Electronic Supplementary Information

Reversible $Na_{15}Sn_4$ alloy compensation for hard carbon anodes to enhance initial coulombic efficiency in sodium-ion full cells†

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1. Experimental Section

1.1 Synthesis $Na_{15}Sn_4$ alloy

Specifically, metallic Na (≥99.7%, Aladdin) and metallic Sn (≥99.99%, Aladdin) were weighed in a molar ratio of 15:4 and placed in a stainless-steel container. The container was then positioned on a stirring heating plate inside a glovebox. The temperature was gradually increased to 350 °C at a rate of 10 °C/ min, allowing both Na and Sn to reach a liquid state. The molten mixture was stirred at 30 r/min for 20 minutes to ensure homogeneity, followed by slow cooling to room temperature. The solidified product was then ground in an agate mortar for 40 minutes to obtain $Na_{15}Sn_4$ alloy powder. All operations were performed within the glovebox, maintaining O_2 and H_2O levels below 0.1 ppm.

1.2 Synthesis NaSn@HC

The NaSn@HC was fabricated by ball mixing prepared $Na_{15}Sn_4$ alloy with commercial hard carbon at a ratio of 1:20 and ground in an agate mortar in the glove box for 30 minutes.

1.3 Preparation of the Cathode Material for the Full Cell

1.3.1 $Na_3V_2(PO_4)_3$@C (NVP):

For a typical synthesis, V_2O_5 and $H_2C_2O_4$ were dissolved into deionized water and vigorously stirred at 70 °C for 1 h to obtain a VOC_2O_4 solution. Then NaH_2PO_4 and glucose were added into the solution, which was further stirred for stirring 5 min. After that, n-propanol was added into the solution stirring was continued for more than 10 min, followed by drying at 70 °C to get nanoflake-assembled flower-like precursor. In the end, nanoflake-assembled hierarchical NVP/C was obtained from the precursor by preheating it at 400 °C for 4 h followed by annealing at 750 °C for 8h in argon atmosphere with a heating rate of 5 °C min^{-1}.

1.3.2 $Na_{2/3}[Fe_{1/3}Mn_{2/3}]O_2$ (NaFeMnO):

The NaFeMnO cathode material used in this work was prepared by the high-temperature solid-state method. Stoichiometric amounts of Na_2CO_3, Mn_2O_3, and Fe_2O_3 were ground thoroughly in an agate mortar for 1 h. The mixture was calcined at 900 ℃ for 10 h at the rate of 5 C min^{-1} in air atmosphere. When the temperature naturally cools to room temperature, the black powders were immediately transferred into a glovebox filled with argon (Ar) atmosphere.

1.3.3 $Na[Ni_{0.3}Mn_{0.55}Cu_{0.1}Ti_{0.05}]O_2$ (NaNMO)

The NaNMO cathode material was prepared by the high-temperature solid-state method. Stoichiometric amounts of Na_2CO_3, Mn_2O_3, Ni_2CO_3, CuO and TiO_2 were ground thoroughly in an agate mortar for 1 h. The mixture was calcined at 900 ℃ for 10 h at the rate of 5 C min^{-1} in air atmosphere. When the temperature naturally cools to room temperature, the black powders were immediately transferred into a glovebox filled with argon (Ar) atmosphere.

1.4 Coin Cell Assembly:

The cathode was prepared using active material, carbon black, and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1, dispersed in N-methyl-2-pyrrolidone (NMP). The resulting slurry was cast into electrodes and cut into circular discs with a diameter of 1.2 cm, achieving an active material loading of 1.0-1.75 mg cm^{-2}. Similarly, the NaSn@HC anode was fabricated using the same composition (7:2:1 weight ratio of active material, carbon black, and PVDF in NMP) and cut into 1.2 cm diameter electrodes. Full cells were assembled with an N/P ratio of 1-1.2, and the specific capacity was calculated based on the cathode.

