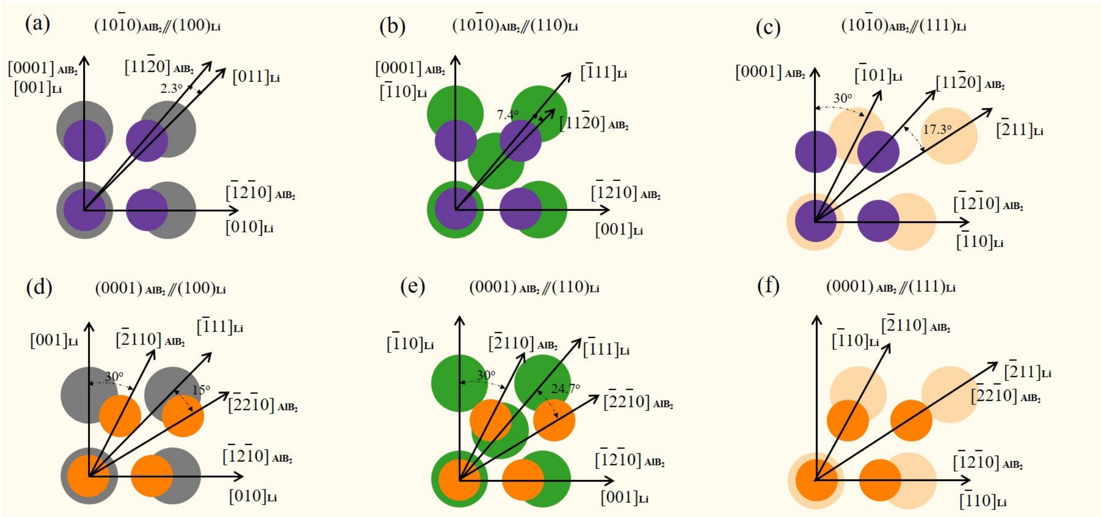


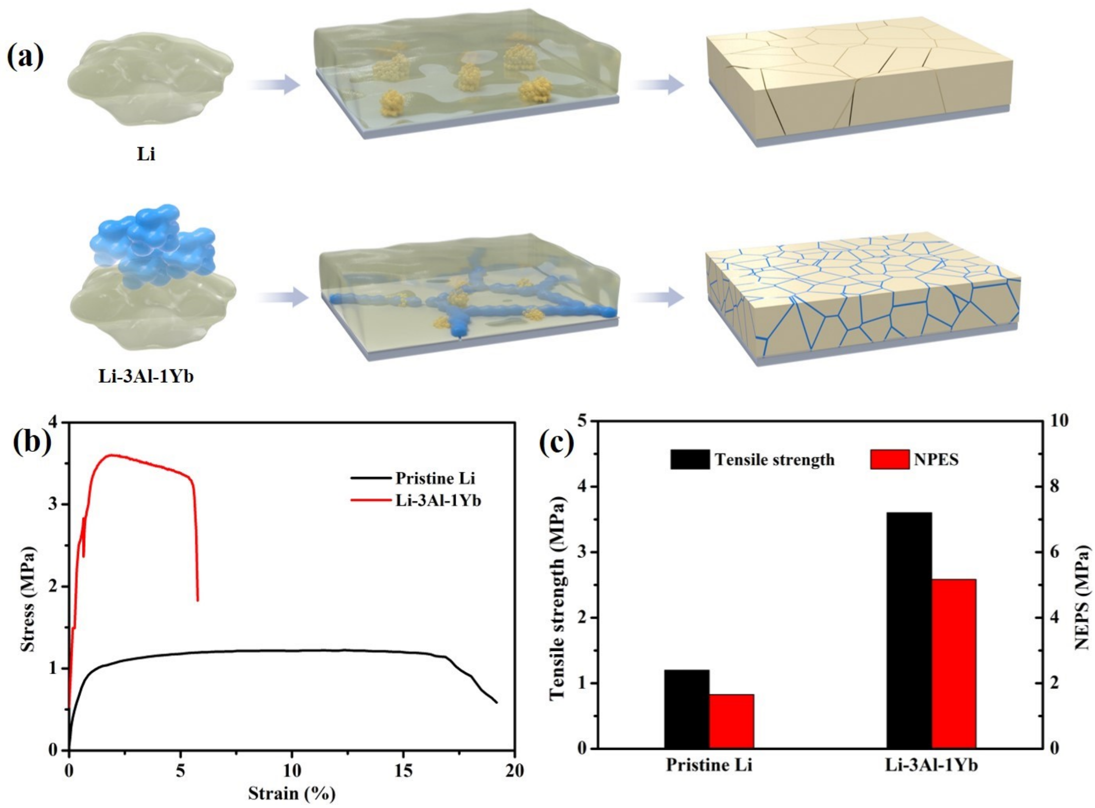
Supplementary Figure 1 The crystallographic orientation relationships between Al_2Yb and *β*-Li (large circle: Al_2Yb atom; small circle: Li atom)



