

## Electronic Supplementary Information

### ZnSb<sub>2</sub>O<sub>6</sub>: An Advanced Anode Material for Li-Ion Batteries

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#### Synthesis of ZnSb<sub>2</sub>O<sub>6</sub>

Typically, ZnSO<sub>4</sub>·7H<sub>2</sub>O (10 mmol) was dissolved in distilled water (200 ml) under mild stirring (solution A), K(SbO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·1/2H<sub>2</sub>O (20 mmol) was dissolved in distilled water (100 ml) under mild stirring (solution B). Then, solution A was added to solution B, followed by adding N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (5 ml). Then the mixed solution was stirred for 12 h, and the white product was collected by centrifugation, washed several times with ethanol and deionized water. After drying in an oven, the white product was annealed at 800 °C at a rate of 5 °C/min and kept at this temperature for 2 h in air to obtain well-crystallized products. Finally, the ZnSb<sub>2</sub>O<sub>6</sub> sample was obtained.

#### Material characterization

The morphologies, particle sizes and elemental compositions of the materials were investigated by scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, Tecnai G2 20ST). X-ray diffraction (XRD, Rigaku3014) with Cu K $\alpha$  radiation was employed to identify the structures of the samples. The X-ray photoelectron spectrum (XPS) was conducted on an X-ray photoelectron spectrometer using a Mg-K $\alpha$  radiation exciting source (AXIS ULTRA DLD, Kratos). Surface area was measured by the N<sub>2</sub> adsorption-desorption isotherms on ASAP 2020/Tristar 3000.

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## Cell assembly and Electrochemical characterizations

The working electrode was made by mixing 70 %  $\text{ZnSb}_2\text{O}_6$ , 15 % carbon black and 15 % sodium alginate in deionized water to form uniform slurry. Then the slurry was pasted onto copper current collector and dried at 60 °C overnight. The loading of each electrode was  $1 \pm 0.05 \text{ mg cm}^{-2}$ . The CR2025 coin-type cells for half and full LIBs were assembled in an argon-filled glove box (Universal 2440/750). The electrolyte of half and full LIBs was a solution of 1 M  $\text{LiPF}_6$  (Aldrich) in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1v/v). For the preparation of full cells, the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  mixed with Super P and polyvinylidene fluoride (8:1:1 by weight) was spread on Al foil and adopted as the cathode. The active material weight ratio between  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{ZnSb}_2\text{O}_6$  was controlled at about 4:1. The anode was firstly activated in half cell for 10 cycles and then were assembled into full cell. Cyclic voltammetry was performed at a scan rate of  $0.2 \text{ mV s}^{-1}$  in the voltage range of 0.01-3.00 V. Galvanostatic charge-discharge tests were carried out on a Land Battery Measurement system (Land CT2001A, Wuhan, China) under set current densities in the fixed voltage range of 0.01-3.00 V for half cells and 1.50-3.75 V for full cells at room temperature.

