Electronic Supplementary Information (ESI) *for*

Tin-based composite anodes for potassium-ion batteries

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Experimental details

Preparation of Sn-C composite

The Sn-C composite was prepared using a magneto-ball mill.[S1] Tin (Johnson Matthey, 99.9%) and graphite (Sigma Aldrich, 282863, < 20 μm) powders were mixed in a 7:3 weight ratio and 5 g of the mixture were loaded into a milling container with 4 stainless steel balls (25.4mm in diameter). The container was filled with an argon gas with an excess gas pressure of 100 kPa. The milling was carried out in the presence of an external magnet located at the bottom of the mill at 135° position in relation to the vertical direction with a rotation speed of 160 rpm for a period of 100h. The milled products were removed from the ball milling container in the presence of an inert Ar atmosphere.

Materials characterisation

X-ray diffraction (XRD) data were collected from powder samples and cycled electrodes on a PANalytical X'Pert Pro instrument using a Cu Kα radiation source (λ = 1.54181 Å) operated at 40 kV with 30 mA current. XRD data were recorded over a range of 10 - 90° by keeping the step angle and dwell time at 0.02° and 2 s. The X'Pert High Score Plus software was used to identify the phases present in the powder. The transmission electron microscopy (TEM) characterisation of the samples was performed using a JEOL JEM 2100F instrument operated at 200 kV. The elastic bright field image and energy filtered TEM (EFTEM) elemental maps of carbon and Sn were obtained using Gatan Quantum ER 965 Imaging Filter. The three-window method was used for the acquisition of the elemental maps that were subsequently combined in a colour-coded energy-filtered image. The quantitative energy-dispersive x-ray spectroscopy (EDS) analysis was performed in a JEOL JSM 7800F scanning electron microscope. Prior to the analysis, the sample was compacted into a pellet with a flat surface. Thermogravimetric analysis (TGA) was performed using a Q50 thermogravimetric analyser in

air atmosphere with the heating rate of 5°C/min to determine the amount of carbon and tin (Sn) in the sample.

Electrochemical characterisation

The Sn-C material was mixed with Super P Li™ carbon black (Timcal Ltd.) and a carboxymethyl cellulose (CMC) binder with a weight ratio of 80:10:10 in a de-ionized water to form a homogeneous slurry. The slurry was spread onto the cupper foil substrate and these coated electrodes were dried in a vacuum oven at 90°C for 24 h. The typical mass loading on the electrodes was 1.3 mg per cm^2. The electrodes was then pressed using a stainless steel metal disc to enhance the contact between the active materials and the Cu foil. Coin cells (CR 2032) were assembled in an Ar-filled glove box (Innovative Technology, USA). Potassium metal was used as counter/reference electrode and Whatman glass microfiber filter (grade GF/F) as a separator. The electrolyte was 0.75 M KPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. The cells were galvanostatically discharged/charged at a current rate of 25 mA g^{-1} in the potential range of 2 – 0.01 V vs K/K$^+$ using a computer controlled LAND battery system (Wuhan LAND Electronics, Ltd, China). Cyclic voltammetry (CV) tests were performed on a Solartron Analytical 1470E workstation and Biologic SP-150 galvanostat/potentiostat. The cycled electrochemical cells were disassembled in an Ar-filled glove box for the ex-situ XRD measurements. The cycled electrodes were taken out and washed with diethyl carbonate to remove the residual electrolyte.
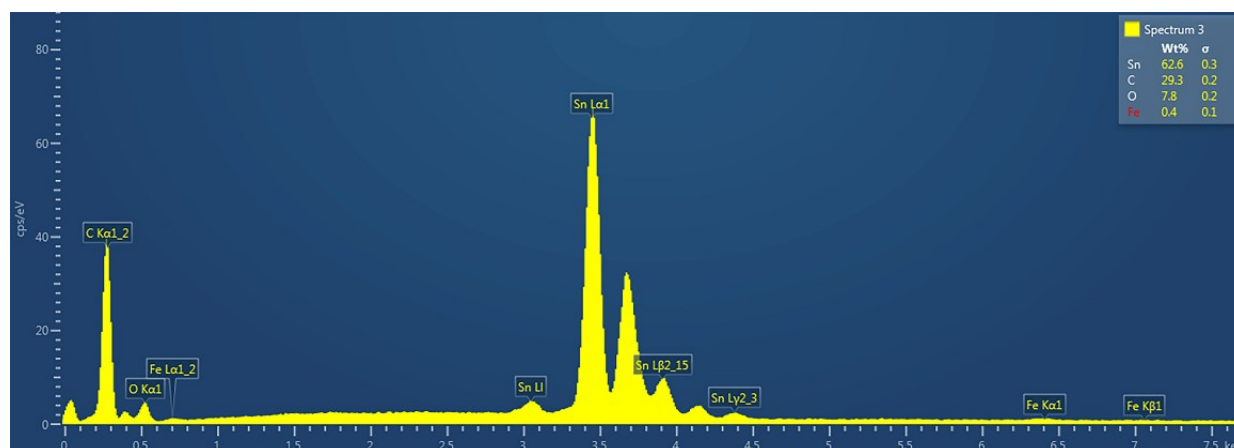
Quantitative EDS analysis

Fig. S1 A representative EDS output obtained from the Sn-C sample.

