

Supporting information for

Copper tetrathiovanadate (Cu_3VS_4): a new emerging electrode for rechargeable aqueous aluminum-ion battery

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Experimental details:

Cu_3VS_4 was prepared by a simple hydrothermal method, as reported in ref [6f]. Briefly, to describe, 1.39 g of vanadium acetylacetonate ($\text{C}_{15}\text{H}_{21}\text{O}_6\text{V}$), 0.301 g thioacetamide (CH_3CSNH_2), and 0.161 g copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were dissolved in 35 ml of methanol solution and stirred for 30 min to form a homogenous solution. The solution was then transferred to a Teflon-lined stainless-steel autoclave and heated at 160 °C for 12 hr and then allowed to cool naturally to room temperature. The final product was collected by centrifugation, and repeatedly washed with ethanol and deionized water for several times, and dried at 80 °C overnight.

Electrode slurry was prepared by mixing Cu_3VS_4 powder, carbon black, and polyvinylidene fluoride in a weight ratio of 7:2:1 using N-methyl-2-pyrrolidone solvent. The slurry was cast on pristine graphite (breadth = 1.5 cm, length = 1 cm) and dried at 80 °C for 12 hr. For the electrochemical measurements, cyclic voltammetry (CV) and galvanostatic charge/discharge experiments were performed in a conventional three-electrode electrochemical glass cell where Pt electrode and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The used electrolyte were 1 M AlCl_3 , 1 M $\text{Al}(\text{ClO}_4)_3$, 0.5 M $\text{Al}_2(\text{SO}_4)_3$, 1 M $\text{Al}(\text{NO}_3)_3$ unless otherwise specially stated. The discharge/charge and CV experiments were performed in a voltage range of -0.8 to 1 V (vs. Ag/AgCl). Electrochemical

impedance spectra (EIS) were recorded in the frequency range of 1 mHz-200 kHz at 10 mV signal amplitude. All the electrochemical tests were performed at room temperature (25 °C).

The composition of the as-prepared samples was evaluated using powder X-ray diffraction (BRUKER AXS D8 FOCUS; Cu-K α radiation, $\lambda = 1.5406 \text{ \AA}$). The morphology of the as-prepared samples was examined by field emission scanning electron microscope (FESEM, JEOL JSM 7200F). X-ray photoelectron spectroscopy (XPS, Thermo-Scientific ESCALAB Xi⁺) was used to analyze the chemical composition and valence states of the constituent elements.

Supplementary figures

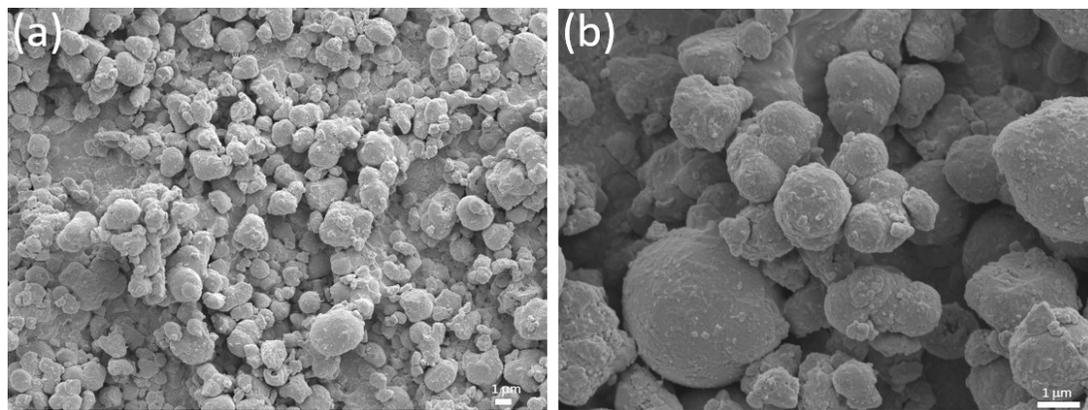


Figure S1: (a-b) FESEM images of Cu₃VS₄.