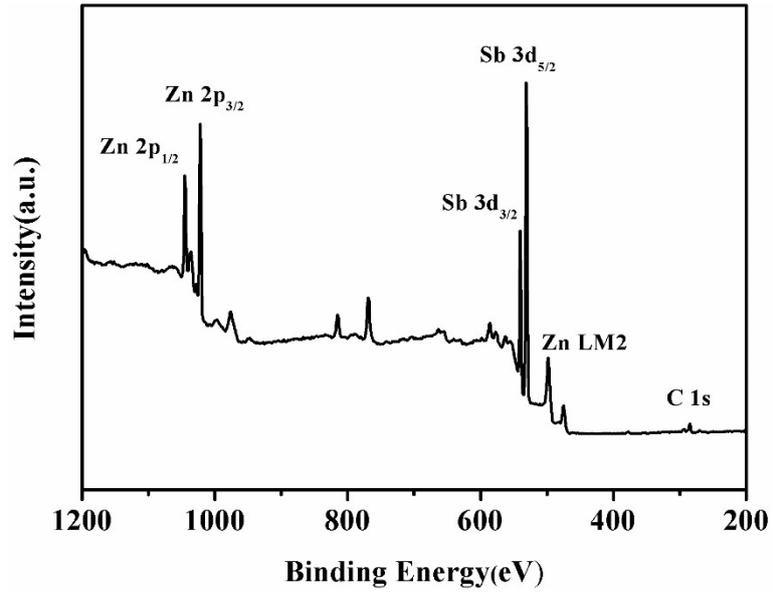


Fig. S1 The survey spectrum of the ZnSb<sub>2</sub>O<sub>6</sub>

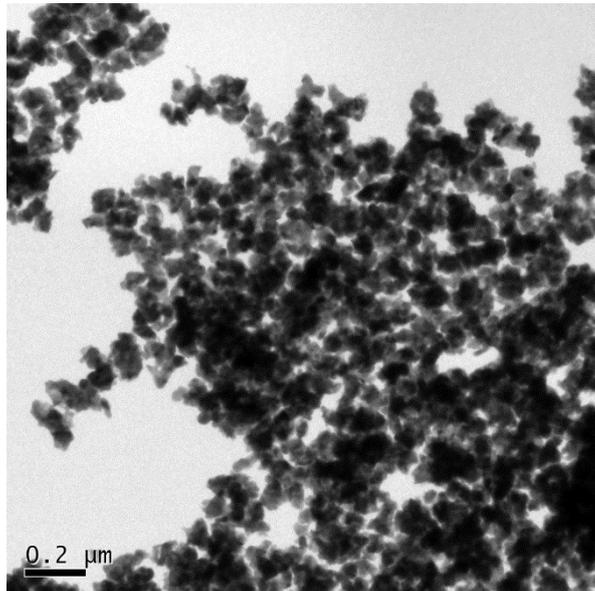


Fig. S2 Low magnification TEM image of the ZnSb<sub>2</sub>O<sub>6</sub>

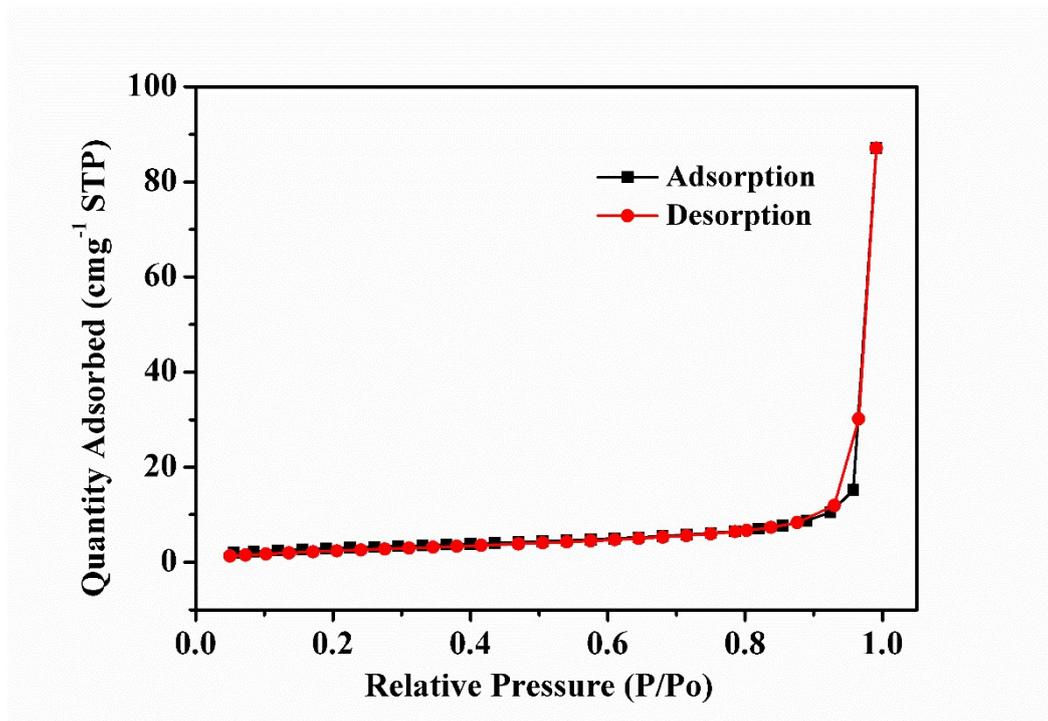


Fig. S3 N<sub>2</sub> adsorption-desorption isotherms of the ZnSb<sub>2</sub>O<sub>6</sub>