Composition estimate from TGA data

To estimate the amount of Sn and carbon in the Sn-C composite, TGA was carried out in air atmosphere. The sample was heated from 50 to 800°C at a rate of 5°C/min. As can be seen from Fig. S2, Sn-C powder started to oxidize slowly in air at temperatures above 200°C, with rapid oxidation above 280°C. It is observed that Sn-C composite powders showed rapid mass loss between 350-500°C, which corresponds to the burning of carbon. The Sn and C contents can be estimated as follows.

X = weight fraction of Sn

Y = weight fraction of C

X+Y=1   equation (S1)

The atomic mass of Sn is 118.7 amu. When Sn is oxidised in air, it forms SnO_2 (150.7 amu) and mass increases by 26.9 %. Assuming that the total mass in the experiment is Z g, carbon burns in air completely, Sn oxidises into SnO_2 and taking into account that the retained mass is 82.2 %, the following equation can be written:

Z (1 - Y + X*0.269) = 0.822*Z

or

Y = 0.269X + 0.178   equation (S2)

Solving equations (S1) and (S2), one may obtain weight fractions of X= 0.65 and Y= 0.35.

Therefore, it can be estimated that the amount of Sn and carbon in the composite is
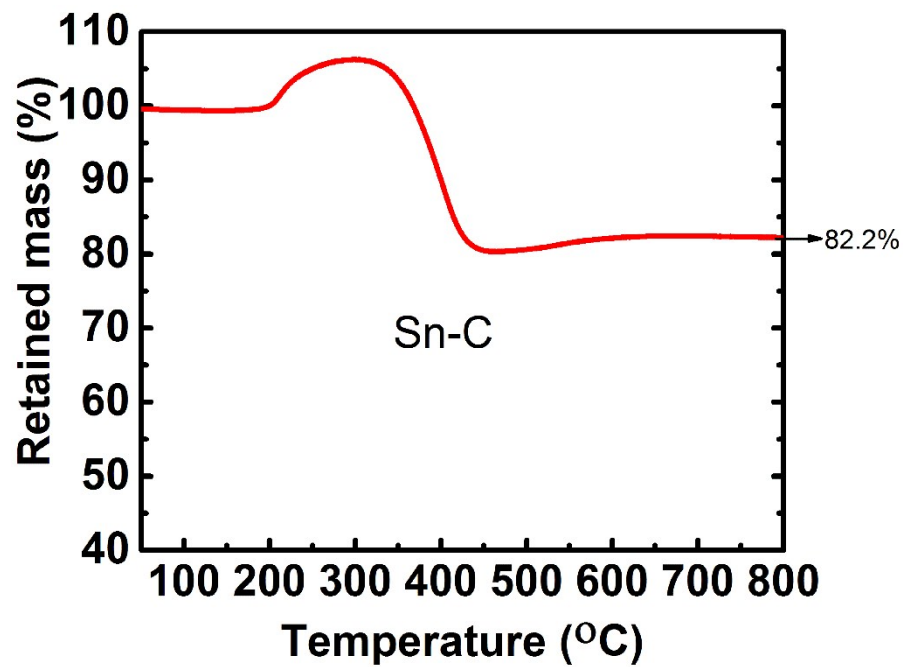
approximately 65 wt. % and 35 wt. %, respectively.

Fig. S2 TGA analysis of the Sn-C sample

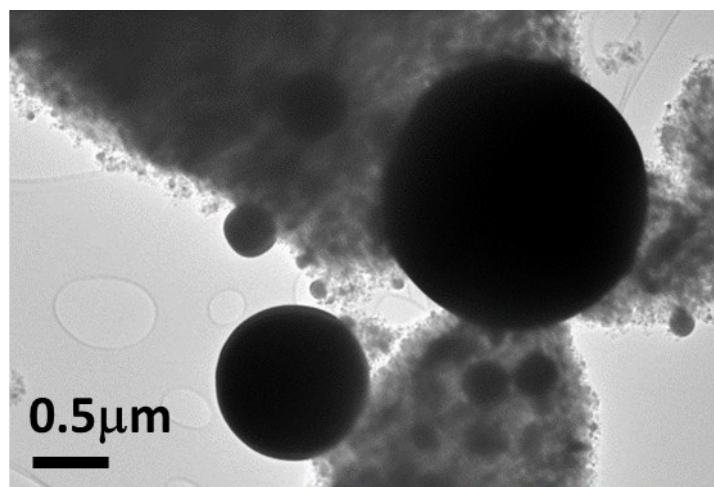**Sensitivity of the Sn-C sample to the electron beam irradiation in the TEM**

Fig. S3 TEM image of Sn balls evolving from the Sn-C composite under concentrated electron illumination.

