

Decreasing the Ion-Diffusion Pathways for the Intercalation of Multivalent Cations into One-Dimensional TiS₂ Nanobelt Arrays

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SUPPORTING INFORMATION

EXPERIMENTAL SECTION

Synthesis

We have previously reported the synthesis of vertically aligned, binder- and carbon-free TiS₂ electrodes.^{1, 2} In this study, the growth substrate was changed from Al foil to carbon paper, as the ionic liquid electrolyte used for the fabrication of Al-TiS₂ electrochemical systems corrodes the Al foil. Oxygen and water exposure were limited by performing all work on a Schlenk-line or in an argon-filled glovebox. All materials were used as received without any further purification. To synthesize TiS₃ nanobelt arrays (which are used as a sacrificial layer for the synthesis of TiS₂), a Denton Discovery 18 sputter system with a titanium (Ti) sputtering target (Kurt J. Lesker 99%, 1.0" Dia. X 0.125" thick) was used to sputter a ~1.6 μm-thick Ti layer on carbon paper (Fuel Cell Store, Sigracet 39 AA). A 5/8" x 3" piece of sputtered Ti-coated carbon paper was then placed in a borosilicate ampule with ~85 mg of sulfur (S) powder (Alfa Aesar 99.5%, ~100 mesh) and evacuated to ~10⁻³ Torr using a vacuum line before flame-sealing. The sealed reaction ampule was heated to 450 °C at 10 °C min⁻¹ and held at 450 °C for 20 h. The ampule was subsequently removed from the oven and placed on an aluminum block to induce rapid quenching of the

reaction. The as-prepared TiS_3 nanobelts were converted to TiS_{2-x} by transferring the substrate to a new borosilicate ampule with ≈ 150 mg Ti powder (Alfa Aesar 99%, ~ 325 mesh) precursor added. The Ti powder acted as a sink for the volatilized sulfur released as the sacrificial TiS_3 was pyrolyzed. A glass wool plug was inserted between the TiS_3 substrate and the Ti powder to block physical contact during handling. This ampule was evacuated and flame-sealed under vacuum. The pyrolysis reaction ampule was placed in a furnace and heated to 450°C at $10^\circ\text{C min}^{-1}$ and held at 450°C for 48 - 144 h. At the end of the reaction time, the pyrolysis reaction ampule containing the TiS_{2-x} nanobelts was cooled to ambient temperature inside of the furnace.

Characterization

The morphologies of the resulting products were examined using a scanning electron microscope (SEM) equipped with a field-emission gun (FEI Nova Nano, FE-SEM 630) operated at an accelerating voltage of 10 keV. Phase identification and purity of the as-synthesized TiS_3 and TiS_{2-x} nanobelts were obtained by x-ray diffraction (XRD) using a Bruker D8 Advance diffractometer, at a scanning rate of $1.2^\circ \text{ min}^{-1}$ in a 2θ range between $5 - 70^\circ$ using monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The operating voltage and current were kept at 40 kV and 40 mA, respectively. The dimensions and crystallinity of the as-synthesized nanobelts were examined using a JEOL JEM 2800 field-emission gun transmission electron microscope (FE-TEM) operated at 200 keV. High-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were independently acquired and provided insights into the crystal growth habits and crystallinity of the TiS_{2-x} nanobelts. To prepare samples for TEM/SAED analysis, the nanobelts were dispersed in isopropanol via sonication and then deposited onto a 400-mesh holey carbon-coated copper grid. The precise Ti/S stoichiometries were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) analyses. The solid samples were digested using a 2.5:2.5:1 $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}$ solution heated to 85°C for 12 h before injection into the ICP-MS column. An error of 1% is expected when determining the stoichiometry of our samples via ICP-MS

Electrochemical studies

Cathodes were fabricated by punching ½” diameter discs from the TiS_{2-x} -coated carbon paper substrate. Each disc had ~0.5 mg TiS_{2-x} nanobelts. CR2032 coin cells were assembled in an argon-filled glove box using the cathode prepared above and Al foil (Alfa Aesar 99.997%, 0.2 mm) as the anode. A glass fiber filter (Whatman) was used as the separator. The electrolyte was prepared by slowly adding anhydrous AlCl_3 (Sigma Aldrich 99.99%) to 1-butyl-3-methylimidazolium chloride (Acros 98+%) in a ratio of 1.5:1 in an argon-filled glovebox. The batteries were constructed in the following manner: bottom cup, Ti disc (Alfa Aesar 99.5%, 0.25 mm), Sigracet 39 AA carbon paper, cathode, electrolyte (20 μL), separator, electrolyte (30 μL), Al anode, Sigracet 39 AA carbon paper, Ti disc, and top cap. Ti discs were added to prevent the corrosion of the stainless-steel battery case by the electrolyte during cycling. All cathodes were soaked in the electrolyte for about 90 minutes. All half-cells were tested three times to ensure reproducibility.