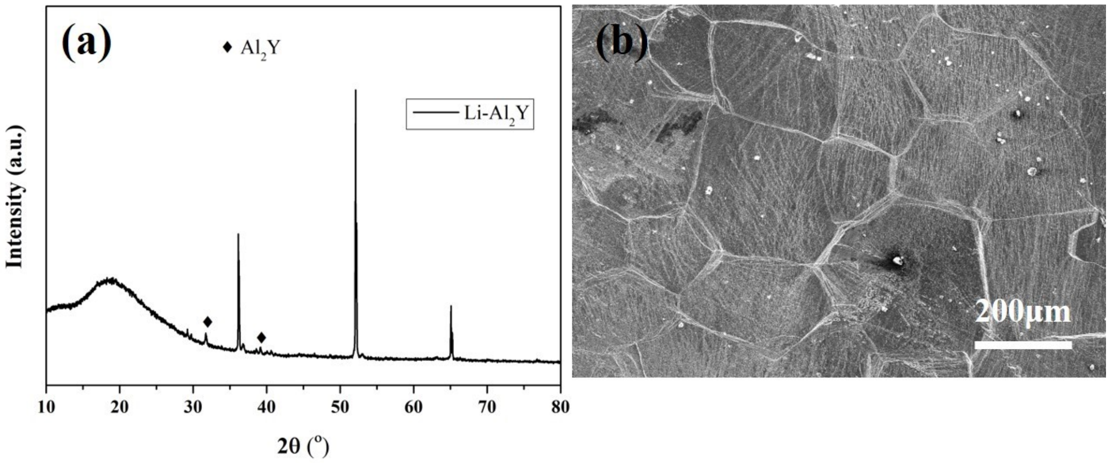
Supplementary Figure 2 The crystallographic orientation relationships between Al_2Y and *β*-Li (large circle: Al_2Y atom; small circle: Li atom)



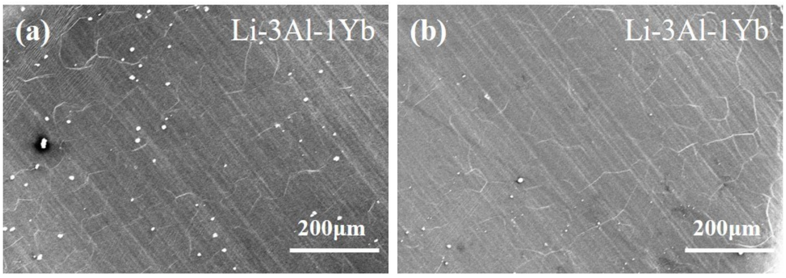
Supplementary Figure 3 The crystallographic orientation relationships between AlB_2 and β-Li (large circle: Li atom; small circle: Al_2B atom)