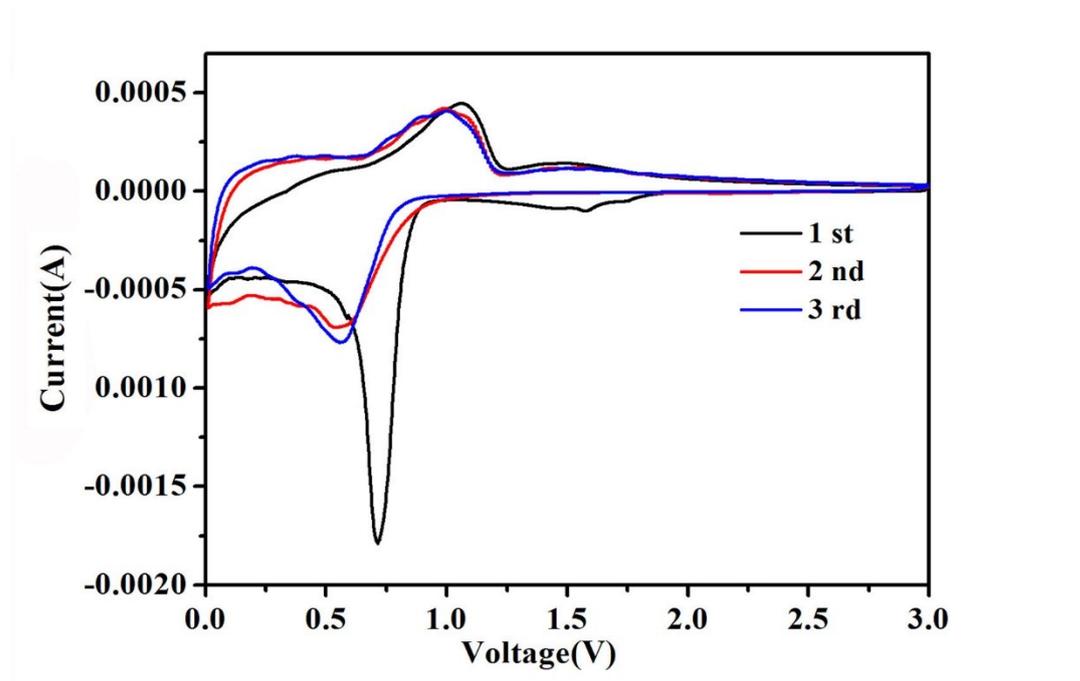


Fig. S4 CV curves of the ZnSb<sub>2</sub>O<sub>6</sub> electrode.

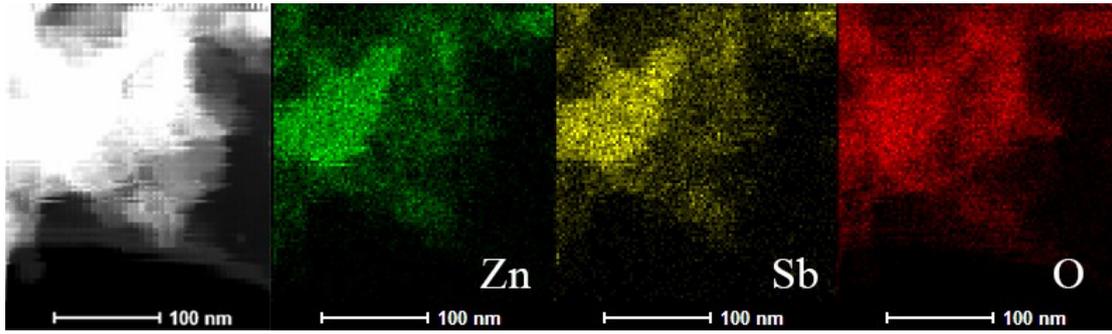


Fig. S5 Elemental mapping images of Zn, Sb and O of the electrode after 100 cycles at 0.5 mA/cm<sup>2</sup> (500 mAh g<sup>-1</sup>)

Tab. S1 The experimental and theoretical *d*-spacings (nm) and the corresponding Miller indices of the products at 0.01 V in discharge.

<i>d</i> -spacing experimental value (nm)	Li <sub>3</sub> Sb (JCPDS 04-0438)		LiZn (JCPDS 65-4082)		Sb (JCPDS 17-0124)		ZnSb <sub>2</sub> O <sub>6</sub> (JCPDS 38-0453)	
	(h,l,k)	d	(h,l,k)	d	(h,l,k)	d	(h,l,k)	d
0.229	(1.0.3)	0.229						
0.236	(1.1.0)	0.235						
0.291	(1.0.2)	0.291						
0.179			(2.2.2)	0.180				
0.265					(0.0.2)	0.263		
0.417							(1.0.1)	0.417

Tab. S2 The experimental and theoretical  $d$ -spacings (nm) and the corresponding Miller indices of the products at 3.00 V after one cycle.

