Electronic Supplementary Material

Nanocrystalline SnS_2 coated onto reduced graphene oxide: demonstrating feasibility of a non-graphitic anode with sulfide chemistry for potassium-ion batteries

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Experimental details

***Preparation of SnS_2-reduced graphene oxide composite*:** The composite material was prepared by H_2S treatment of a peroxostannate - graphene oxide composite in accordance with a previously reported procedure (P.V. Prikhodchenko, D.Y. W. Yu, S.K. Batabyal, V. Uvarov, J. Gun, S. Sladkevich, A.A. Mikhaylov, A.G. Medvedev and O. Lev, Nanocrystalline Tin Disulfide Coating of Reduced Graphene Oxide Produced by the Peroxostannate Deposition Route for Sodium Ion Battery Anodes. *J. Mater. Chem. A* **2014**, *2*, 8431-8437.).

***Characterization*:** X-ray powder diffraction (XRD) measurements were performed on a D8 Advance Diffractometer (Bruker AXS) with a goniometer radius 280 mm and Cu Kα radiation. XRD patterns were processed using DIFFRAC.SUITE software package. The morphology of the material was analyzed using a FEI Sirion high-resolution scanning electron microscope coupled with an x-ray energy dispersive spectrometer (EDS, Oxford Instruments). Transmission electron microscopy (TEM) analysis was conducted on JEOL JEM 2100F and FEI Tecnai F20 G2 electron microscopes. Energy-filtered images were obtained using a Gatan Quantum ER 965 Imaging Filter attached to the JEOL JEM 2100F instrument. Scanning transmission electron microscopy (STEM) imaging was performed on the same JEOL JEM 2100F instrument and also at 20 kV using an FEI Magellan 400L extra high-resolution scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra X-ray photoelectron spectrometer (Manchester, UK) with a monochromated Al Kα (1486.6 eV) X-ray source with 0˚ takeoff

angle. Data analysis was performed with Vision processing data reduction software (Kratos Analytical Ltd) and CasaXPS (Casa Software Ltd).

***Electrochemical testing*:** SnS_2 - reduced graphene oxide powder was mixed with Super P Li™ carbon black (Timcal Ltd) and sodium carboxymethyl cellulose (CMC, Aldrich) binder with a weight ratio of 80:10:10 in a de-ionized water to form a homogeneous slurry. The slurry was then coated onto round Cu foils with a diameter of 1.5 cm. The coated electrodes were dried at 100 °C in a vacuum oven for 12 hours. The CR2032 coin cells were fabricated inside an argon-filled glove box (Innovative Technology, USA). Potassium metal was used as counter/reference electrode and glass microfiber filter paper (Whatmann GF/F, USA) was used as the separator. An electrolyte consisting of 0.75M KPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 was used. The same electrolyte with 3 vol.% of fluoroethylene carbonate (FEC) was also used in a comparative test. The cells were galvanostatically discharged and charged at different current ranges in the potential range of 2 – 0.01 V vs K/K^+ using a LAND battery system (Wuhan LAND Electronics Ltd, China). The temperature for testing was maintained at 25 °C. Mass loadings of the electrodes were controlled in the range of 0.8 - 0.93 mg cm^{-2} (counting the total mass of the electrode coatings on copper foils). The currents and capacities in this work are reported per total mass of the electrode (including active material, binder and carbon black). The cyclic voltammetry experiment was carried out on an Ivium-n-stat instrument (Ivium Technologies, the Netherlands) at a scan rate of 0.5 mV s^{-1}.

XPS data

The XPS spectrum of the electrode material is shown in Figure S1. The scan of S 2p binding energies (Figure S1a) of the material reveals, after deconvolution, two pairs of binding energies at 162.1/163.3 and 164.1/165.3 eV, corresponding to the sulfide and a minor amount of elemental sulfur, respectively. The Sn 3d spectrum (Figure S1b) shows that Sn 3 d5/2 (and Sn 3 d3/2) can be deconvoluted to two peaks separated by less than 0.1 eV, and these peaks can be attributed to the tin in the SnS_2 and SnO_2 phases. SnO_2 is indeed an intermediate in our preparation route and it is quite possible that a minor amount of tin oxide is present in the resultant sample as an impurity.

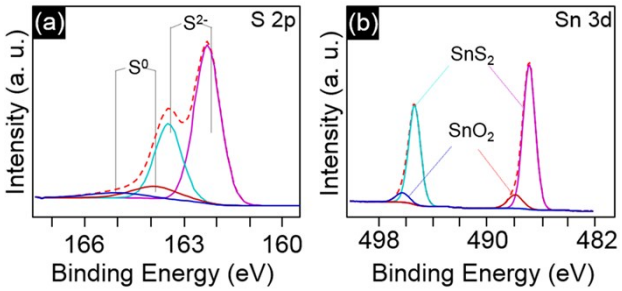

Figure S1. XPS analysis of the material: S 2p (a) and Sn 3d (b) spectra.

