

## Electronic Supplementary Information (ESI)

### Sn-Carbon Nanocomposite Anode for All-Solid-State Chloride-ion Batteries Operating at Room Temperature

Hyeonsu Yang,<sup>a,b</sup> Seonghee Kim,<sup>a</sup> Sungho Lee,<sup>a</sup> Liwei Zhao,<sup>c</sup> Atsushi Inoishi,<sup>\*c</sup> Hikari Sakaebe,<sup>\*c</sup> Ken Albrecht<sup>\*c</sup> and Oi Lun Li<sup>\*a</sup>

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- a Department of Materials Science and Engineering, Pusan National University, 2 Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 46241, Republic of Korea. E-mail: helenali@pusan.ac.kr
- b Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen Kasuga-shi Fukuoka 816-8580, Japan.
- c Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-koen 6-1, Kasuga, Fukuoka 816-8580, Japan.  
E-mail: inoishi@cm.kyushu-u.ac.jp, sakaebe@cm.kyushu-u.ac.jp, albrecht@cm.kyushu-u.ac.jp

## Experimental section

### 1 Synthesis of the Sn@NC

The synthesis of Sn@NC was achieved using plasma engineering process. This method involved a plasma reactor containing the precursor solution and a pair of Sn electrodes facing each other. A high-voltage bipolar pulse generator (MPP-HV02, KURITA) was utilized to apply a 2.0 kV bipolar pulse to the electrodes. The electrodes were insulated with ceramic tubes, and each electrode was exposed by 1 mm at the liquid end to concentrate the applied energy. The pulse width and frequency were maintained at 1.0  $\mu$ s and 100 kHz, respectively. N,N-Dimethylmethanamide (DMF, Sigma-Aldrich) solution and Sn electrodes served as the precursors for Carbon and Sn, respectively. The entire synthesis process was conducted at atmospheric pressure and room temperature. The result solution was filtered using a 0.45  $\mu$ m pore size polytetrafluoroethylene filter and then washed several times with ethanol to remove residual precursor. Subsequently, the filtered powder was dried in an oven at 80°C for 12 hours.

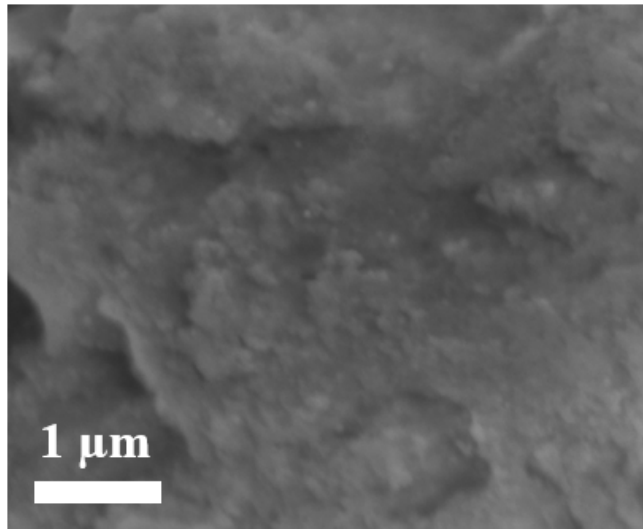
### 2 Materials characterization

Optical emission spectroscopy (OES) was performed using a spectrometer (Ocean Optics, FLAME-S-UV-VIS-ES). The surface morphology of synthesized material was observed using scanning electron microscopy (SEM, TESCAN Clara), transmission electron microscope (TEM, JEM-2100F) and high-resolution TEM (HR-TEM, JEM-2100F). Thermogravimetric analysis (TGA) was conducted using a Q600 analyzer (TA Instruments) at a heating rate of 10 °C min<sup>-1</sup> in an air atmosphere to determine the Sn concentration in the synthesized materials. Structural properties were analyzed by an X-ray diffractometer (XRD, SmartLab, RIGAKU) using filtered Cu K $\alpha$  radiation. Raman spectra were recorded using a microscope (DXR, Thermo Fisher Scientific) with laser irradiation at 532 nm. The N<sub>2</sub> adsorption–desorption isotherm was measured at 77 K using an N<sub>2</sub> adsorption analyzer (BELSORP-max, MicrotracBEL Corp.). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and the pore sizes were determined using the Barrett–Joyner–Halenda (BJH) methods. Prior to measurement, the sample was degassed at 300 °C for 3 hours.