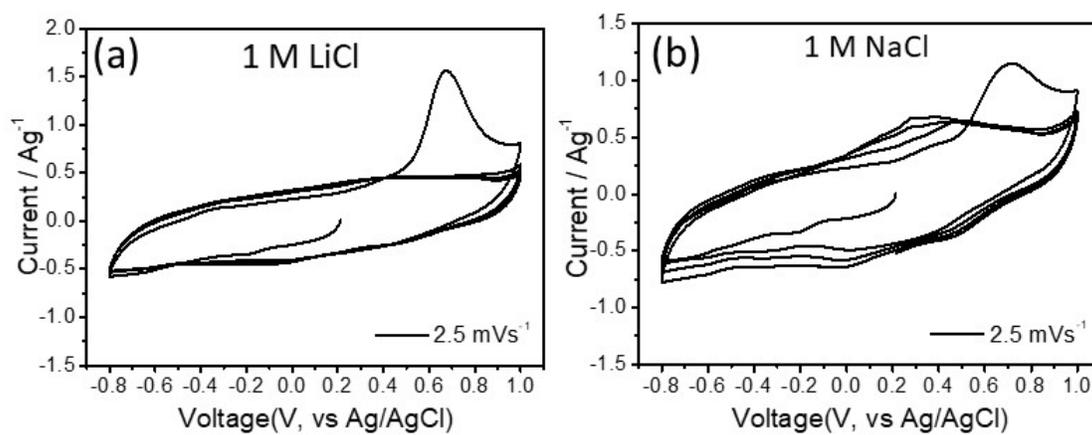


Figure S2: CV profiles of Cu₃VS₄ in (a) 1 M LiCl and (b) 1 M NaCl aqueous electrolytes at a scan rate of 2.5 mVs⁻¹.

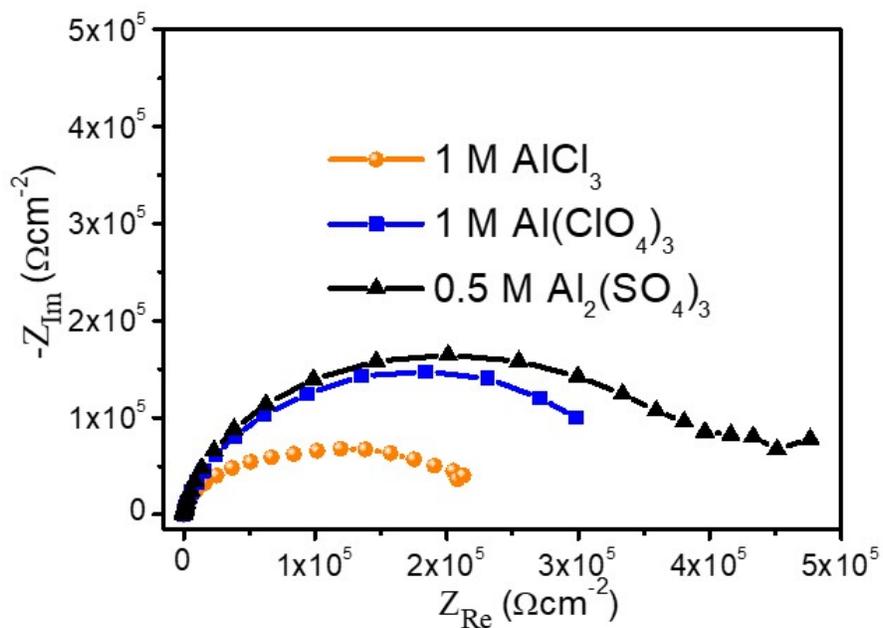


Figure S3: EIS spectra of Cu_3VS_4 in three different aqueous electrolytes.