Coin-type (2032) full cells were assembled in an argon-filled glovebox, maintaining water and oxygen levels below 0.01 ppm. The electrolyte consisted of 1 M $NaClO_4$ dissolved in a 1:1 (v/v) mixture of EC and DEC, with 5 wt% FEC as an additive. In half-cells, metallic sodium served as both the counter and reference electrode, while binder-free glass microfiber filters (Whatman, Grade GF/D) were used as separators.

1.5 Materials characterization

The cells were tested at room temperature Neware test system (CT-4008Tn-5V20mA-164). The Cyclic Voltammetry test (CV) was obtained using the Donghua electrochemical workstation (DH7006). The materials were studied using a Scanning Electron Microscope, Fourier Transform Infrared Spectrometer, Raman Spectra (SEM, FTIR and Raman: the test in shiyanjia.com) and X-ray Photoelectron Spectroscopy (XPS: the test in www.zkec.cc).

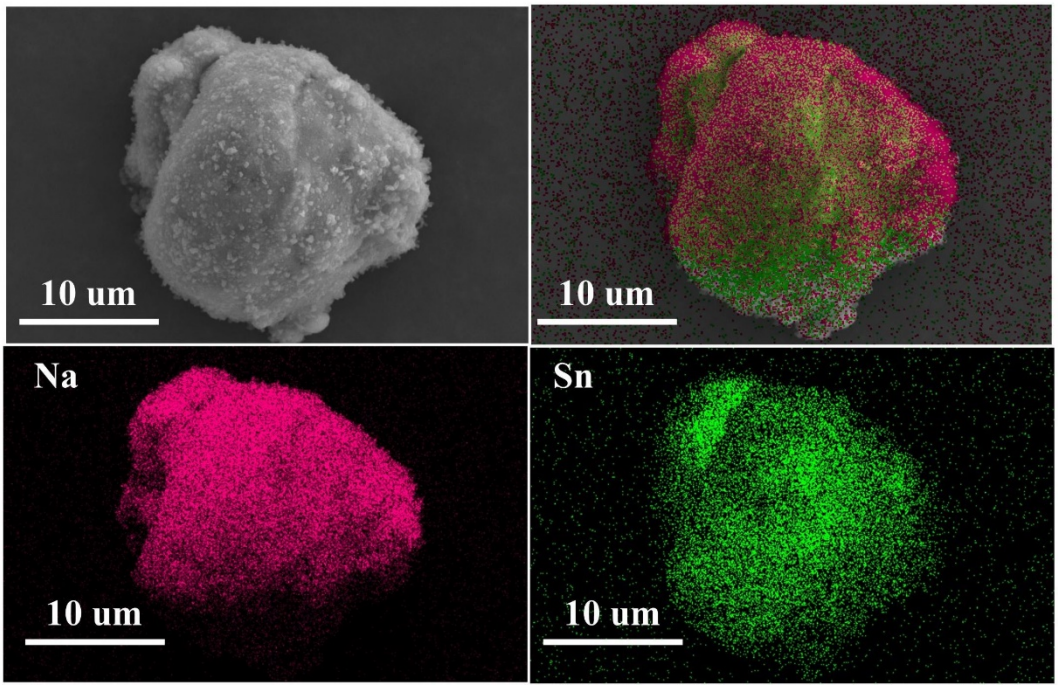

Fig. S1. EDS maps of $Na_{15}Sn_4$.

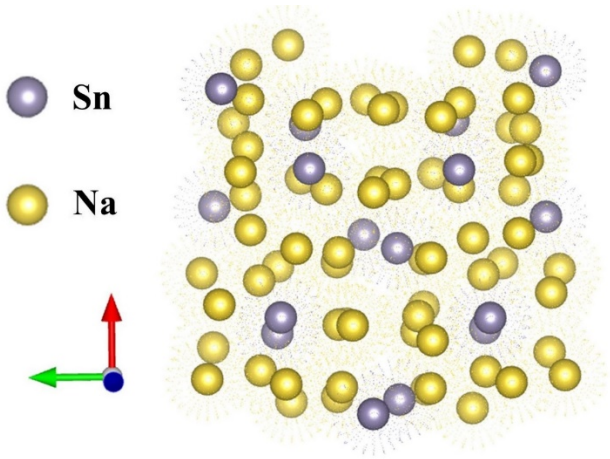

Fig. S2. crystal structures of $Na_{15}Sn_4$.