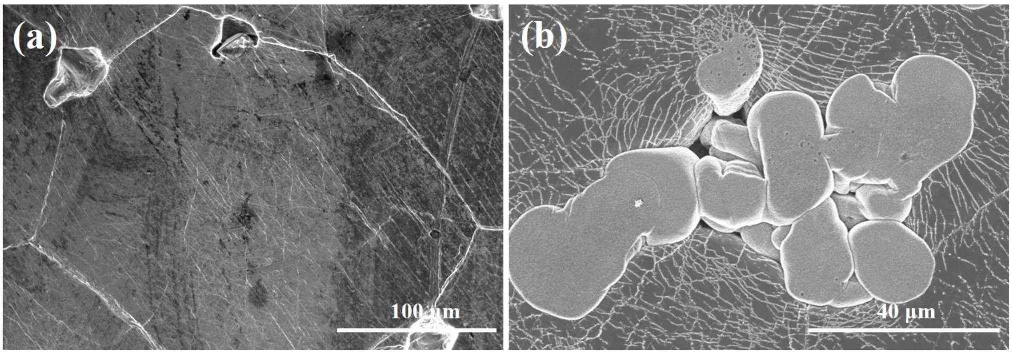
Supplementary Figure 4 (a) The formation process of composite alloy anode materials; (b) The stress strain curve; (c) The tensile strength and the Non-Proportional Extensional Strength.



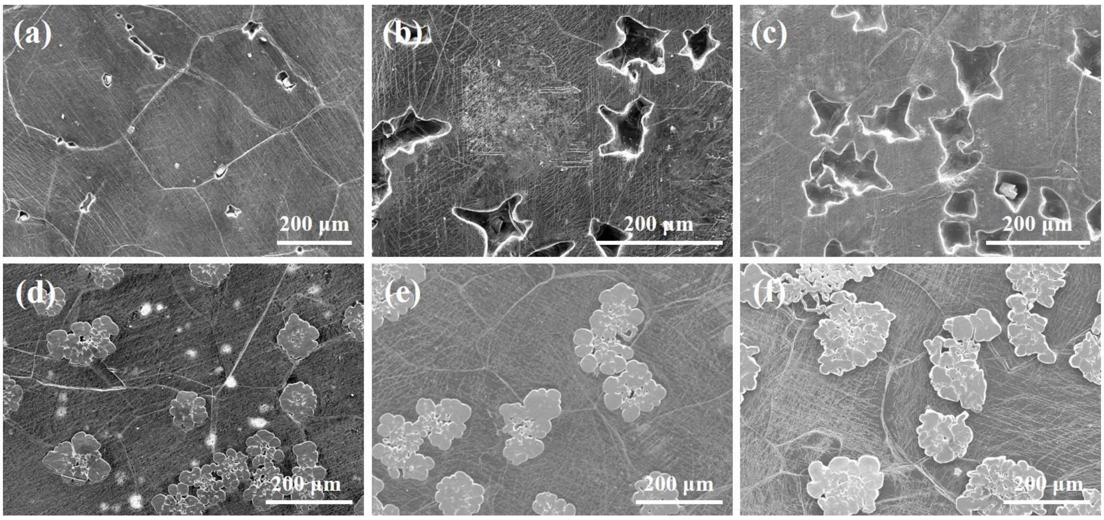
Supplementary Figure 5 (a) The XRD patterns of the Li-Al_2Y sample; (b) The SEM image for the surface of Li-Al_2Y alloy material after etching.