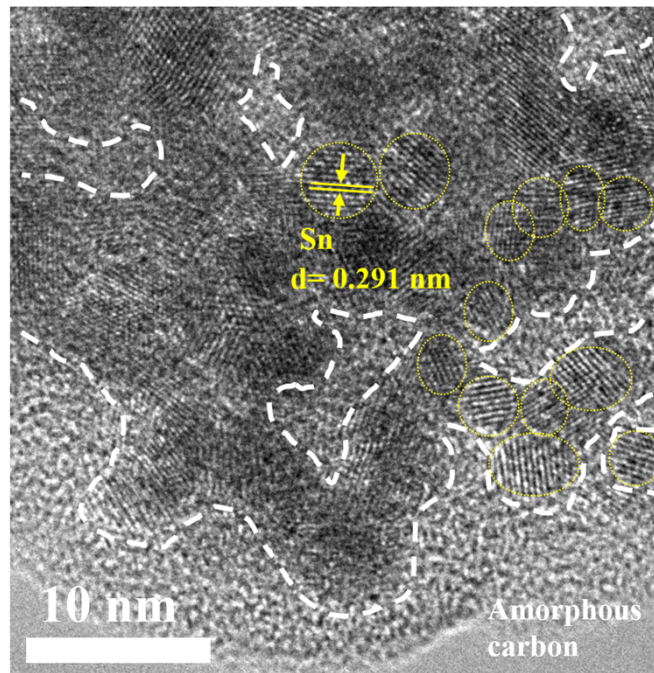
### 3 Electrochemical measurements

An all-solid-state chloride-ion battery cell consists of a CsSn<sub>0.95</sub>Y<sub>0.05</sub>Cl<sub>3.05</sub> (CSYC) solid electrolyte, a BiCl<sub>3</sub> cathode mix, and a Sn@NC anode mix. To prepare the CSYC, CsCl (Sigma-Aldrich), SnCl<sub>2</sub> (Sigma-Aldrich), and YCl<sub>3</sub> (Sigma-Aldrich) were used. These components were mixed in their respective ratios to form 1 g of the mixture, which was placed in a grinding vessel with a volume of 80 mL, along with 60 g of zirconia balls (diameter: 3 mm). The vessel was assembled in an Ar-filled glove box to prevent the ingress of oxygen and moisture. The mixture was mechanically rotated for 12 hours at a speed of 600 rpm using a planetary ball-mill apparatus. The cathode mix was prepared by mixing BiCl<sub>3</sub> (Sigma-Aldrich), CSYC, and acetylene black (AB) in a ratio of 4:5:1. The anode mix was synthesized by mixing Sn@NC, CSYC, and AB in a 4:5:1 ratio. The mixture was prepared by ball-milling at 150 rpm for 12 hours, using a powder-to-ball mass ratio of 1:40. For the cell with conventional Sn anode, Sn powder (99.5%, Wako Pure

