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Exploring the electrochemical stability mechanism of SnS_2-based composite in dimethoxyethane electrolyte for potassium ion batteries

Jizu Zhang,[a] Sibo Chen,[a] Zuhang Huang,[b] Wanggang Zhang,[c] Zhicong Yuan,[d] Yiming Liu,*[c] Wenjie Mai[a] and Jinliang Li*[a]

[a]*Siyuan Laboratory, Guangzhou Key Laboratory of Vacuum Coating Technologies and New Energy Materials, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics, Jinan University, Guangzhou 510632, People's Republic of China.*

[b]*College of Chemistry and Materials Science, Jinan University, Guangzhou, 510632 People's Republic of China.*

[c]*College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China.*

[d]*Dongguan Power Supply Bureau, Guangdong Power Grid Co., Ltd, Dongguan 523000, People's Republic of China.*

Corresponding authors: E-mail: lijinliang@email.jnu.edu.cn (J.L. Li); liuym812@163.com (Y.M. Liu)

Experimental section

Synthesis

Graphene oxide (GO) was obtained by a modified Hummers' method, which has been described in our previous work [1, 2]. Firstly, 10 mmol of $SnCl_4$•$5H_2O$ and 30 mmol thioacetamide (TAA) were added into a 170 mL water/ethanol (7/3, v/v) mixed solution with 480 mg GO under vigorously stirring at 60 °C for 4 h. After that, placed 60 mL of the above-mixed solution in each 100 mL Teflon-lined stainless-steel autoclave for solvothermal treatment at 180 °C for 12 h. Whereafter, the precipitate was collected and washed with deionized water by centrifuge after cooling to room temperature. Then the precipitate was transferred to a container for freeze drying (-50 °C, pressure < 20 Pa) for 2 days, specified as SnS_2-GO. Subsequently, the obtained SnS_2-GO was moved to a tube furnace for heat treatment at 500 °C for 2 h with a heating rate of 5 °C min^{-1} in a nitrogen atmosphere, denoted as SnS_2-RGO. The corresponding synthesis schematic is shown in Figure 1a.

Characterization

The morphologies of SnS_2-RGO composites were characterized by field emission scanning electron microscopy (SEM, Zeiss Ultra 55) and transmission electron microscopy (TEM, JEOL 2100F). The structural and surface properties were confirmed by X-ray diffraction (XRD, Rigaku, MiniFlex600), X-ray photoelectron spectra (XPS, Thermo Fisher Scientific, K-Alpha), and Raman spectroscopy (Horiba T64000) with a wavelength of 532 nm.

Electrochemical test

For the preparation of the electrode, the active materials, super P and carboxymethylcellulose sodium with the proportion of 8:1:1 were mixed into moderate deionized water to form a homogeneous sizing agent and then coated onto the coarse copper foil. After fully drying, the electrode was sliced into a disc with a diameter of 14 mm. The average mass of the active materials in each disc was about 1 mg cm^{-2}. The coin-type CR2032 half-batteries were assembled in an Ar-filled glove box (Etelux Lab 2000, O_2 and H_2O < 0.1 ppm), using metallic potassium as a counter electrode and Whatman glass fiber as the separator. Different concentrations of KFSI dissolved into DME were used as the electrolyte. The electrochemical performance of batteries was evaluated by the battery test system (Neware BTS-4000) in the voltage range from 0.01 V to 3 V at 100 mA g^{-1} except as otherwise noted. Cyclic voltammetry (CV) measurements were conducted by a Chenhua electrochemical workstation (CHI 1030C) at a scan rate of 0.2 mV s^{-1}. Electrochemical impedance spectra (EIS) were recorded by a Princeton electrochemical workstation (Veras STAT 3-400) with a frequency range from 10^{-1} Hz to 100 kHz.

In-situ Raman measurement

We used the same electrode in battery measurement for the In-situ Raman measurement. The glass fiber membrane was punched into a hole with a diameter of 2 mm as a separator and Metallic K foil was punched into a hole with a diameter of 2 mm as a counter electrode. After that, the corresponding electrolyte was injected from the hole, and then used quartz glass to encapsulate the battery for the in-situ Raman

measurement. During the measurement, the 532 nm laser was transmitted to the quartz glass and hole to reach the electrode.