The sample was sensitive to e-beam in the TEM during observation. Care was taken not to concentrate the intensity on the sample excessively in order to obtain proper images. When the beam intensity was concentrated on a small local area, real-time evolution of Sn balls (confirmed by energy-dispersive X-ray analysis) was observed (Fig. S2).

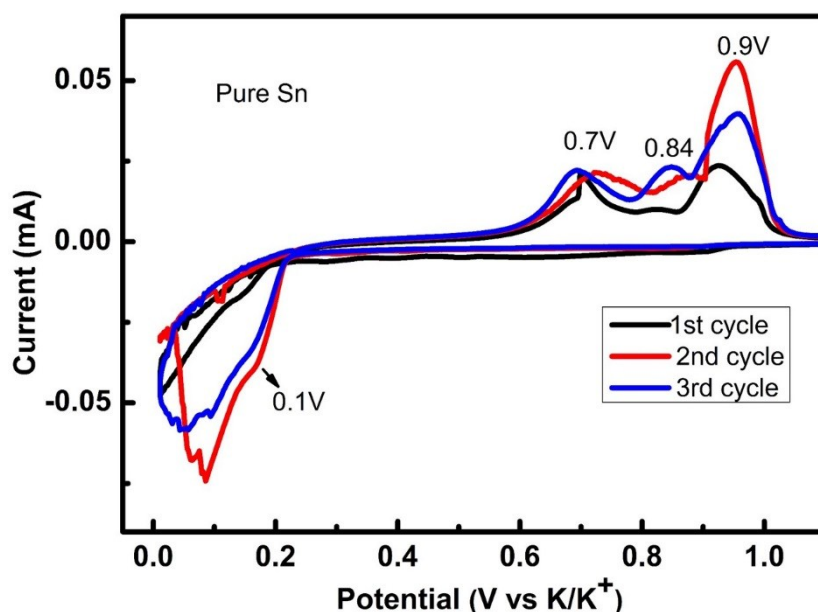**Cyclic voltammetry analysis of an electrode assembled with pure Sn**

Fig S4. CV curves of an electrode assembled with pure Sn. Alloying electrochemical process is visible, similar to that observed in Sn-C electrodes. An indicative range of $1.1 - 0.01$ V vs K/K^+ is shown.

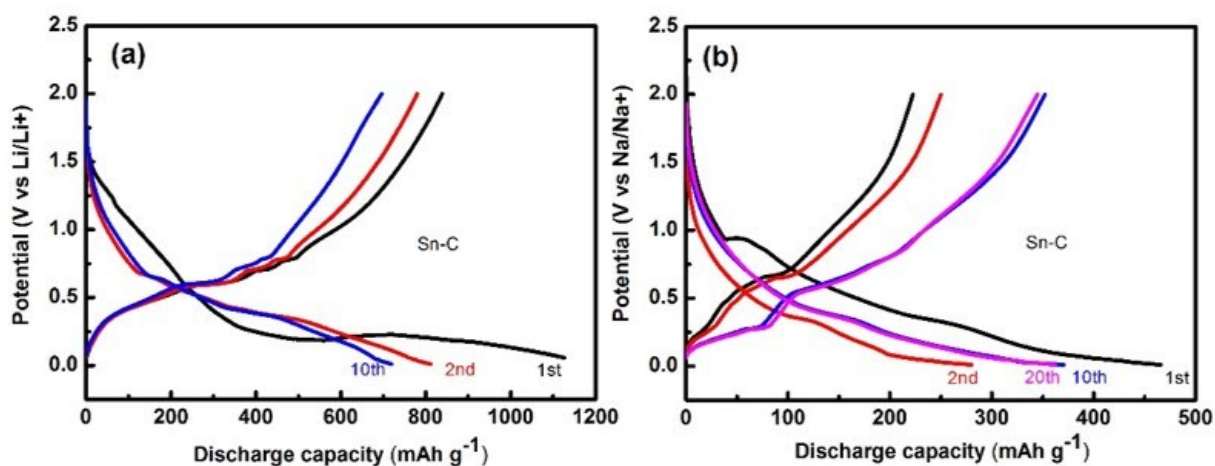**Discharge –charge curves of the Sn-C sample in lithium and sodium half-cells.**

Fig S5. Discharge-charge curves of the Sn-C electrode in lithium and sodium cells: (a) Li half-cell; (b) Na half-cell. Expected theoretical capacity is achieved in the lithium cell, while the capacity is the sodium cell is below the expected theoretically predicted capacity.

Supporting Information references:

S1 A. Calka and A. P. Radlinski, *Mater. Sci. Eng. A*, 1991, **134**, 1350.