Electronic Supplementary Information

Distinct Nanoscale Reaction Pathways in a Sulfide Material for Sodium and Lithium Batteries

Matthew G. Boebinger¹, Michael Xu¹, Xuetian Ma², Hailong Chen², Raymond R. Unocic³, Matthew T. McDowell*^{1,2}

¹School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA, 30332

²George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 801 Ferst Drive, Atlanta, GA, 30332

³Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN, 37831

*Corresponding author, mattmcdowell@gatech.edu

1. *In situ* **TEM videos.** The video entitled *Video_Figure_5* shows the *in situ* TEM sodiation process for the particles in Fig. 5 in the main text. This video is presented at 12 times actual speed.

The video entitled *Video_Figure_6* shows the *in situ* TEM sodiation process for the particles in Fig. 6 in the main text. This video is presented at 12 times actual speed.

2. Electrochemical data. Figure S1 shows cyclic voltammograms from the 1^{st} , 2^{nd} , and 5^{th} cycles of a Na/Cu₂S cell with diglyme electrolyte.



Figure S1. 1^{st} , 2^{nd} , and 5^{th} CV cycles for a Na/Cu₂S cell in diglyme electrolyte. The redox peaks change position over these first few cycles.

Figure S2 shows electrochemical data from a typical Na/Cu₂S cell using an electrolyte consisting of 1.0 M NaPF₆ in monoglyme (DME) solvent. The curves are quite similar to the diglyme case shown in the main text, and the specific capacity remains approximately constant after the first cycle.



Figure S2. Cycling of a Na/Cu₂S cell with an electrolyte consisting of monoglyme solvent with 1.0 M NaPF₆ salt at a rate of C/20. a) Galvanostatic discharge/charge curves. b) Specific capacity with cycle number.

Figure S3 shows electrochemical data from a typical Na/Cu₂S cell using an electrolyte consisting of 1.0 M NaClO₄ in a mixed carbonate (ethylene carbonate/diethyl carbonate, EC/DEC) solvent. The specific discharge capacity decreases quickly over the first five cycles from 350 mAh g⁻¹ in the first cycle to less than 100 mAh g⁻¹ in the fifth cycle.



Figure S3. Galvanostatic cycling (the first, second, and fifth cycle) of a Na/Cu₂S cell with EC/DEC solvent and 1.0 M NaClO₄ salt at a rate of C/5.

Figure S4 shows electrochemical cycling data from a Li/Cu₂S cell using an electrolyte consisting of 1.0 M LiTFSI in DOL/DME (i.e., dioxolane/monoglyme) solvent. Cycling in this

electrolyte results in the retention of much greater capacity over 20 cycles compared to EC/DEC, which is used in Fig. S5.



Figure S4. Galvanostatic cycling of a Li/Cu₂S half cell using an electrolyte consisting of 1.0 M LiTFSI in DOL/DME. The cell was cycled at a rate of C/20. **a)** Discharge-charge curves from the 10^{th} cycle. **b)** Specific capacity over 20 cycles.

Figure S5 shows typical electrochemical cycling data from a Li/Cu_2S cell using an electrolyte consisting of 1.0 M LiPF₆ in an EC/DEC solvent. The cycling stability is inferior to the case of Fig. S4 (dioxolane/monoglyme solvent).



Figure S5. Galvanostatic cycling (the first, second, and fifth cycle) of a $\text{Li/Cu}_2\text{S}$ cell with EC/DEC solvent and 1.0 M LiPF₆ salt at a rate of C/10.

To demonstrate that the current collector metal (Al vs. Cu) does not impact the electrochemistry, Fig. S6 shows electrochemical cycling data from Li/Cu₂S cells tested using Cu and Al current collectors for the active electrode. The shapes of the curves are very similar in both cases, and both cells show similar capacity decay.



Figure S6. Li/Cu₂S cells tested with different current collectors: a) Cu, b) Al. The cells were tested with an electrolyte consisting of 1.0 M LiPF₆ in an EC/DEC solvent at a rate of C/5.

3. XRD data. Figure S7 shows labeled XRD data of the pristine Cu₂S material used in half cell electrochemical experiments. The material primarily takes the low chalcocite phase (JPCDS no. 04-007-1284), with a minority component of djurleite (JPCDS no. 00-023-0959). Figure S8 shows labeled XRD data of the pristine Cu₂S nanocrystals synthesized herein. This material is also primarily low chalcocite, with a smaller djurleite component.



Figure S7. XRD trace of the as-purchased Cu₂S material.



Figure S8. XRD trace of the synthesized Cu₂S nanocrystals.

4. Electrochemical data from in situ XRD. Figure S9 shows the galvanostatic discharge curves

from the *in situ* XRD experiments shown in Fig. 4 in the main text.



Figure S9. Galvanostatic discharge curves from *in situ* XRD experiments. a) Discharge of a Li/Cu_2S cell with EC/DEC electrolyte. The initial voltage portion above ~1.6 V vs. Li/Li^+ is likely due to side reactions in this cell; the XRD peaks did not change during this section. b) Discharge of a Na/Cu₂S cell with diglyme electrolyte.

5. SEM imaging of electrodes. Figure S10 shows SEM images of Cu₂S electrodes before reaction (Fig. S10a), after discharge in lithium or sodium cells (Fig. S10b and c, respectively), and after charge in lithium and sodium cells (Fig. S10d and e, respectively). These experiments utilized EC/DEC electrolyte for the Li cells and diglyme for the Na cells. After discharge, one-dimensional wire-like Cu structures are visible on the surface of the lithiated electrode, but such structures are not visible in the sodiated electrode. These Cu structures are more clearly shown in Fig. S11, which shows the color-coded EDS signal intensity overlaid on the SEM image of the lithiated electrode. After delithiation, some Cu wire structures are still visible (Fig. S10d), which indicates that the reaction is not fully reversible.



Figure S10. *Ex situ* SEM images of Cu_2S electrodes in the pristine state (a), after discharge in lithium (b) or sodium (c) cells, and after charge in lithium (d) or sodium (e) cells.



Figure S11. a) Magnified SEM image of the lithiated Cu_2S electrode from Fig. S10b. b) The same image colorized with EDS signal emitted from different parts of the sample. Red corresponds to sulfur EDS signal, and green corresponds to Cu EDS signal. From the morphology and the EDS signal, it is clear that the Cu_2S material has phase separated after lithiation.

SEM Methods: Lithiated, sodiated, delithiated, and desodiated samples were extracted from coin cells and rinsed with the solvents corresponding to the electrolyte used (EC/DEC or diglyme) and dried within an Ar-filled glove box. Samples were mounted onto SEM stubs, sealed in an airtight container, and transferred to the SEM. Atmospheric exposure was limited due to the reactive nature of the discharged samples, and total exposure exceeded no more than 5 seconds during transfer into the SEM chamber. Imaging was performed using a Zeiss Ultra 60 Field Emission SEM (Carl Zeiss, Germany) with accelerating voltages between 1 and 15 kV. Energy Dispersive Spectroscopy (EDS) was performed using an Oxford 50mm SDD EDS detector attached to the Zeiss Ultra 60 FE SEM.

6. Histogram of average Cu particle sizes after in situ TEM sodiation.



Figure S12. Histogram of the measured area of Cu particles after sodiation of the Cu_2S nanocrystals from the data in Fig. 5 of the main text.