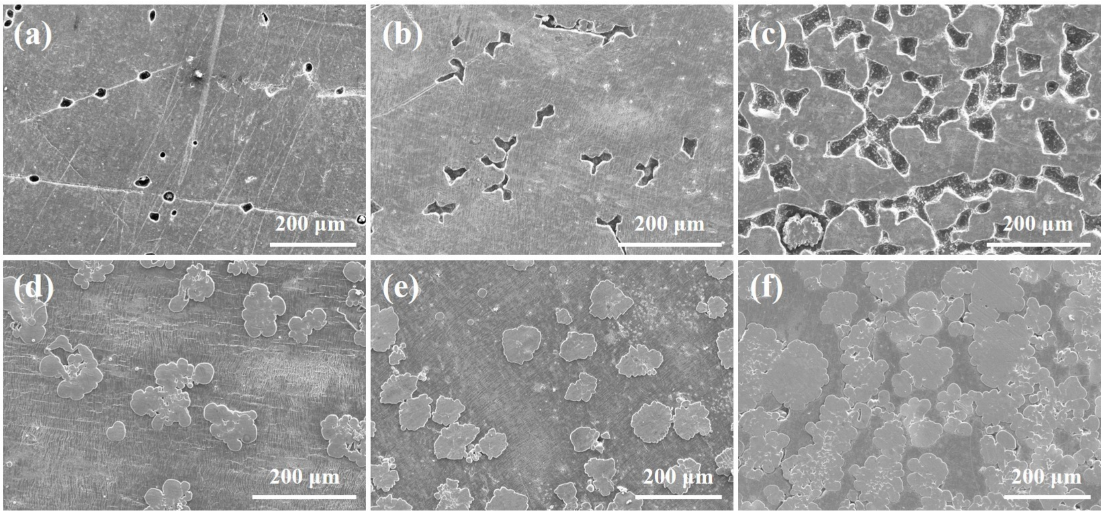
Supplementary Figure 6 (a) and (b) the surface of Li-3Al-1Yb alloy electrode materials from various areas.



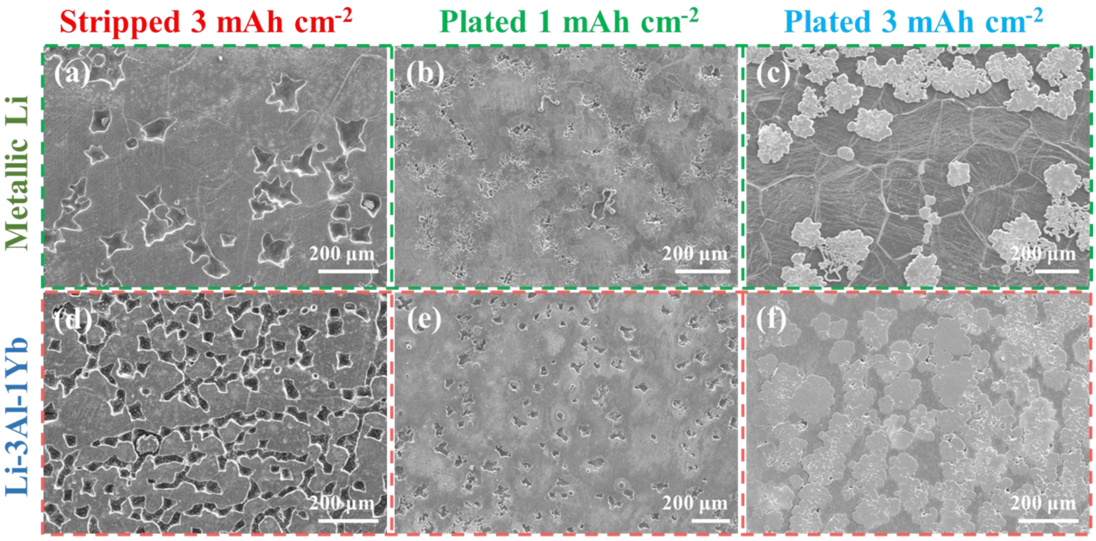
Supplementary Figure 7 Scanning electron microscopy (SEM) images for metallic Li anode material: (a) stripping and (b) platting at 0.5 mA cm^{-2}.



