Electronic supporting information (ESI)

A high-stability biphasic layered cathode for sodium-ion batteries

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Experiments

Material synthesis

$Na_{0.62}Ni_{0.33}Mn_{0.62}Sb_{0.05}O_2$ and $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ were synthesized by solid state methods. The reagent grade Na_2CO_3 (5% excess), NiO, MnO_2 and Sb_2O_5 were added to the ball milling tank according to the stoichiometric ratio grinding at 300 rpm for 450 min. The powder obtained after drying was pressed into discs under the pressure of 10 MPa, which subsequently was calcined in air at 950 °C for 15 h. The sample was cooled to room temperature after calcination and then ground into powder.

Material characterization

The structure characterization of NNMS and NNM was collected on a D8 Advance diffractometer (Bruker) with Cu Kα radiation. Rietveld refinement of the XRD data were performed with general structural analysis system (GSAS). The exact element composition of the sample was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The morphology of samples was observed by scanning electron microscopy (SEM, Hitachi SU8010). High-resolution transmission electron microscopy (HRTEM, FEI TECNAI F20) and energy dispersive spectroscopy (EDS) were employed to confirm the microstructure and the distribution of elements. X-ray photoelectron spectroscopy (XPS) were conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer.

Electrochemical measurements

The active material, acetylene black and the PVDF binder were fully mixed in a weight ratio of 8:1:1 and then casted on the Al foil. The electrode was dried in a vacuum oven at 120°C for 5 h, after that the dried electrode sheet was cut into a disc with a diameter of 12 mm. 1 M NaClO4 in propylene carbonate (PC) which dissolved with 5 wt% fluorinated ethylene carbonate (FEC) served as the electrolyte, and a glass fiber membrane was used as the separator. Using Na metal as anode and the prepared electrode as cathode, assembled into a CR2032 coin-type cells in a glove box filled

with argon. Electrochemical impedance spectroscopy (EIS) measurements were detected by solartron 1260-1287.

Tab. S1. Crystallographic parameters of NNMS refined by the Rietveld method.

Sample		NNMS		
Phase	P2-type		O3-type	
Space Group	P63/mmc		$R\bar{3}m$	
Fraction(%)	68.775		31.225	
Cell Parameters	a(Å)	2.8939(0)	a(Å)	3.0111(7)
	b(Å)	2.8939(0)	b(Å)	3.0111(7)
	c(Å)	11.2584(1)	c(Å)	16.6867(9)
	α(°)	90.000	α(°)	90.000
	β(°)	90.000	β(°)	90.000
	γ(°)	120.000	γ(°)	120.000
	Volume(Å^3)	81.65(4)	Volume(Å^3)	131.03(1)
Agreement Factors	R_{wp}(%)		7.17	
	R_p(%)		4.81	

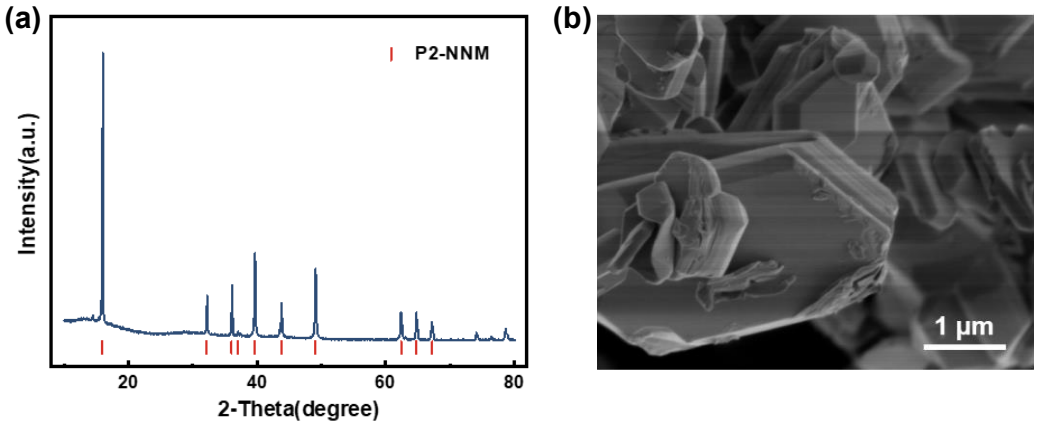

Fig. S1 (a) X-ray diffraction pattern and (b) SEM images of P2-NNM.