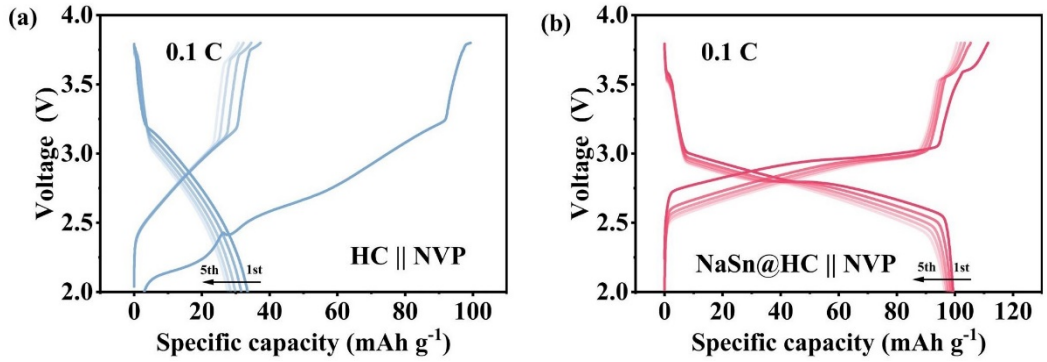

Fig. S3. (a) HC || NVP and (b) NaSn@HC || NVP cyclic curve diagrams.

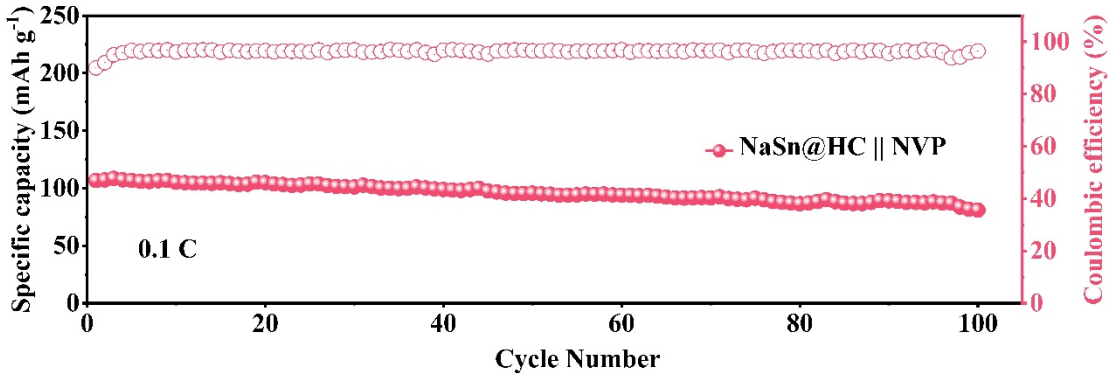

Fig. S4. Cycling performance of NaSn@HC || NVP at 0.1c.