$d$ -spacing	Sb <sub>2</sub> O <sub>3</sub>		Sb <sub>2</sub> O <sub>5</sub>		ZnO	
experimental value (nm)	(JCPDS 65-2426)		(JCPDS 33-0110)		(JCPDS 36-1451)	
	(h,l,k)	d	(h,l,k)	d	(h,l,k)	d
0.319	(1.3.0)	0.318				
0.312	(0.4.0)	0.312				
0.261			(0.0.2)	0.264		
0.290/0.291			(3.1.-1)	0.293		
0.261					(0.0.2)	0.260

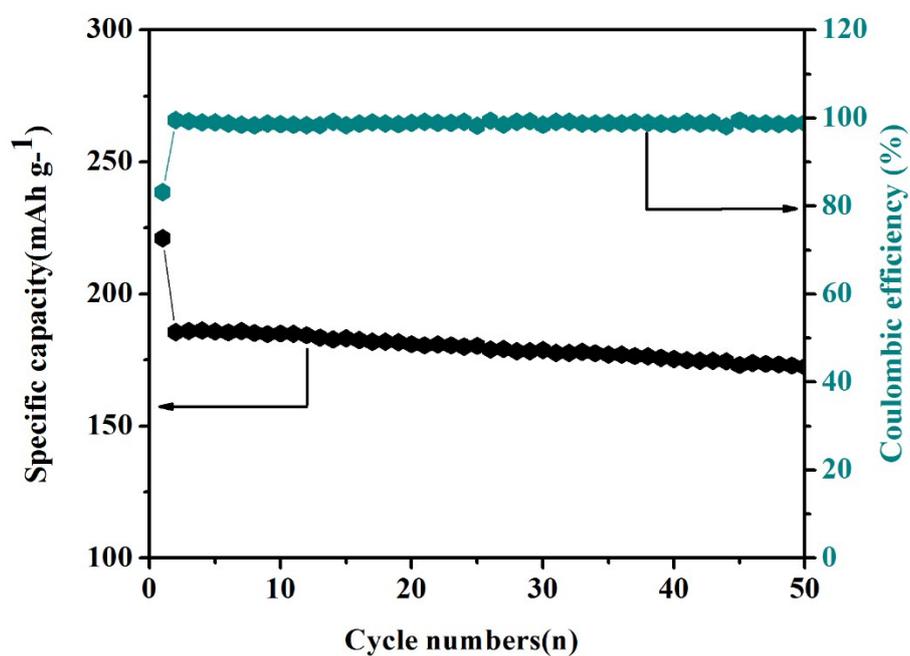


Fig. S6 Cycling performance of the LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathode in half cells at 200 mA/g

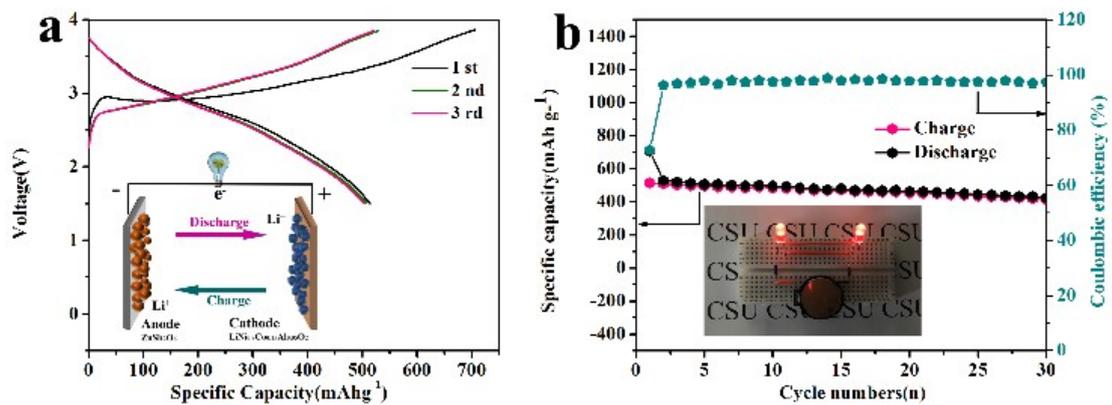


Fig. S7 Charge/discharge curves (a); Cycling performance (b) of ZnSb<sub>2</sub>O<sub>6</sub>/

LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> full cell.