
Supporting Information

Room-Temperature Fabrication of Liquid Na-K Alloy-Based Membrane Electrode for Sodium Ion Batteries

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Experimental Section

Fabrication of Na-K-Sn@Cu mesh. Cu mesh (#200, Asone) was cut into discs, i.e., circular stainless steel with a diameter of 1.1 cm (0.95 cm^2) by a punch machine. The fabrication of Na-K-Sn@Cu mesh membrane electrodes was conducted in an argon-filled glove box with less than 1 ppm O_2 and H_2O . Typically, 0.50 g solid sodium (99.9%, Sinopharm) and 1.00 g solid potassium (99.9%, Sinopharm) were stacked together in mortar followed by soft squeezing by pestle to form the liquid Na-K alloy. Then, 0.38 g Sn powder (99.9%, Sinopharm) was added to Na-K alloy with gentle grinding to let alloy slowly adsorb Sn powder to obtain the final liquid alloy in the low-surface-tension state. At last, circular Cu mesh was immersed into the liquid alloy using tweezers, slowly adsorbing the mixture. The final membrane electrode was separated with tweezers from the remaining liquid alloy, which would be reused to prepare more Na-K-Sn@Cu mesh membrane electrodes. The Na-K-Sn@mesh membrane electrodes were fabricated in the same way except the current collector replaced by the stainless steel mesh (#500, Alfa).

Fabrication of Na-K@Cu foam. The Cu foam (Innochem) was also cut into circular shape (diameter of 1.1 cm, 0.95 cm^2) while the preparation of the Na-K alloy is the same as described in **Fabrication of Na-K-Sn@Cu mesh**. Then, some Cu foams were placed on and beneath the Na-K alloy ready for vacuum infiltration process. The mortar with Cu foam and the liquid alloy was put into the transferring chamber of the glovebox. Next, a vacuum is applied to the transferring chamber for 1 min, followed by the argon gas refilled. The argon gas would push the Na-K liquid into the porous membrane, making the scattered Na-K alloy stable in those small pores of the porous matrix.

Materials Characterization. The Na-K-Sn@Cu mesh was sealed with tape on the glass slide for materials characterization. $\text{Na}_{15}\text{Sn}_4$ phase detection was conducted by X-ray diffraction (XRD, PANalytical diffractometer) with Cu $K\alpha$ radiation ($\lambda = 1.5416\text{ \AA}$). The microscopic images were taken on an optical microscope of the Horiba Jobin-Yvon LabRAM ARAMIS system. Digital images were taken using the camera of the author's cell phone (MIUI 4).

Synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. Typically, 2.34 g NH_4VO_3 (99%, Sinopharm), 3.60 g NaH_2PO_4 (99%, Sinopharm) and 3.0 g citric acid (99.5%, Sinopharm) were dissolved into 50 mL distilled water, which was directly dried with vigorous stirring at $80\text{ }^\circ\text{C}$ on the hot plate. After gradual evaporation, the solution became sol that was too sticky to stir and transferred into air-circulating oven for deeper drying at $90\text{ }^\circ\text{C}$ for 24 h. Next, the as-prepared powder precursor was grounded and then calcined in a tube furnace for 8 h min at $750\text{ }^\circ\text{C}$ under a N_2 atmosphere to get the final $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ black powders.

Electrochemical Measurements. The 2032 coin-type cells were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. The $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes (loading of 1 mg cm^{-2}) were fabricated by putting the mixture of 70 wt% active material, 20 wt% carbon black, and 10 wt% PVDF with an appropriate amount of N-methyl-2-pyrrolidone (NMP) on an Al foil with 100 μm doctor blade. The slurry was dried at $90\text{ }^\circ\text{C}$ in an air-circulating oven. Some disks (11 mm in diameter) were tailored from the dried Al foil and then rolled as the electrodes while the high-loading ones (the free-standing $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode) were prepared in the same way except changing the ratio of active material, carbon black and PVDF to 80, 10 and 10 wt% and the thickness of the doctor blade to 1000 μm . The free-standing $\text{Na}_3\text{V}_2(\text{PO}_4)_3$

electrode would fall out from Al foil by enforced rolling process. All electrodes were further dried in vacuum at 120 °C for 12 h for cell assembly.