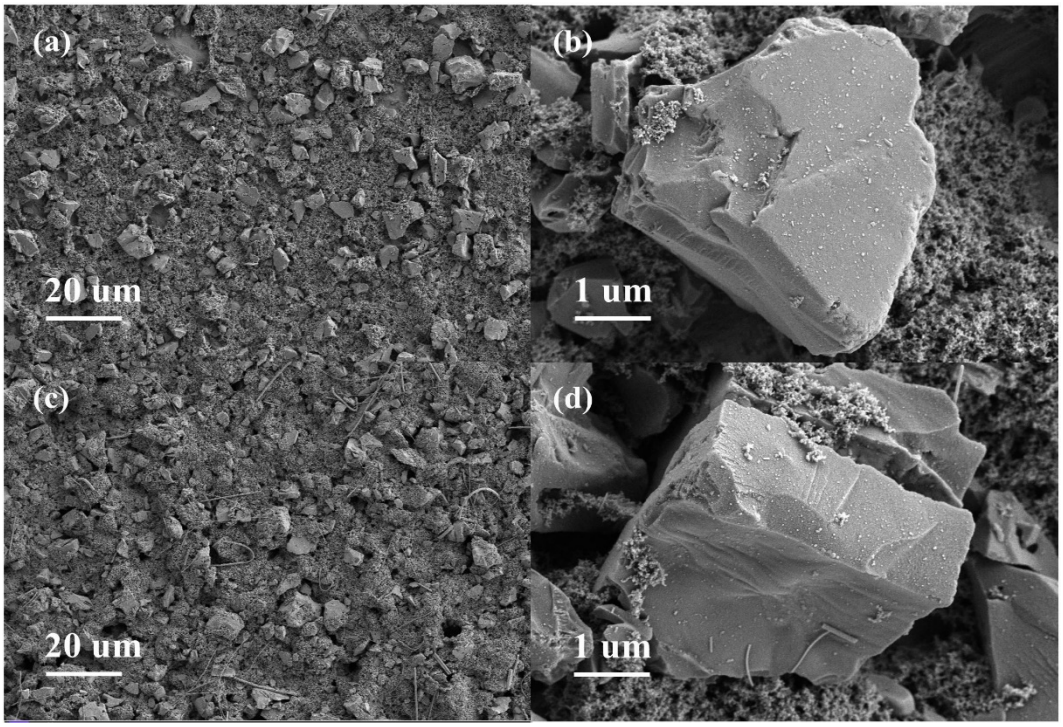

Fig. S5. The SEM image of the NaSn@HC anode, (a, b) before cycling and (c, d) after 100 cycles in the full cell.