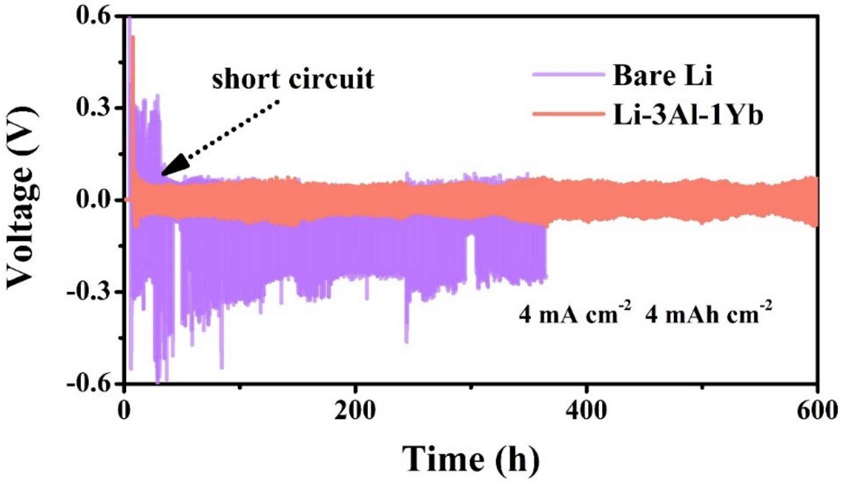
Supplementary Figure 8 Large-scale scanning electron microscopy (SEM) images for metallic Li anode: stripping for (a) 0.5 mAh cm^{-2}, (b) 1 mAh cm^{-2} and (c) 3 mAh cm^{-2}; plating for (d) 0.5 mAh cm^{-2}, (e) 1 mAh cm^{-2} and (f) 3 mAh cm^{-2}.



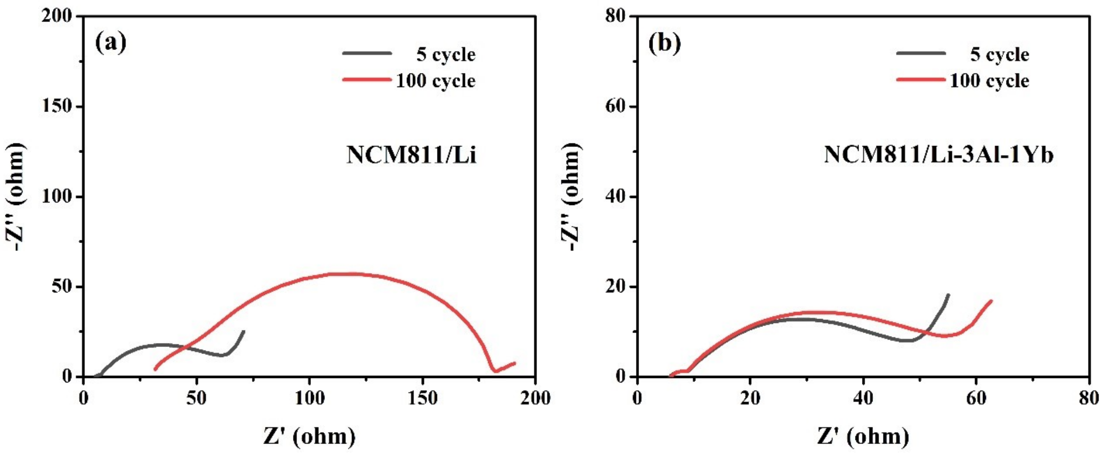
Supplementary Figure 9 Large-scale scanning electron microscopy (SEM) images for Li-3Al-1Yb alloy anode: stripping for (a) 0.5 mAh cm^{-2}, (b) 1 mAh cm^{-2} and (c) 3 mAh cm^{-2}; plating for (d) 0.5 mAh cm^{-2}, (e) 1 mAh cm^{-2} and (f) 3 mAh cm^{-2}.