The cell assembly was based on a sandwich configuration:

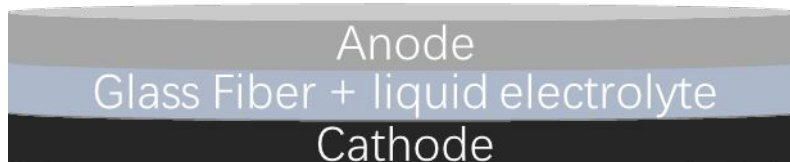


Figure S1. The sandwich configuration for cell assembly.

All cells were assembled using disk-type electrodes (11 mm in diameter) with 100 μL 1.0 mol L^{-1} solution of NaClO_4 in propylene carbonate (PC, Energy Chemical) with 5 vol% fluoroethylene carbonate (FEC, Energy Chemical) as electrolyte and a diameter of 16 mm glass fiber (GF/F, Whatman) as the separator.

In symmetric cells, the sodium metal and the Na-K-Sn@mesh were used as the electrodes on both sides. Each cell was cycled at 2.0 mA cm^{-2} for 0.5 h half-cycles on a battery test system (LAND CT2001A).

In the full cells with 1 mg cm^{-2} $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode, the sodium foil and the Na-K-Sn@mesh were used as the anodes while the 1 mg cm^{-2} $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode as the cathode. The galvanostatic charge-discharge tests were carried out at 2 C (1 C = 117 mAh g^{-1}) at a voltage window of 2.0-4.0 V on a battery test system (LAND CT2001A).

In the full cells with high-loading $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ material, the Na-K-Sn@mesh and the stacked free-standing $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode (Figure S6) were used as the anode and the cathode, respectively, a 1.0 mol L^{-1} solution of NaClO_4 in PC with 5 vol% FEC as electrolyte and glass fiber as the separator. The galvanostatic charge-discharge tests were carried out at 0.25 mA cm^{-2} at a voltage window of 2.0-4.0 V on a battery test system (LAND CT2001A).