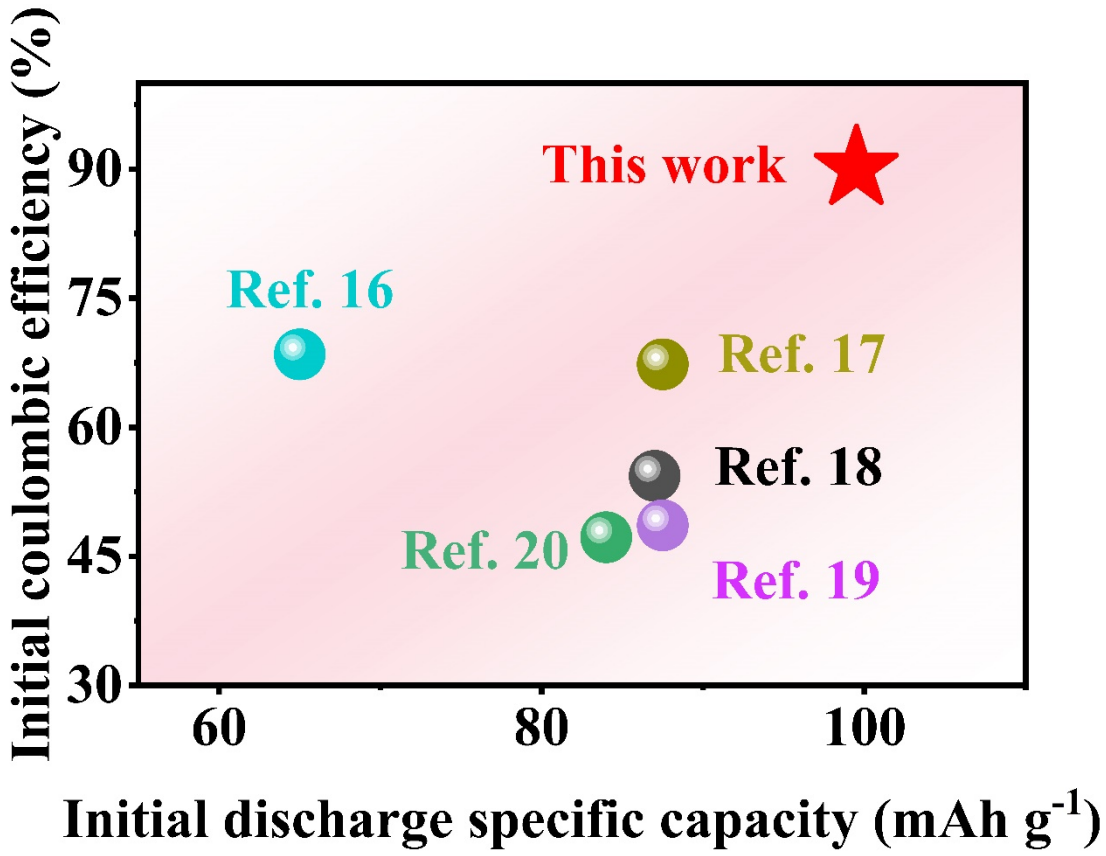

Fig. S6. The NaSn@HC || NVP full-cell performance and published various pre-sodiation techniques full-cell performance graph.

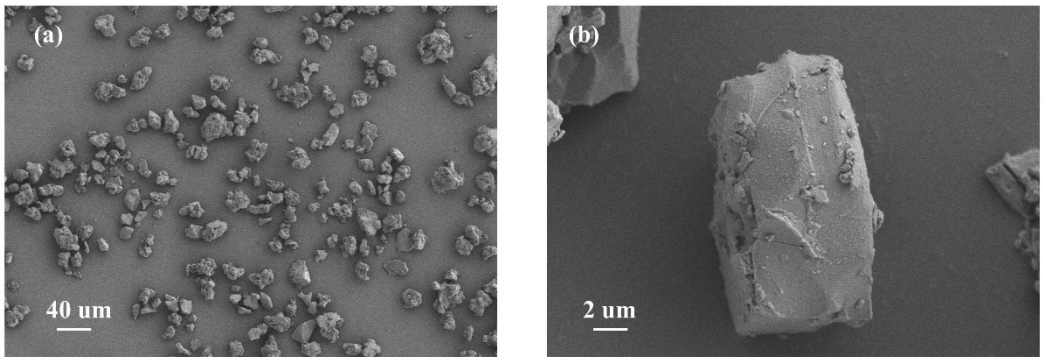

Fig. S7. The scanning electron microscopy of $Na_{2/3}[Fe_{1/3}Mn_{2/3}]O_2$ material.