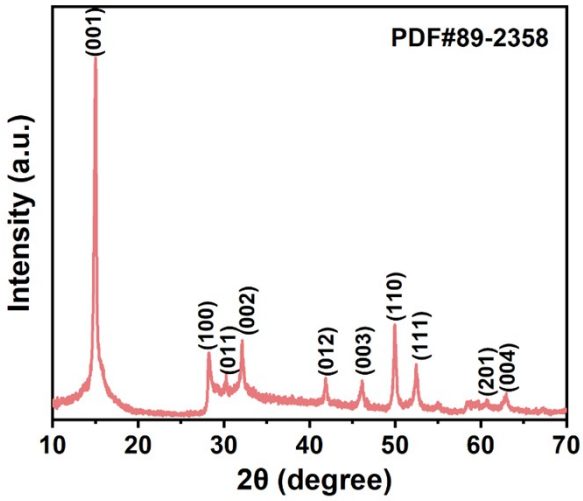

Figure S1 XRD pattern of SnS_2-RGO composite.

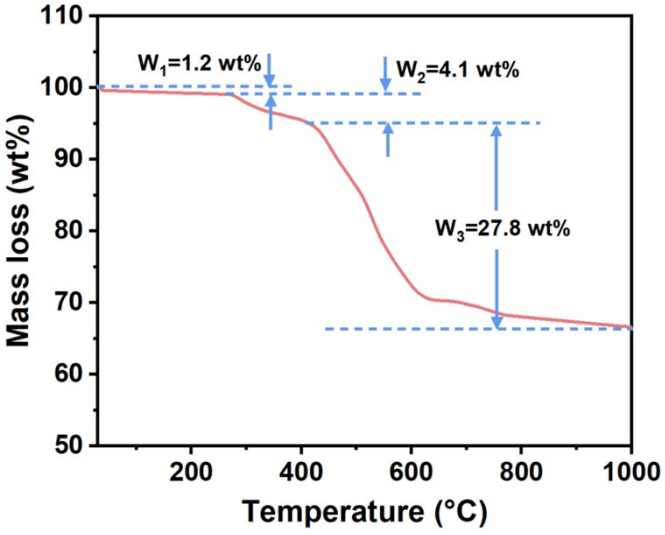

Figure S2 TGA curve of SnS_2-RGO composite.

From the TGA curve, the W_1 should be the water evaporation, W_2 is deemed to be the combustion of RGO, and W_3 is designated to the combustion of RGO and the oxidation of SnS_2. Since the final product of the SnS_2-RGO composite after high-temperature treatment is SnO_2, we can obtain the content of RGO in the composite

according to this result. From the TGA, the RGO content is 17.9% in the composites after calculation.