Galvanostatic measurements were conducted at room temperature and at 50 °C using a Neware BT-4008 battery testing system. Al-ion cells were cycled between 0.2 V and 1.3 V *versus* Al^{3+}/Al . The capacity retention study was cycled at different rates ranging from 1 - 5 C. The long-term capacity fade study was cycled at a theoretical rate of 1 C. For all capacity studies, the cells were charged and discharged at the same C rates. The specific capacity and coulombic efficiency calculations are determined within a $\pm 1\%$ uncertainty error. The GITT study was discharged at a theoretical rate of 0.1 C. All batteries tested for the GITT study were discharged for 60 s and then allowed to rest for 3 h before the next discharge. Cyclic voltammetry (CV) studies were performed on a CH Instrument (CHI660E) electrochemical workstation. Each test was performed using a CR2032 coin cell with the cathode as the working electrode and the anode as the counter and reference electrodes. All GITT measurements were acquired three times for each coin cell tested.

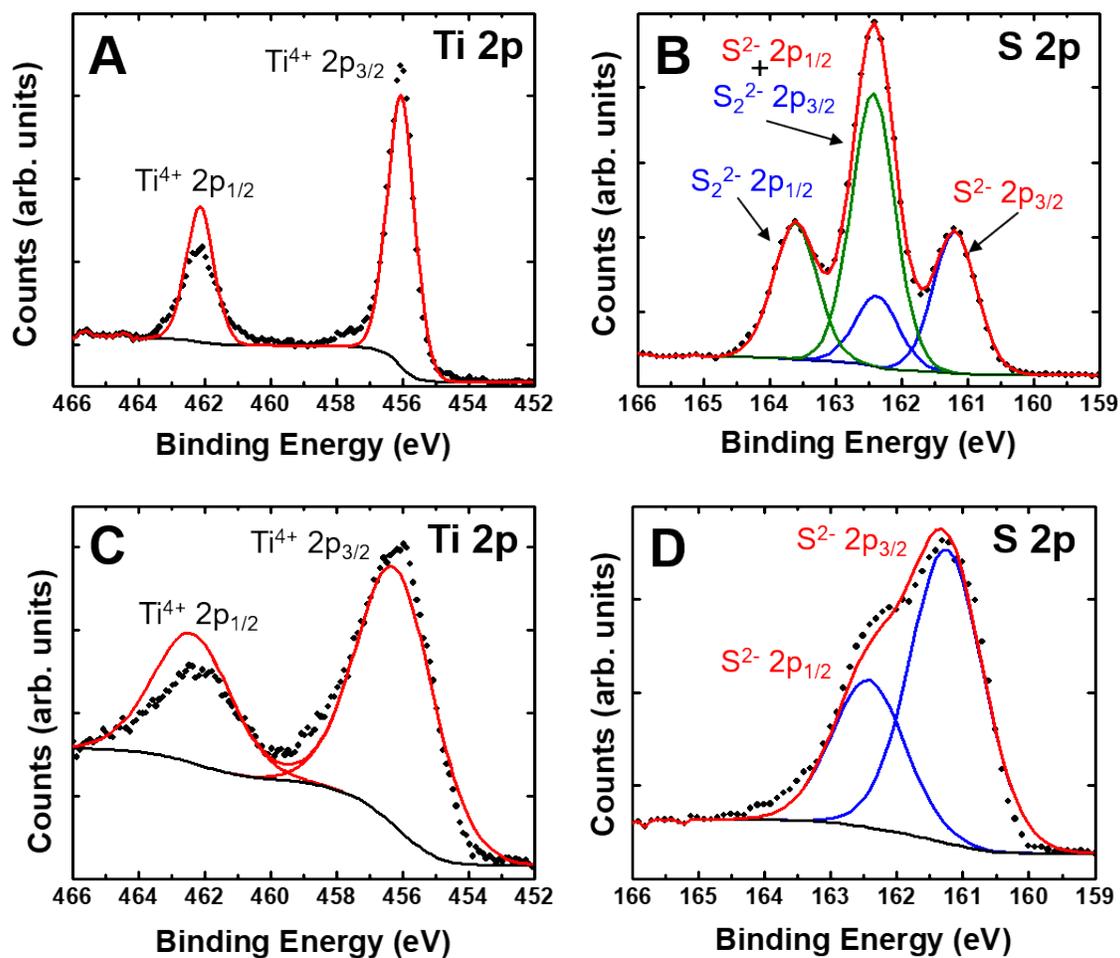


Figure S1. XPS spectra for vertically oriented TiS₃ and TiS_{2-x} nanobelt arrays. (A,B) Ti 2p and S 2p regions, respectively, for TiS₃. (C,D) Ti 2p and S 2p regions, respectively, for TiS_{2-x}. The sample used for acquiring the XPS data in C and D was pyrolyzed at 450 °C for 48 h to yield TiS_{1.98} as per previous published works.^(1,2)

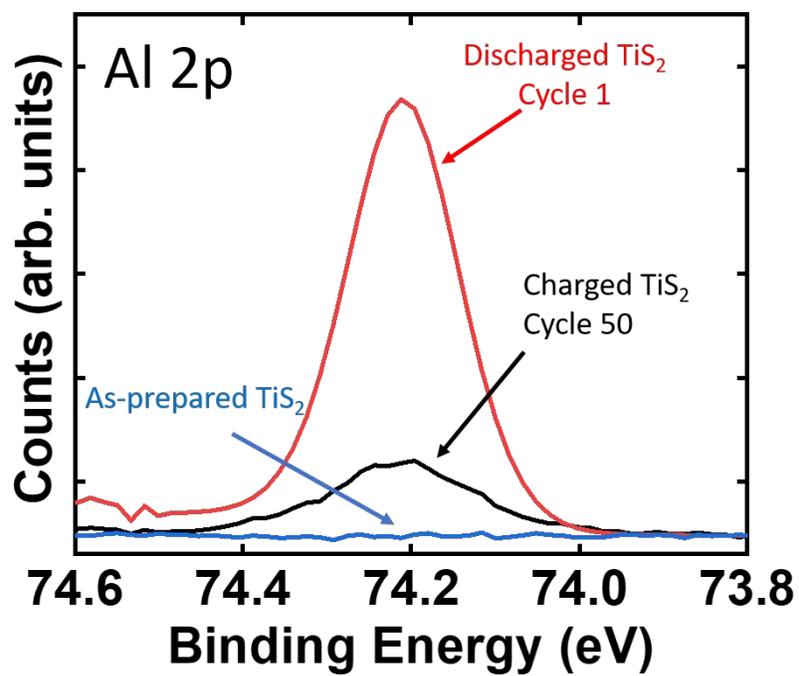


Figure S2. Al 2p XPS spectra for TiS_{2-x} nanobelts upon discharging and charging. As-prepared TiS_{2-x} is presented as a control.

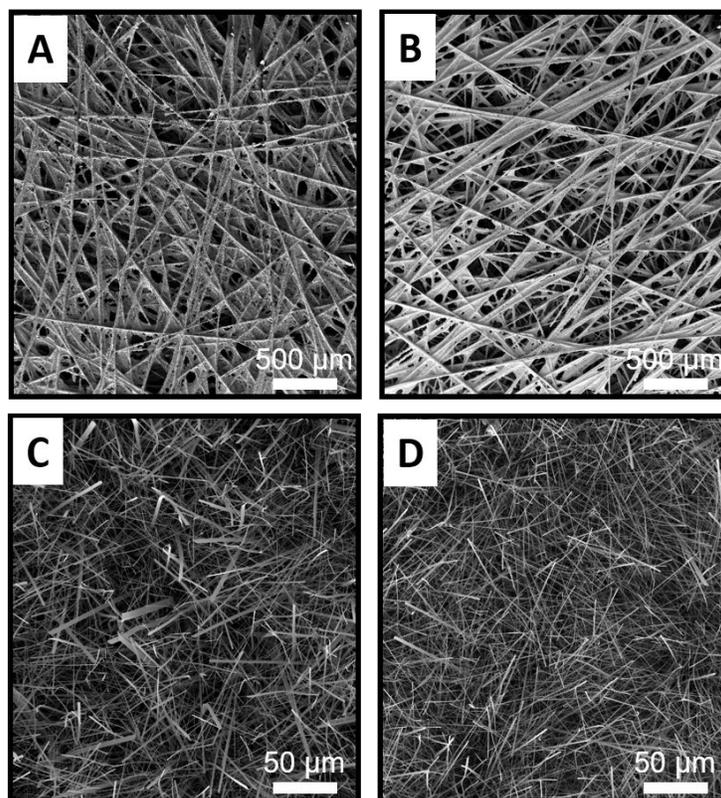


Figure S3. SEM images for a pristine Sigracet 39 AA carbon substrate (A), Ti-coated Sigracet 39AA carbon substrate (B), as-synthesized TiS_3 (C) and TiS_{2-x} nanobelt arrays (D) atop the Sigracet 39AA layer.