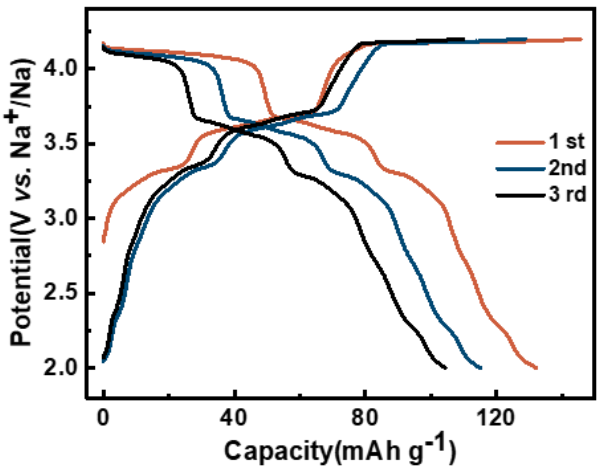

Fig. S2 The typical charge-discharge profiles between 2.0 and 4.2 V at a 0.2C rate of NNM.

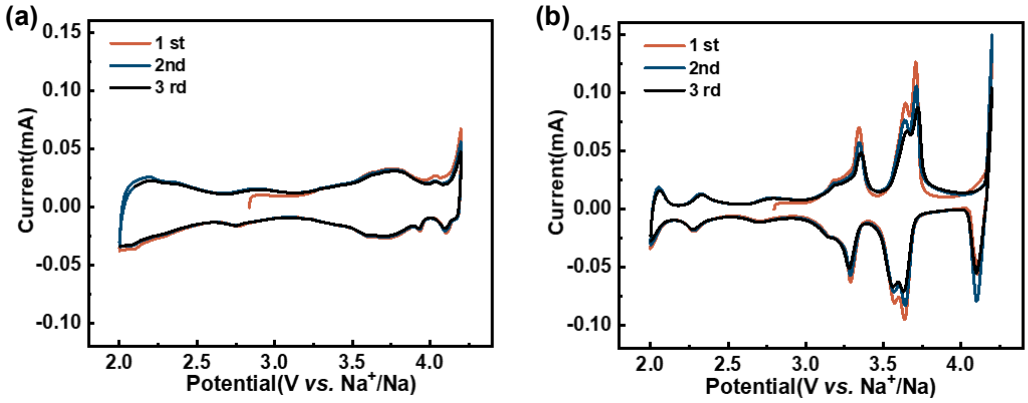

Fig. S3 Cyclic voltammogram of (a) NNMS and (b) NNM at a scan rate of 0.2 mV s^{-1} in voltage ranges of 2.0-4.2V.