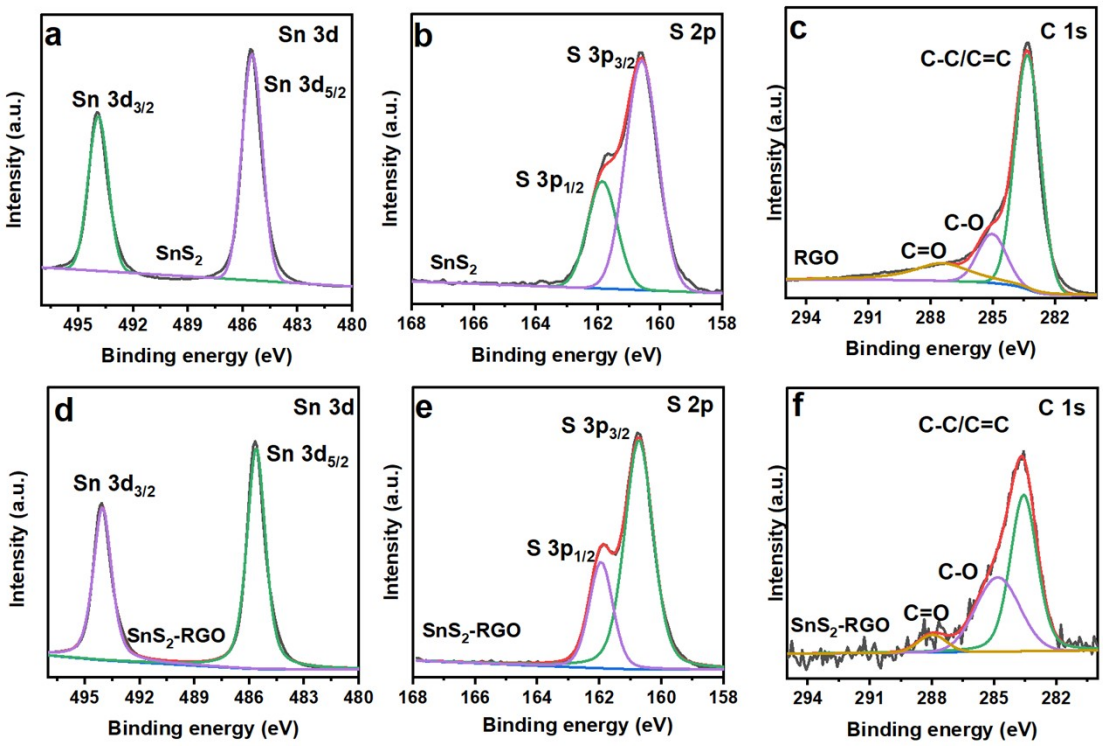

Figure S3 (a) Sn 3d and (b) S 2p XPS of SnS_2; (c) C 1s XPS of RGO; (d) Sn 3d, (e) S 2p and (f) C 1s XPS of SnS_2-RGO composite.

Figure S4 Photograph of DME-9.

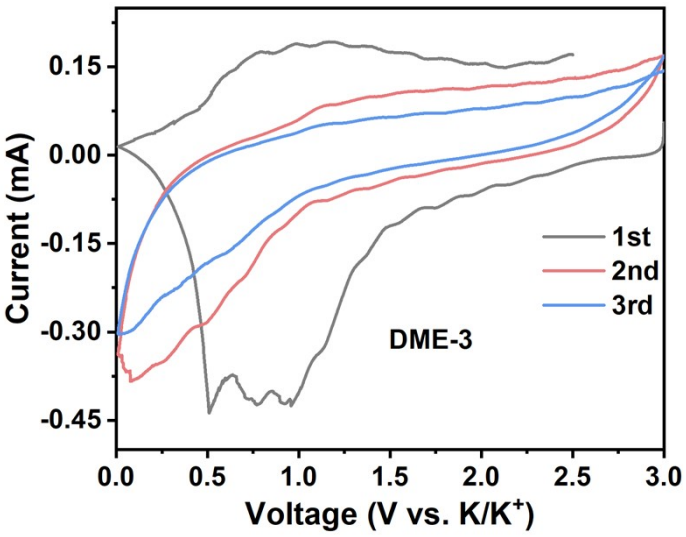

Figure S5 CV curves SnS_2-RGO composite with DME-3 electrolyte.

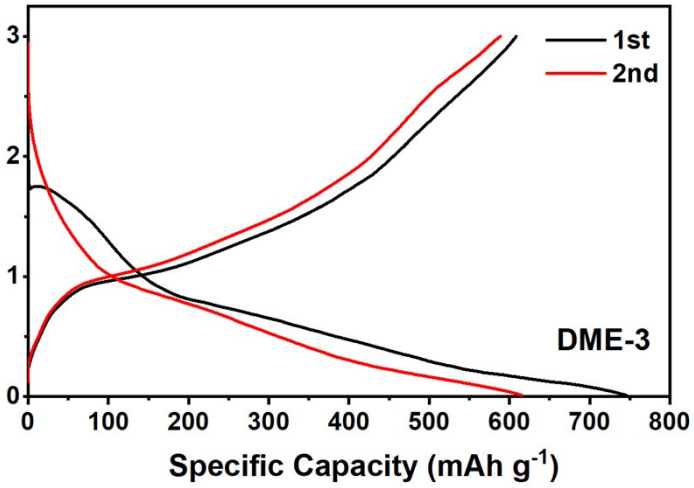

Figure S6 GCD curves SnS_2-RGO composite with DME-3 electrolyte.