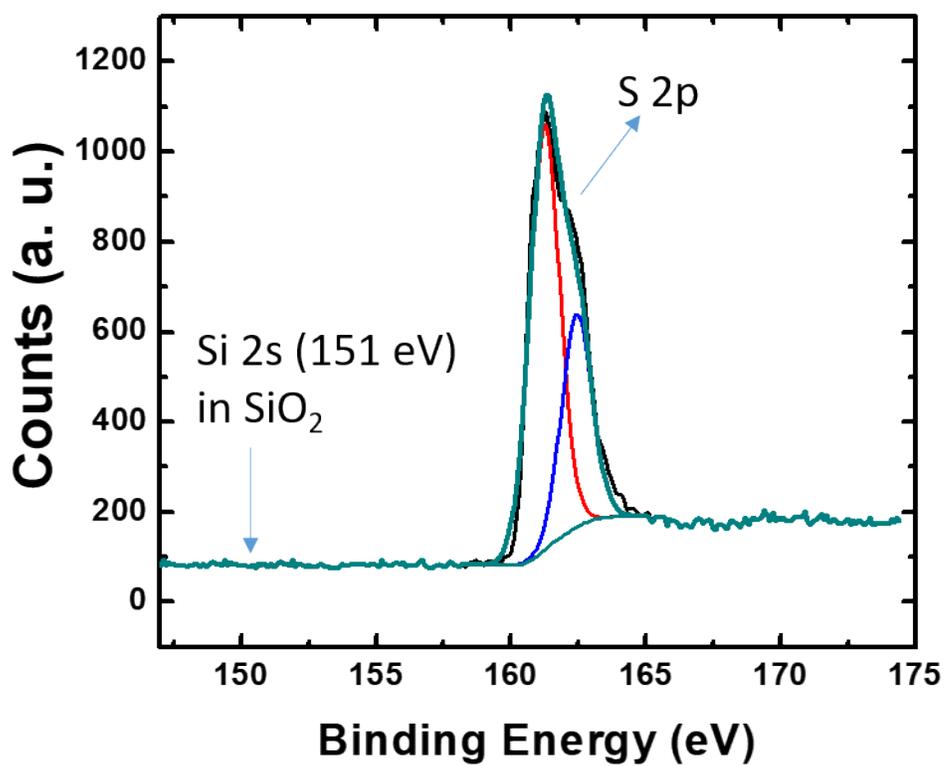


Figure S4. XPS spectrum for S 2p and Si 2s regions for mechanically sanded Al underneath TiS_{1.98} nanobelts.