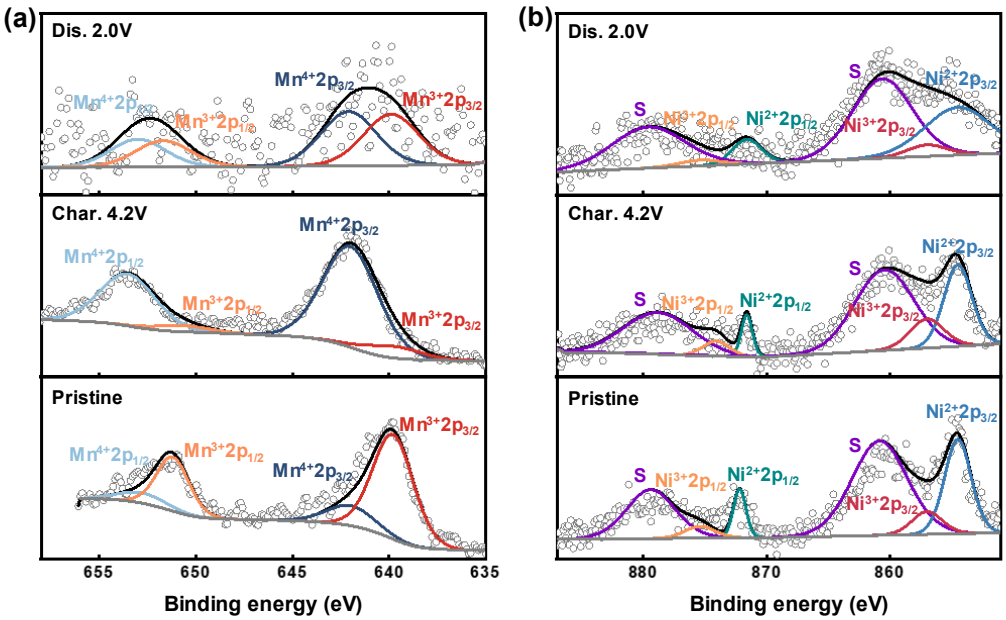

Fig. S4 XPS spectra of NNMS: (a) Mn 2p spectra (b) Ni 2p spectra.

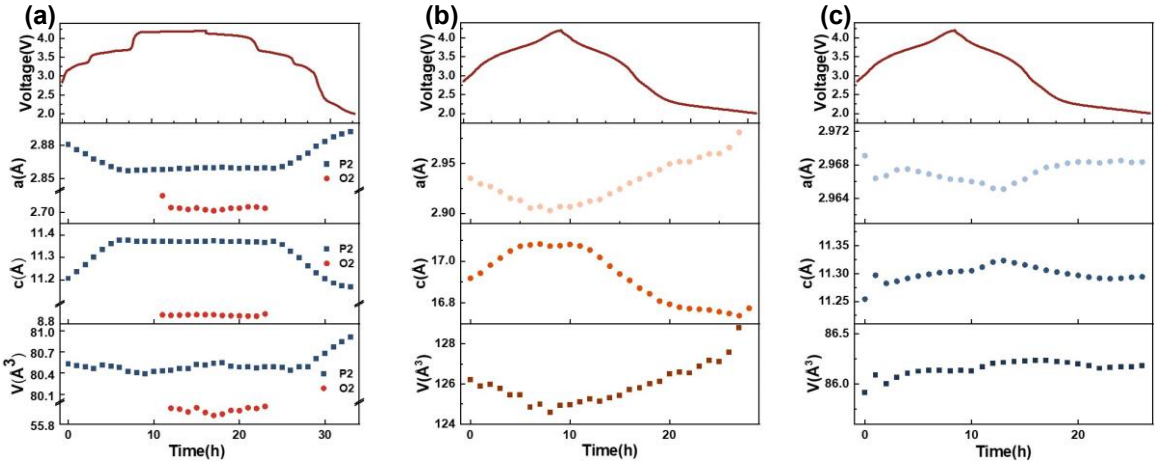

Fig. S5 (a) The variation of lattice constants and unit-cell volume of the NNM cathode with the extraction and insertion of sodium ions. The variation of lattice constants and unit-cell volume of O3-NNMS (b) and P2-NNMS (c) cathode in synchronous electrochemical cycles.

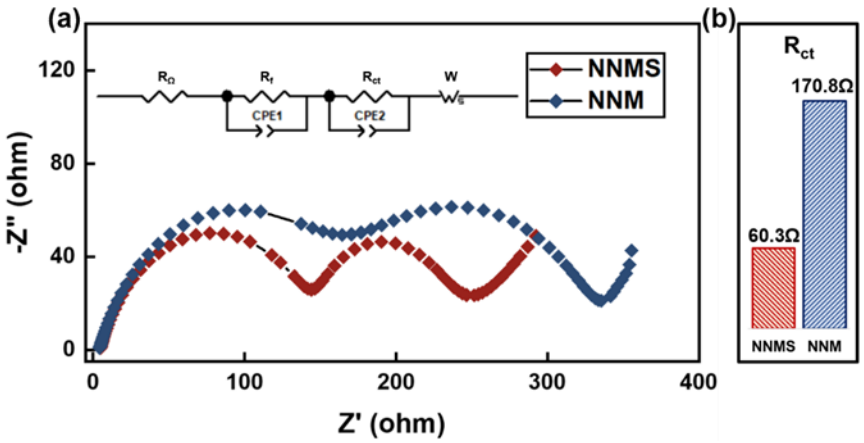

Fig. S6 (a) Nyquist plots of EIS and the fit for NNMS and NNM cathode. (b) The R_{ct} of NNMS and NNM cathodes.