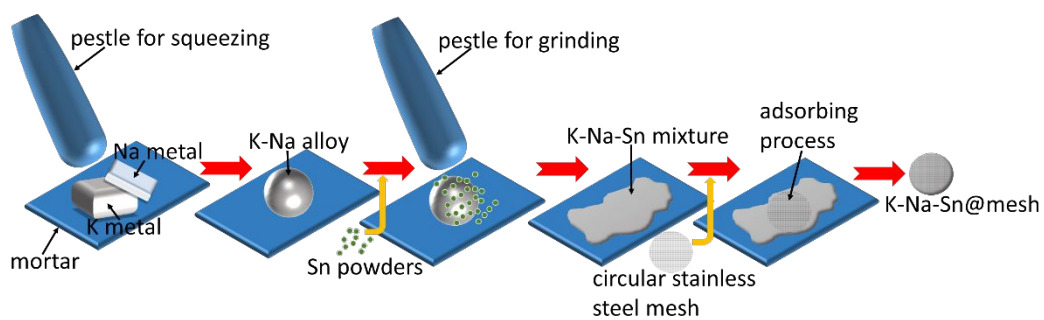


Figure S2. Preparation process of the Na-K-Sn@mesh membrane electrode

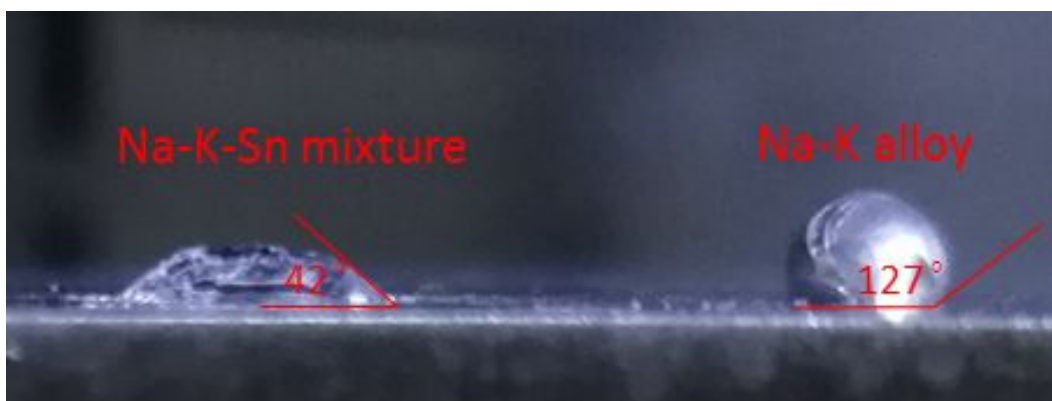


Figure S3. Photos of the Na-K-Sn mixture and the Na-K alloy on the stainless steel plate at room temperature.

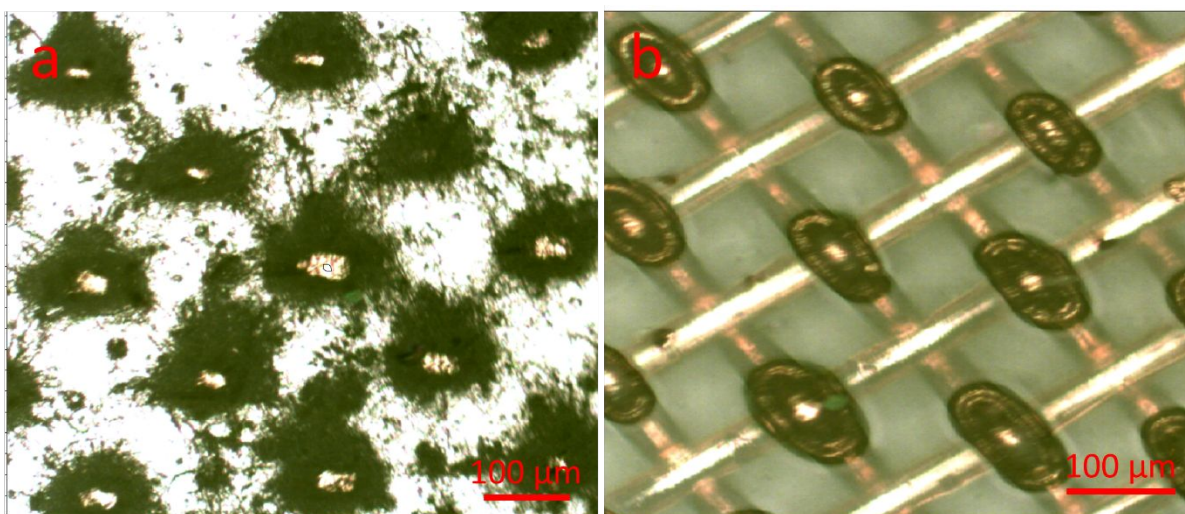


Figure S4. The microscopic images of the Na-K-Sn@Cu mesh (a) and pure Cu mesh (b) sealed with tape.



Figure S5. The successful immobilization of Na-K-Sn into (a) carbon felt, (b) carbon paper and (c) carbon cloth.



Figure S6. Experiment image of using vacuum infiltration method to reproduce Na-K@Cu foam.



Figure S7. Successful preparation of the Na-K@Cu foam membrane electrode using the transferring chamber of the glovebox as the special chamber of the vacuum infiltration method.



Figure S8. Unsuccessful preparation of the Na-K@Cu mesh. The experiment was conducted utilizing the same experiment design in Figure S4 with Cu foam and Cu mesh both beneath the Na-K alloy.