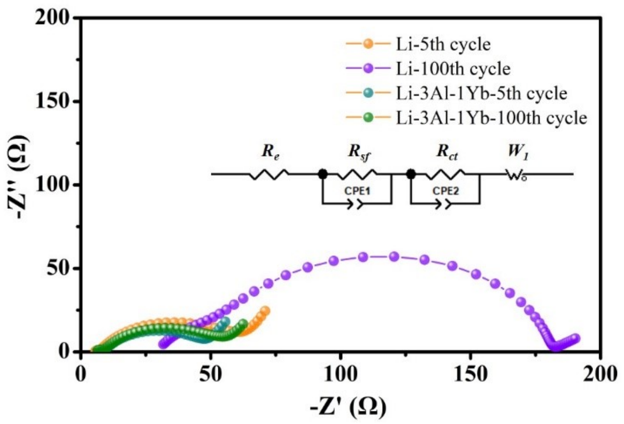
Supplementary Figure 10 Scanning electron microscopy (SEM) images: stripped 3 mAh cm^{-2} for (a) Li and (d) Li-3Al-1Yb at 0.5 mA cm^{-2}; plated for (b, c) Li and (e, f) Li-3Al-1Yb at 0.5 mA cm^{-2}.



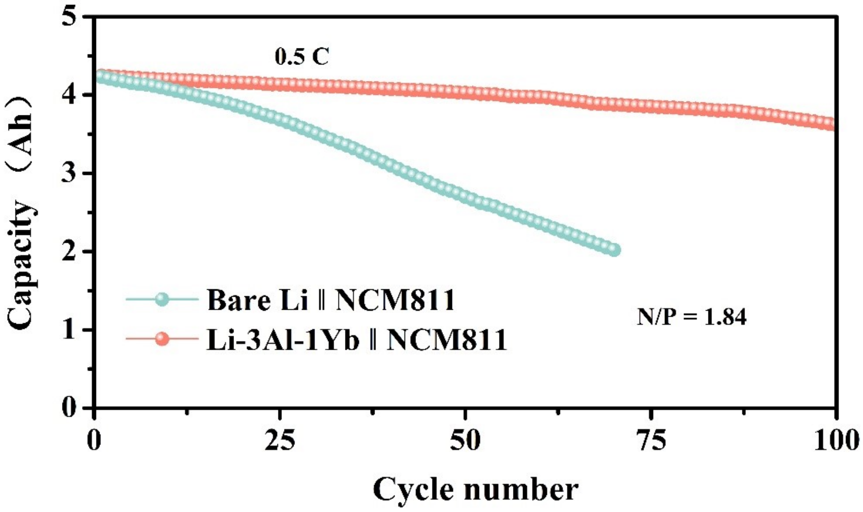
Supplementary Figure 11 the cycle performance at the current density of 4 mA cm^{-2} (plating/stripping capacity: 4 mAh cm^{-2}) for bare Li and Li-3Al-1Yb anode in Li||Li symmetrical cell systems.



Supplementary Figure 12 The impedance spectroscopy of the Li||NCM811 and Li-3Al-1Yb||NCM811 at 5th cycle and 100th cycle.



Supplementary Figure 13 Nyquist plots of the Li||NCM811 and Li-3Al-1Yb||NCM811 at 5th cycle and 100th cycle after fitting.



Supplementary Figure S14 Cycling performances of pouch cells (Li||NCM811 and Li-3Al-1Yb||NCM811) at 0.5 C.

Table S1 the crystal structure, lattice parameters and atomic radius of Al_2Yb, Al_2Y, AlB_2 and β-Li.

Compound	Crystal structure	Lattice parameters	
		a	*c*
Al_2Yb	fcc	0.788	0.788
Al_2Y	fcc	0.786	0.786
AlB_2	hex	0.301	0.326
β-Li	bcc	0.351	0.351

Table S2 the disregistries of matched crystal plane between (100)Al_2Yb with (100)β-Li, (110)β-Li and (111)β-Li.

	(100)Al_2Yb//(100)Li			(100)Al_2Yb//(110)Li			(100)Al_2Yb//(111)Li		
[uvw]Al_2Yb	[001]	[011]	[010]	[001]	[011]	[010]	[001]	[011]	[010]
d[uvw]Li	[001]	[011]	[010]	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]
[uvw]Al_2Yb	0.788	0.557	0.788	0.788	0.557	0.788	0.788	0.557	0.788
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	0	0	0	0	10°	0	30°	15°	0
δ		87.10%			87.94%			44.63%	

Table S3 the disregistries of matched crystal plane between (110)Al_2Yb with (100)β-Li, (110)β-Li and (111)β-Li.