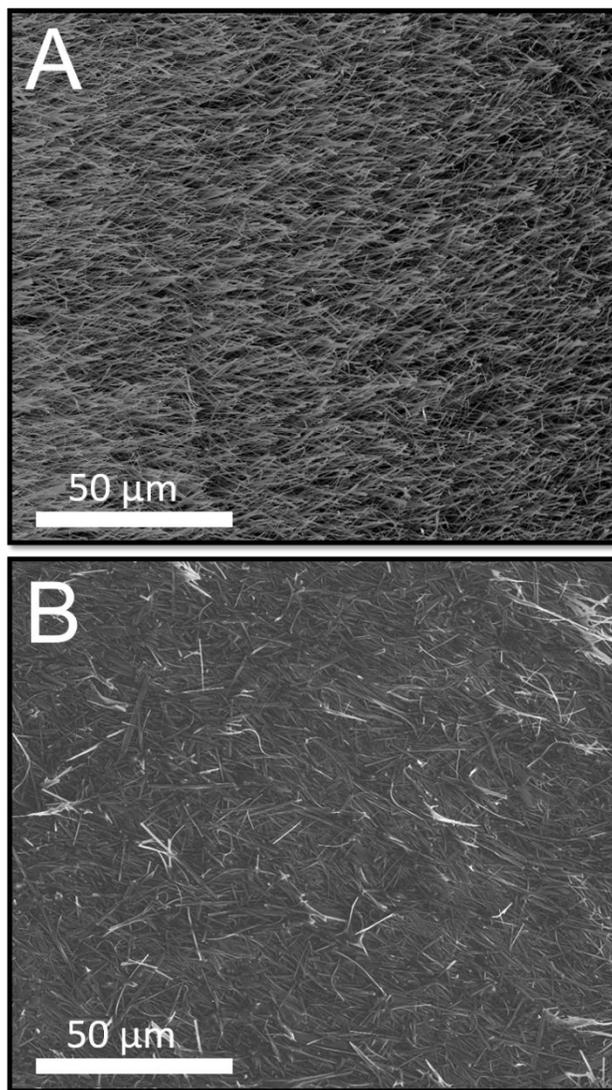


Figure S5. SEM images for Al-TiS_{1.98} half-coin cells before (A) and after 80 cycles (B). After closing the coin cell, we observe that the top layer of the TiS_{1.98} layer is completely pressed against the cap. This causes the nanobelts to lay flat. However, we do not observe any substantial morphological degradation of the nanobelt morphology upon cycling.

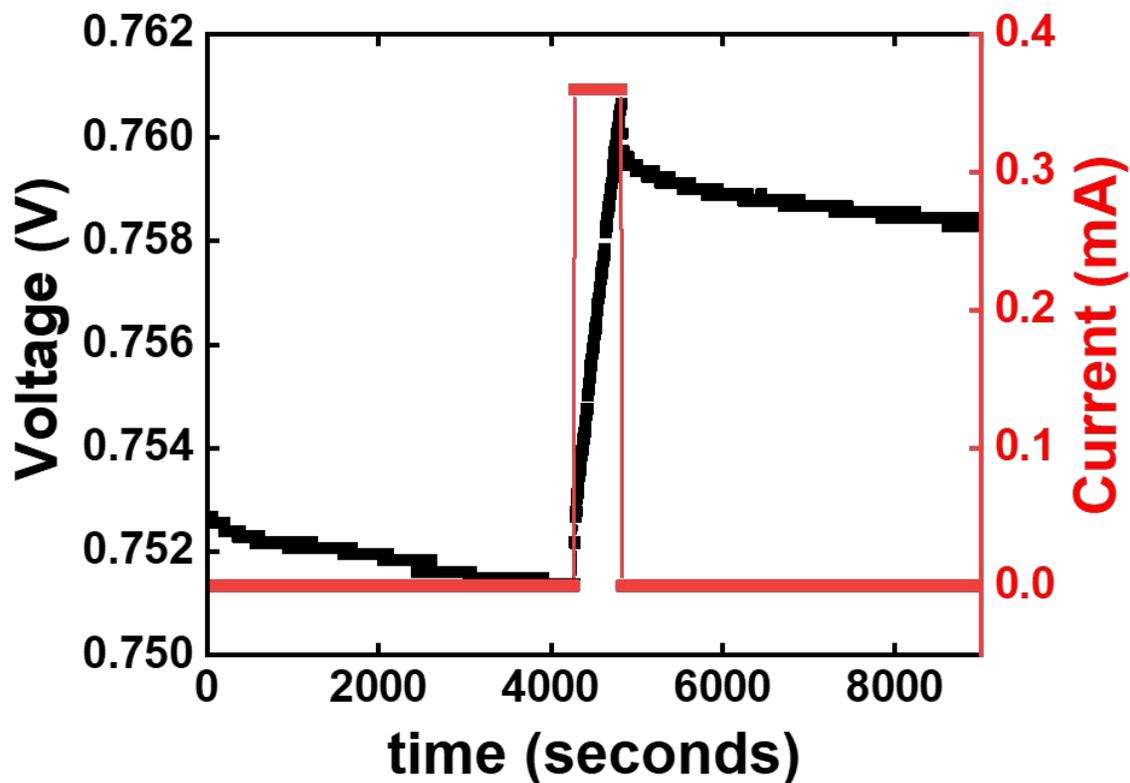


Figure S6. Voltage and current as a function of time for a rest-charge-rest step of the GITT dataset.

References

1. Hawkins, C. G.; Whittaker-Brooks, L., Vertically Oriented TiS_{2-x} Nanobelt Arrays as Binder- and Carbon-Free Intercalation Electrodes for Li- and Na-based Energy Storage Devices. *J. Mater. Chem. A* **2018**, *6*, 21949-21960.
2. Hawkins, C. G.; Whittaker-Brooks, L., Controlling Sulfur Vacancies in TiS_{2-x} Cathode Insertion Hosts via the Conversion of TiS_3 Nanobelts for Energy-Storage Applications. *ACS Appl. Nano Mater.* **2018**, *1*, 851-859.