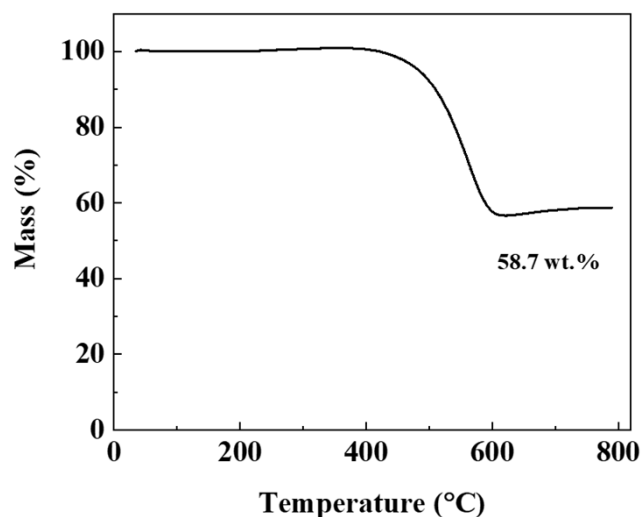
Chemical Industries, Ltd.) was used as the anode active material. To prepare the all-solid-state chloride-ion battery cell, 100 mg of CSYC electrolyte was pressed at 128 MPa with an internal diameter of 10 mm. Subsequently, this solid electrolyte was sandwiched between 25 mg of BiCl<sub>3</sub> cathode mix and 40 mg of Sn@NC anode mix and pressed at 510 MPa. For the conventional Sn anode cell, 18.4 mg of the Sn anode mix was loaded into the cell, matching the Sn content of the Sn@NC-based anode. Cell assembly was performed in an Ar-filled glove box. Galvanostatic charge-discharge tests were conducted at a current density of 20  $\mu\text{A cm}^{-2}$  in the voltage range of 0.01 to 0.8 V. The tests were conducted in a vacuum chamber.



**Fig. S1.** SEM image of Sn@NC



**Fig. S2.** HR-TEM image of Sn@NC

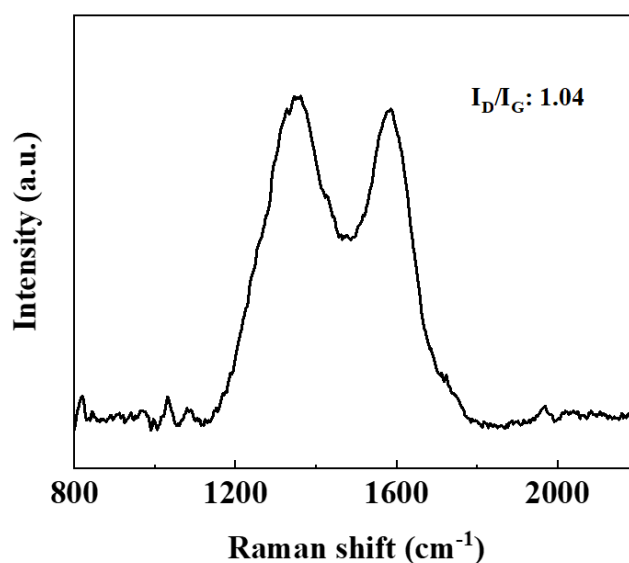


**Fig. S3.** TGA curve of Sn@NC

To confirm the mass content of Sn in Sn@NC, thermogravimetric analysis (TGA) was performed at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in an air atmosphere. The TGA curve of Sn@NC exhibits minimal changes up to approximately  $220\text{ }^{\circ}\text{C}$ , indicating stability at lower temperatures. A marginal mass increase is observed in the range of approximately  $220\text{--}400\text{ }^{\circ}\text{C}$ , which can be attributed to the oxidation of Sn. In contrast, a substantial weight loss occurs in the temperature range of approximately  $400\text{--}600\text{ }^{\circ}\text{C}$ , which corresponds to the decomposition of the carbon matrix. Assuming that Sn in Sn@NC is converted to  $\text{SnO}_2$  during the TGA process, the Sn concentration in Sn@NC can be calculated using equation (1) as follows:

$$\text{Sn(wt.\%)} = 100 \times \frac{\text{molecular weight of Sn}}{\text{molecular weight of SnO}_2} \times \frac{\text{final weight of SnO}_2}{\text{initial weight of Sn@C}} \quad (1)$$

Therefore, the Sn concentration in Sn@NC is calculated to be 46.2 wt.% based on the TGA results.



**Fig. S4.** Raman spectra of Sn@NC