Additional electron microscopy data

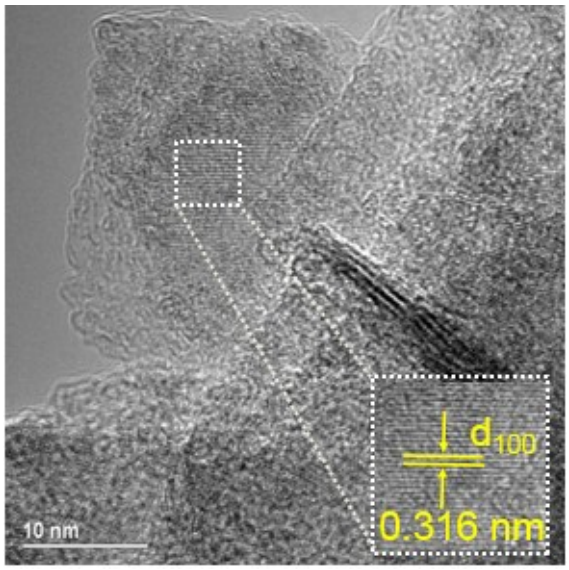

Figure S2. High resolution TEM image demonstrating a lattice image of a SnS_2 nanocrystal.

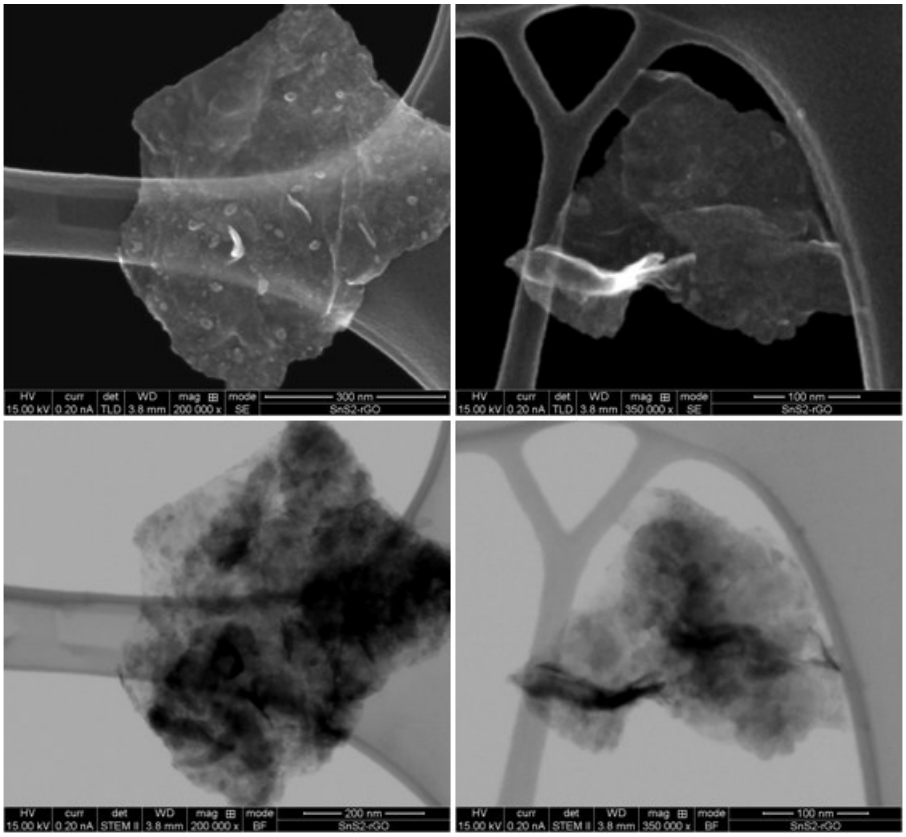

Figure S3. SEM and STEM images of two flakes of SnS_2-rGO: top row – SEM images; bottom row – STEM images

Additional electrochemical data

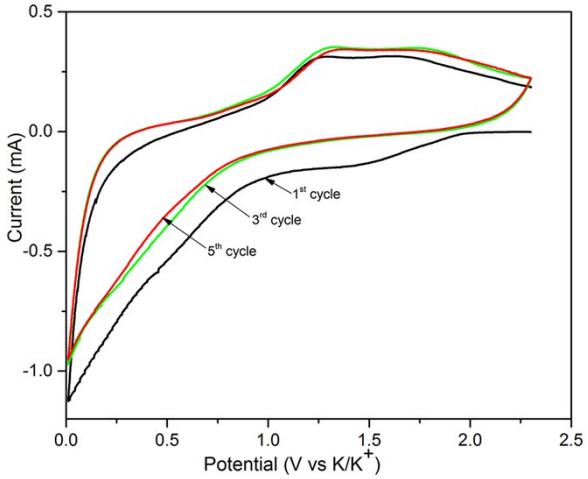

Figure S4. Cyclic voltammetry curves of SnS_2-rGO at a scan rate 0.5 mVs^{-1}.