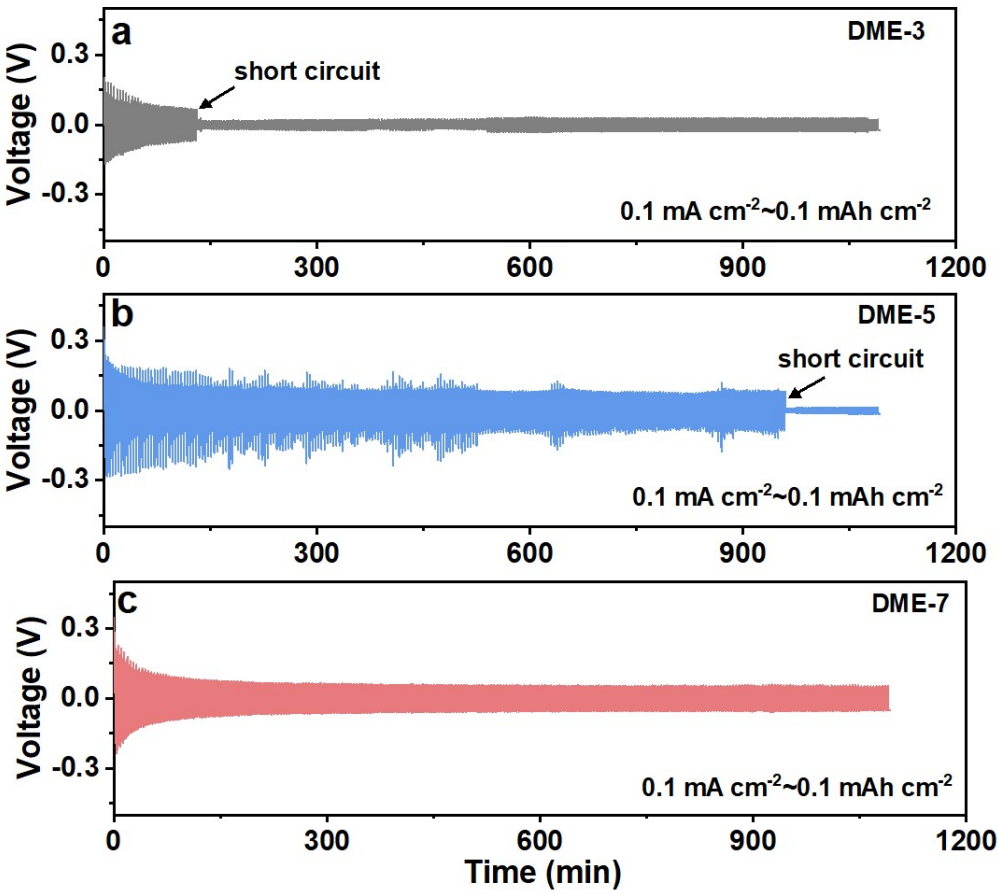

Figure S7 The electrochemical performance of K||K symmetrical batteries with (a) DME-3, (b) DME-5, and (c) DME-7 electrolytes at 0.1 mA cm^{-2}~0.1 mAh cm^{-2}.

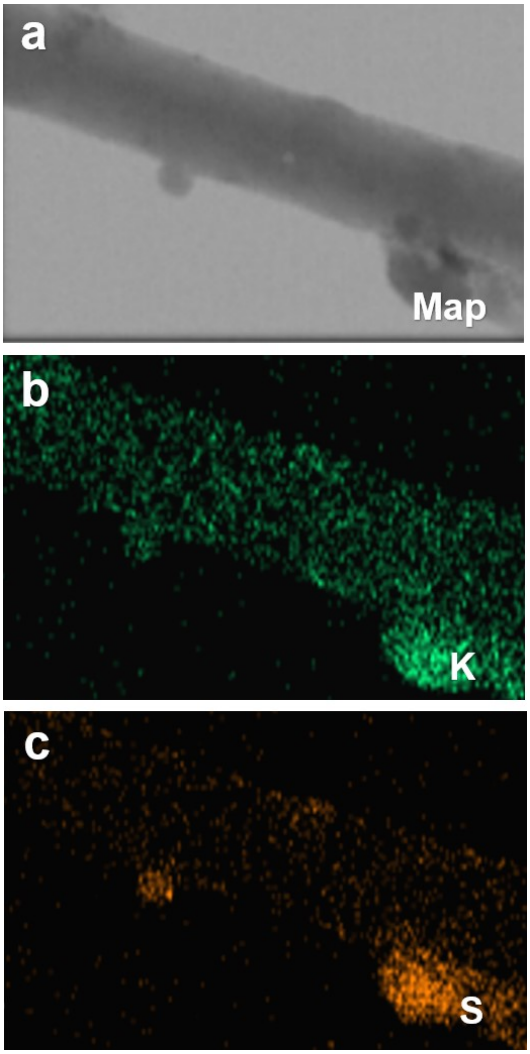

Figure S8 (a) Map (b) K and (c) S element mapping of needle-like by-product in the SnS_2-RGO electrolyte with DME-3 electrolyte after 50 cycles.

[1] J. Xie, Y. Zhu, N. Zhuang, H. Lei, W. Zhu, Y. Fu, M.S. Javed, J. Li, W. Mai, Rational design of metal organic framework-derived FeS_z hollow nanocages@reduced graphene oxide for K-ion storage, Nanoscale, 10 (2018) 17092-17098.

[2] J. Li, W. Qin, J. Xie, H. Lei, Y. Zhu, W. Huang, X. Xu, Z. Zhao, W. Mai, Sulphur-doped reduced graphene oxide sponges as high-performance free-standing anodes for K-ion storage, Nano Energy, 53 (2018) 415-424.