	(110)Al_2Yb//(100)Li			(110)Al_2Yb//(110)Li			(110)Al_2Yb//(111)Li		
[uvw]Al_2Yb	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$10]	[$\bar{1}$11]	[001]
d[uvw]Li	[001]	[011]	[010]	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]
[uvw]Al_2Yb	0.557	1.365	0.788	0.557	1.365	0.788	0.557	1.365	0.788
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	0	10°	0	0	0	0	30°	25°	0
δ		118.07%			161.94%			35.16%	

Table S4 the disregistries of matched crystal plane between (111)Al_2Yb with (100)β-Li, (110)β-Li and (111)β-Li.

	(111)Al_2Yb//(100)Li			(111)Al_2Yb//(110)Li			(111)Al_2Yb//(111)Li		
[uvw]Al_2Yb	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]
d[uvw]Li	[001]	[011]	[010]	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]
[uvw]Al_2Yb	0.557	0.965	0.557	0.557	0.965	0.557	0.557	0.965	0.557
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	30°	15°	0	30°	25°	0	0	0	0
δ		61.34%			83.04%			12.27%	

Table S5 the disregistries of matched crystal plane between (100)Al_2Y with (100)*β*-Li, (110)*β*-Li and (111)*β*-Li.

	(100)Al_2Y//(100)Li			(100)Al_2Y//(110)Li			(100)Al_2Y//(111)Li		
[uvw]Al_2Y	[001]	[011]	[010]	[001]	[011]	[010]	[001]	[011]	[010]
d[uvw]Li	[001]	[011]	[010]	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]
[uvw]Al_2Y	0.786	0.556	0.786	0.786	0.556	0.786	0.786	0.556	0.786
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	0	0	0	0	10^o	0	30^o	15^o	0
δ		86.65%			87.44%			44.44%	

Table S6 the disregistries of matched crystal plane between (110)Al_2Y with (100)β-Li, (110)β-Li and (111)β-Li.

	(110)Al_2Y//(100)Li			(110)Al_2Y//(110)Li			(110)Al_2Y//(111)Li		
[uvw]Al2Y	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$10]	[$\bar{1}$11]	[001]
d[uvw]Li	[001]	[011]	[010]	[$\bar{1}$10]	[$\bar{1}$11]	[001]	[$\bar{1}$01]	[$\bar{2}$11]	[$\bar{1}$10]
[uvw]Al2Y	0.556	1.361	0.786	0.556	1.361	0.786	0.556	1.361	0.786
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	0	10^o	0	0	0	0	30^o	25^o	0
δ		117.56%			161.24%			34.89%	

Table S7 the disregistries of matched crystal plane between (111)Al_2Y with (100)β-Li, (110)β-Li and (111)β-Li.

	(111)Al_2Y//(100)Li			(111)Al_2Y//(110)Li			(111)Al_2Y//(111)Li		
[uvw]Al_2Y	$[\bar{1}01]$	$[\bar{2}11]$	$[\bar{1}10]$	$[\bar{1}01]$	$[\bar{2}11]$	$[\bar{1}10]$	$[\bar{1}01]$	$[\bar{2}11]$	$[\bar{1}10]$
d[uvw]Li	[001]	[011]	[010]	$[\bar{1}10]$	$[\bar{1}11]$	[001]	$[\bar{1}01]$	$[\bar{2}11]$	$[\bar{1}10]$
[uvw]Al_2Y	0.556	0.963	0.556	0.556	0.963	0.556	0.556	0.963	0.556
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	30°	15°	0	30°	25°	0	0	0	0
δ		61.07%			82.80%			12.06%	

Table S8 the disregistries of matched crystal plane between (100)AlB_2 with (100)*β*-Li, (110)*β*-Li and (111)*β*-Li.