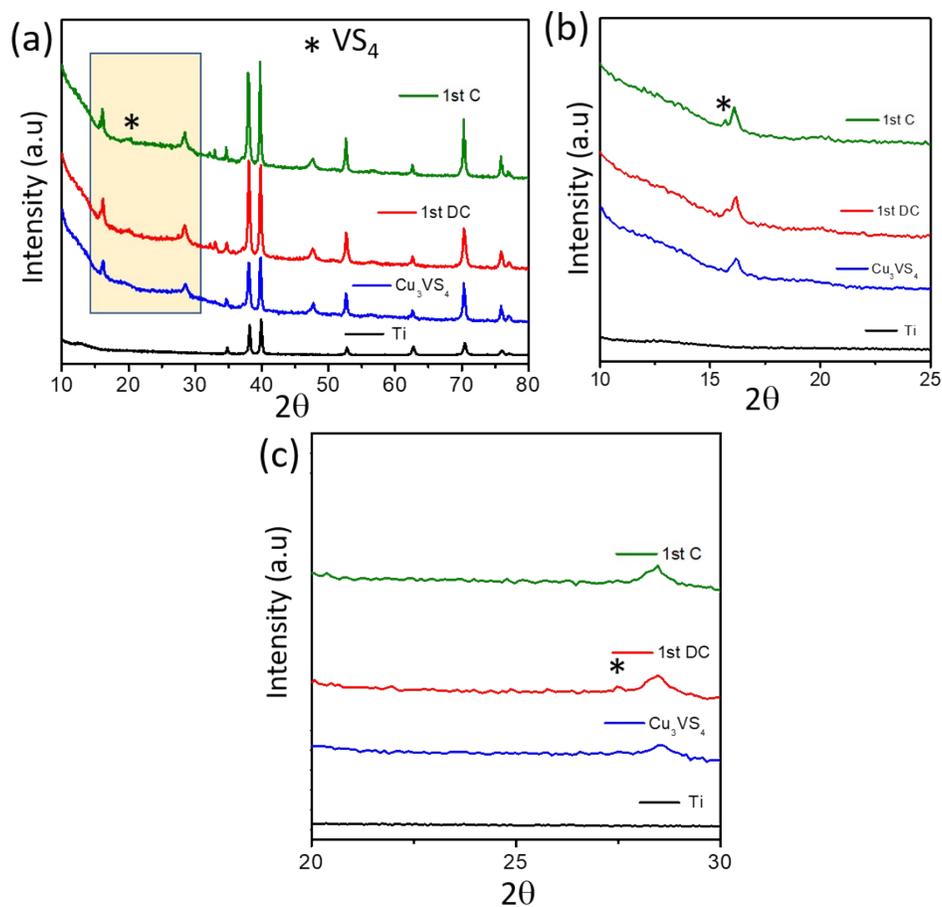


Figure S4: (a) Ex-situ XRD patterns of Cu_3VS_4 before and after 1st discharge/1st charge state, and (b-c) enlargement of degree from 10° to 30° respectively.

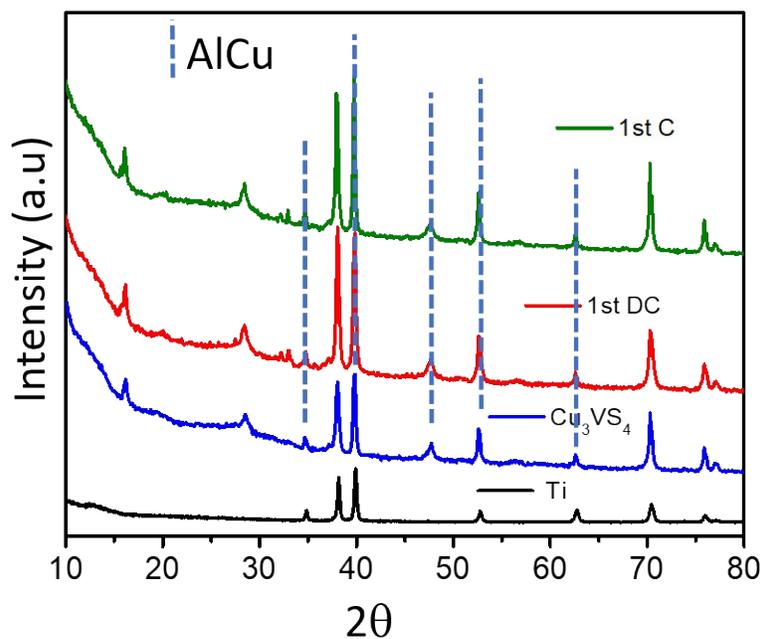


Figure S5: Ex-situ XRD patterns of Cu_3VS_4 before and after 1st discharge/1st charge state. The dotted line indicates the AlCu peaks.