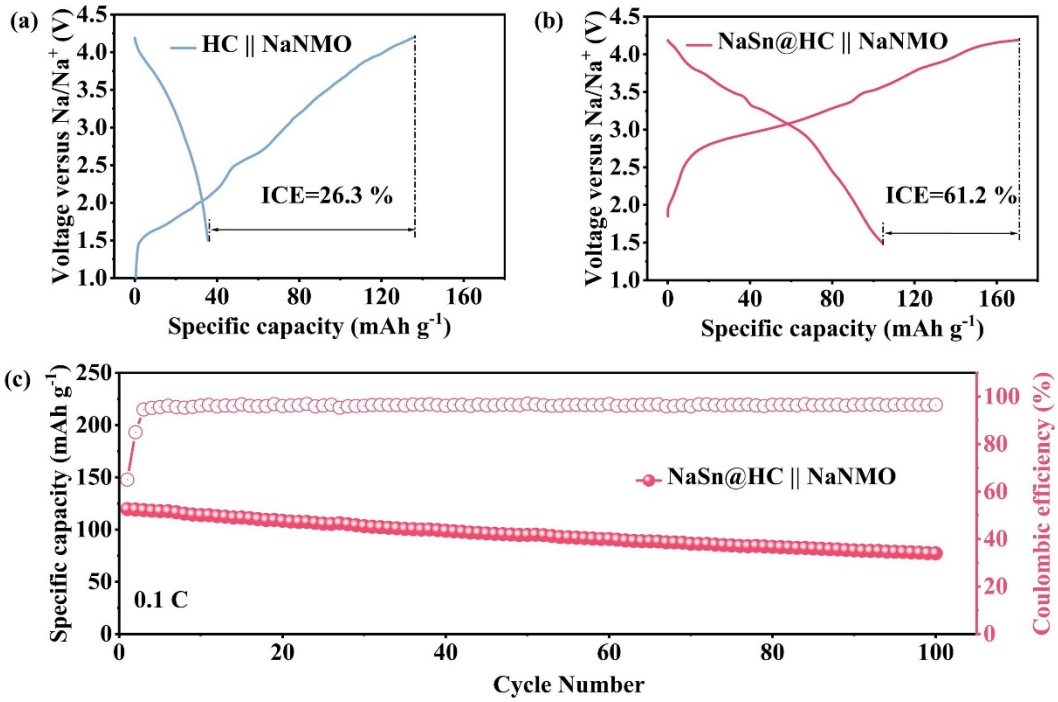

Fig. S8 (a) First loop charge-discharge curve of NaNMO || HC full cell and (b) NaNMO || NaSn@HC full cell; (c) The long-term cycling performance of NaNMO || NaSn@HC full cell.

Table S1. Structural parameters of $Na_{15}Sn_4$ from Rietveld refinement.

Sample	$Na_{15}Sn_4$	
Crystal system	Cubic	
Space group	I-43d	
Lattice parameters	a=b=c=13.1946Å	
Rp=12.7	Rwp=19.0	Chi2=10.9

Table S2. Atomic positions of $Na_{15}Sn_4$ alloy deduced from Rietveld refinement of XRD data.

Atom	Wyckoff	x	y	z	Occupancy
Na1	12a	0.37500	0.00000	0.25000	1
Na2	48e	0.65480	0.46700	0.46700	1
Sn	16c	0.70830	0.70830	0.70830	1

Table S3. Summary of initial Coulomb efficiency (ICE) of various Sn-based alloy anodes full cell Electrochemical performance in previously published literature

Anode	Cathode	ICE	Reference
SbSn@NCNFs	$Na_3V_2(PO_4)_2F_3$	79.5	[1]
Sn/$FeSn_2$@C	$Na_3V_2(PO_4)_3$	79.7	[2]
SnO_2@C/RGO	n-$Na_3V_2(PO_4)_2F_3$	77.9	[3]
Sn_4P_3-C	$Na_2C_6O_6$	85.0	[4]
α-Sn	$Na_3V_2(PO_4)_3$/rGO	80.0	[5]
SnO	$Na_3V_2(PO_4)_2F_3$	63.7	[6]
Cu_2Sn@Cu	$Na_3V_2(PO_4)_3$	87.5	[7]
NaSn@HC	**$Na_3V_2(PO_4)_3$**	**90.1**	**This work**

Table S4. Summary of initial Coulomb efficiency of various advanced sodium-ion anodes available in previously published literature

Anode	Cathode	ICE	Reference
CFS/CS@C	$Na_3V_2(PO_4)_3$	83.1	[8]
Mn-BiOCl	$Na_3V_2(PO_4)_3$	78.2	[9]
HC	$Na_3V_2(PO_4)_3$	63.6	[10]
Mo_3Sb_7@C	$Na_3V_2(PO_4)_3$@C	57.3	[11]
MnHC	$Na_3V_2(PO_4)_3$	86.5	[12]
MGO-Si	$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$	45.1	[13]
Activated carbon	$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	74.5	[14]
Na_4PTC@Bi	$Na_3V_2(PO_4)_2F_3$	89.6	[15]
NaSn@HC	**$Na_3V_2(PO_4)_3$**	**90.1**	**This work**

Table S5. Summary of various pre-sodiation techniques in previously published literature

Cathode	Anode	Pre-sodiation Techniques	Ref.
$Na_3(VO)_2(PO_4)_2F$	HC	Additive	16
$Na_{3.5}V_2(PO_4)_2F_3$	HC	Ball milling	17
$Na_3V_2(PO_4)_2F_3$/rGO	HC	Sef-Sacrificial	18
$Na_{2/3}Ni_{1/3}Mn_{1/3}Ti_{1/3}O_2$	HC	Sef-Sacrificial	19
$Na_{2/3}Ni_{1/3}Mn_{1/3}Ti_{1/3}O_2$	HC	Sef-Sacrificial	20
$Na_3V_2(PO_4)_3$	**HC**	**Alloy**	**This work**

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