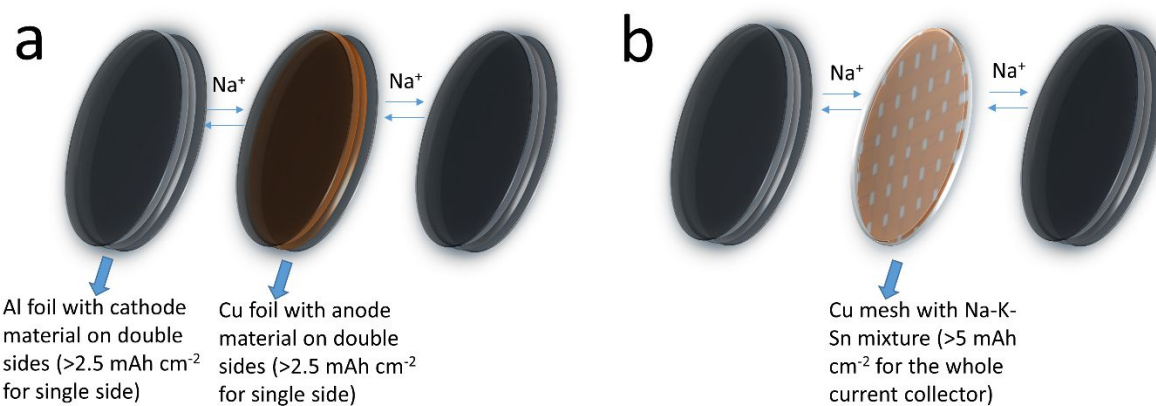


Figure S9. a) Conventional LIBs use double-printed metal foil with $>2.5 \text{ mAh cm}^{-2}$ loading for single side. b) For mesh-type current collector, it is actually storing Na^+ from two cathode sides with the requirement of $>5 \text{ mAh cm}^{-2}$.

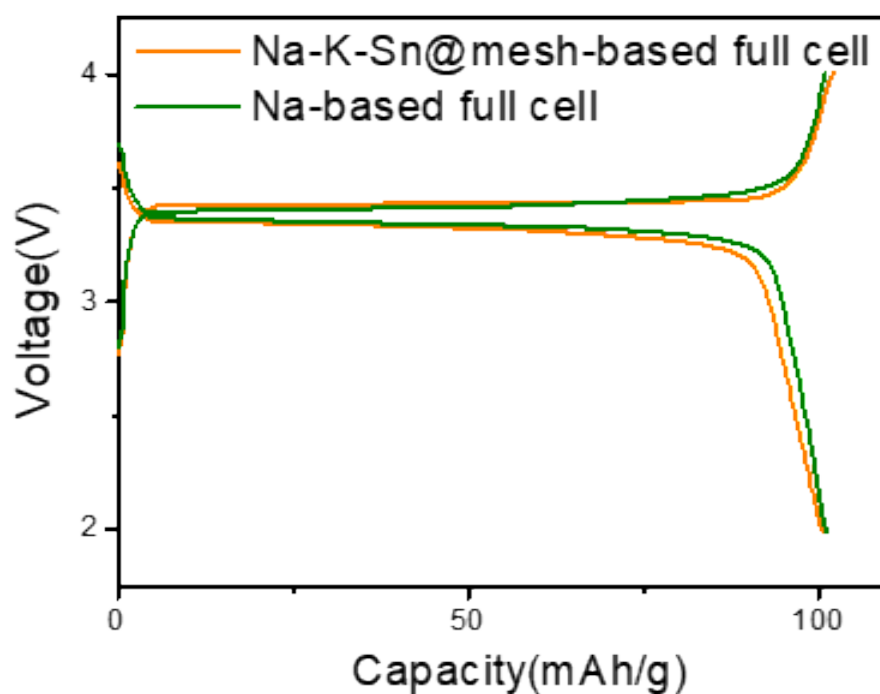


Figure S10. Charge/discharge curve at 2 C of the Na-K-Sn@mesh and pure Na foil. (1 C = 117 mA g^{-1})



Figure S11. The free-standing $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode used for the Na-K-Sn@mesh- $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ full cell with high areal loading of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ active material.