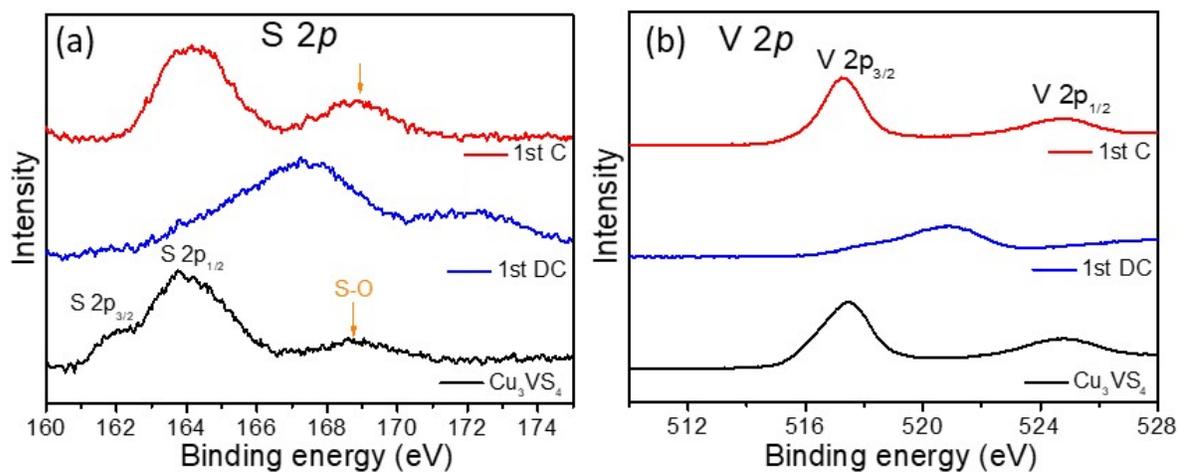


Figure S6: Ex-situ XPS spectra of (a) S 2p, and (b) V 2p before and after 1st discharge/1st charge states.

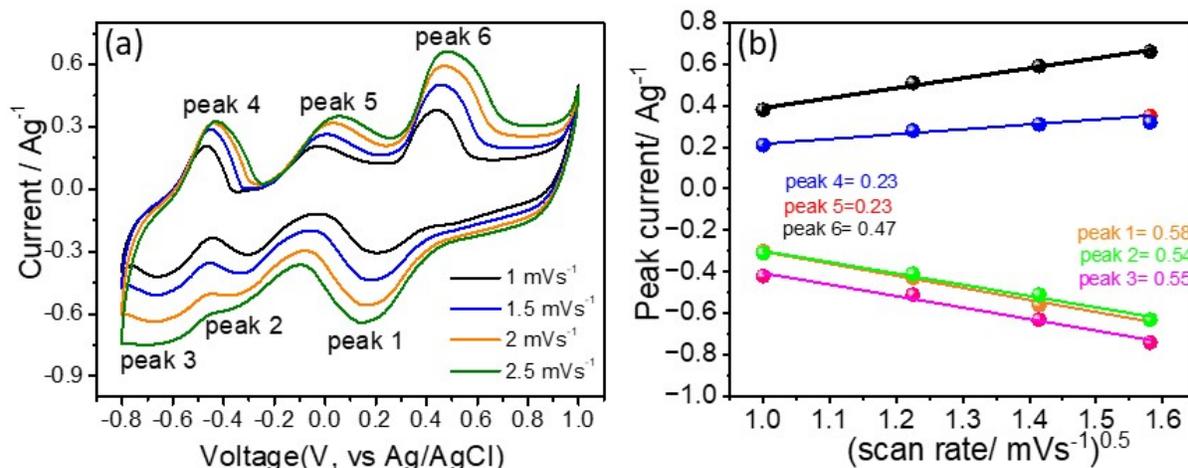


Figure S7: CV profiles of Cu_3VS_4 at different scan rates in 1 M AlCl_3 aqueous electrolyte, and (b) the corresponding linear dependence plots between peak current versus square root of scan rates using the equation $I = k\nu^{0.5}$ (k is a constant).

Table S1: The electrochemical performances of vanadium sulfides-based cathode materials

Cathode materials	Discharge capacity	Cycle number	Type of electrolyte	Reference
	(mAh g^{-1}) /current density (mA g^{-1})			
G- VS_2	50/100	50	Chloroaluminate electrolyte	S1
VS_4/rGO	80/100	100	Chloroaluminate electrolyte	S2
VS_4 nanowire	129.24/400	120	Chloroaluminate electrolyte	S3
Tremella VS_4	322.2/200	120	Chloroaluminate electrolyte	S4
Hierarchical $\text{VS}_2@\text{VS}_4$	116.5/300	500	Chloroaluminate electrolyte	S5
Cu_3VS_4	77/2000	300	Aqueous electrolyte	This work

Reference:

- S1: L. Wu, R. Sun, F. Xiong, C. Pei, K. Han, C. Peng, Y. Fan, W. Yang, Q. An, L. Mai, *Phys. Chem. Chem. Phys.*, 2018, **20**, 22563-22568.
- S2: X. Zhang, S. Wang, J. Tu, G. Zhang, S. Li, D. Tian, S. Jiao, *ChemSusChem*, 2018, **11**, 709-715.
- S3: L. Xing, K. A. Owusu, X. Liu, J. Meng, K. Wang, Q. An, L. Mai, *Nano Energy*, 2021, **79**, 105384.
- S4: X. Han, F. Wu, R. Zhao, Y. Bai, C. Wu, *ACS Appl. Mater. Interfaces*, 2023, **15**, 6888–6901.
- S5: Y. Wang, Z. Shen, X. Lin, Q. Ding, X. Huang, T. Han, H. Zhang, J. Liu, *Chem. Commun.*, 2022, **58**, 11677-11680