	(100)AlB_2//(100)Li			(100)AlB_2//(110)Li			(100)AlB_2//(111)Li		
[uvw]AlB_2	[0001]	[110]	[20]	[0001]	[110]	[20]	[0001]	[110]	[20]
d[uvw]Li	[001]	[011]	[010]	$[\bar{1}10]$	$[\bar{1}11]$	[001]	$[\bar{1}01]$	$[\bar{2}11]$	$[\bar{1}10]$
[uvw]AlB_2	0.326	0.444	0.301	0.326	0.444	0.301	0.326	0.444	0.301
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	0	2.3°	0	0	7.4°	0	30°	17.3°	0
δ		10.64%			31.18%			44.36%	

Table S9 the disregistries of matched crystal plane between (0001)AlB_2 with (100)*β*-Li, (110)*β*-Li and (111)β-Li.

	$(0001)AlB_2//(100)Li$			$(0001)AlB_2//(110)Li$			$(0001)AlB_2//(111)Li$		
$[uvw]AlB_2$	[110]	[20]	[20]	[110]	[20]	[20]	[110]	[20]	[20]
d[uvw]Li	[001]	[011]	[010]	$[\bar{1}10]$	$[\bar{1}11]$	[001]	$[\bar{1}01]$	$[\bar{2}11]$	$[\bar{1}10]$
$[uvw]AlB_2$	0.301	0.521	0.301	0.301	0.521	0.301	0.301	0.521	0.301
d[uvw]Li	0.351	0.496	0.351	0.496	0.304	0.351	0.496	0.860	0.496
θ	30°	15°	0	30°	24.7°	0	0	0	0
δ		13.87%			39.13%			39.35%	

Table S10 Cell parameters of the Li‖NCM811 pouch cell.

	Parameter	Value
NCM811 cathode	Discharge capacity	200 mAh g^{-1}
	Active naterial loading	95.94%
	Area weight (each side)	14 mg cm^{-2}
	Area capacity (each side)	2.8 mAh cm^{-2}
	Electrode desity	3.41 g cm^{-3}
	Electrode thickness (each side)	48.3 μm
Al foil	Thickness	12 μm
Li anode	Specific capacity	3860 mAh g^{-1}
	Anode thickness (each side)	25 μm
	Area capacity (each side)	5.15 mAh cm^{-2}
	N/P ratio	1.84
Electrolyte	E/C ratio	2.5 g Ah^{-1}
Separator	Thickness	16 μm
	Average voltage	3.8 V
	Capacity	⩾4.1Ah
	Energy density	⩾390 Wh kg^{-1}

Cathode mass = (14 * 7.7 * 9.7 * 2 * 10 / 1000) g = 20.91 g

Anode mass = (0.534 * 7.7 * 9.7 * 2 * 25 * 10 /10000) g = 1.99 g

Al foil mass = (2.7 * 7.7 * 9.7 * 12 * 10 / 10000) g = 2.41 g

Separator mass = (1.43 * 16 * 7.7 * 9.7 * 10 / 10000) g = 1.70 g

Electrolyte mass = (4.15 * 2.5) g = 10.37 g

Package foil mass = (0.0181*8*10*2) g = 2.89 g

The total mass = 40.27 g

The total energy density = (4.148*3.8/40.27)*1000 = 391.6 Wh kg^{-1}

Table S11 the fitting results of Nyquist plots for Li||NCM811 and Li-3Al-1Yb||NCM811 at 5th cycle and 100th cycle.

Sample	R_e (ohm)	R_{sf} (ohm)	R_{ct} (ohm)
Li-5th cycle	5.434	1.372	46.4
Li-100th cycle	29.61	27.91	122.6
Li-3Al-1Yb-5th cycle	5.967	2.553	38.37
Li-3Al-1Yb-100th cycle	6.17	2.907	40.76