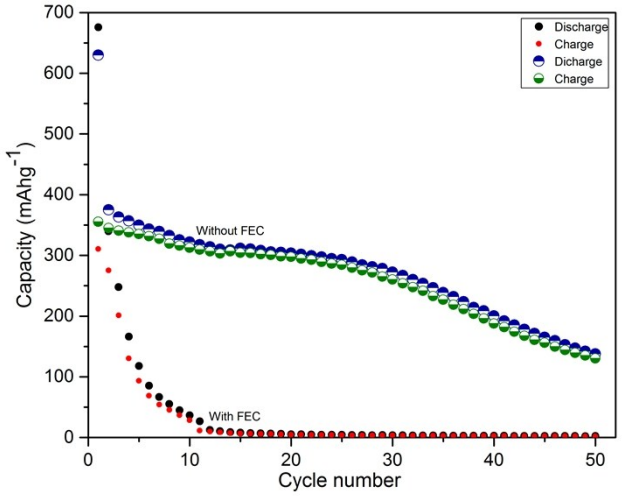

Figure S5. Comparative cycling stability analysis of SnS_2-rGO cell with and without 3 vol.% fluoroethylene carbonate additive.

X-ray diffraction studies of discharged and charged electrodes

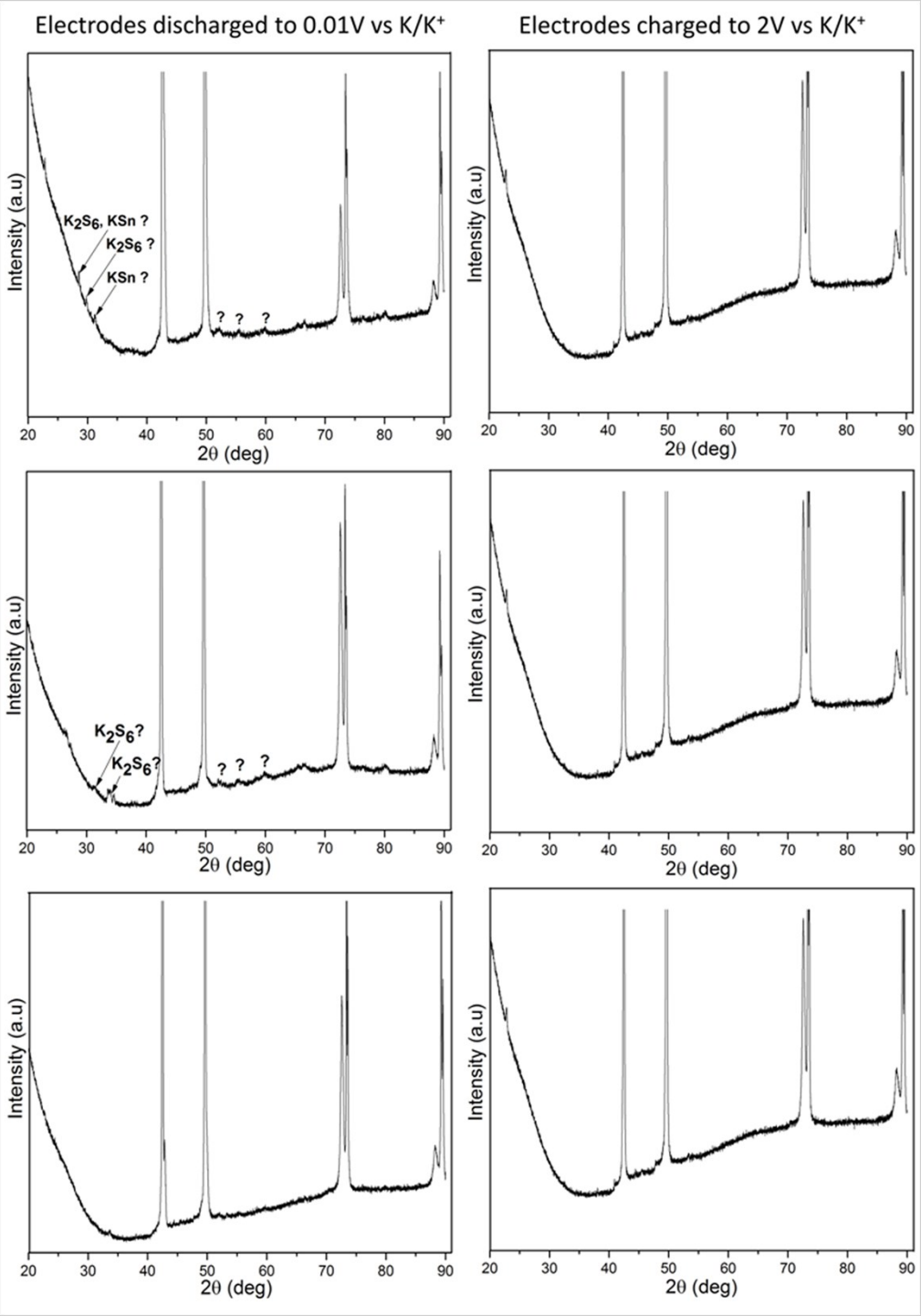

Figure S6. XRD patterns of SnS_2-rGO electrodes after the first discharge (left-hand side column) and first charge (right-hand side column) potassium cells with materials loadings 1.95-2.15 mg/cm^2. The data from electrodes extracted from three cells are shown in each case.