



# Facile Synthesis of Binder-Free Three-Dimensional Cu<sub>x</sub>S Nanoflowers for Lithium Batteries

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Copper sulfides (Cu<sub>x</sub>S) with different stoichiometry are considered as prospective cathode materials for lithium batteries owing to their large energy storage capability. In this work, three-dimensional Cu<sub>x</sub>S cathodes were synthesized via introducing commercially available copper foam into the solution of dimethyl sulfoxide (DMSO) and sulfur powder. The synthesis procedures were straightforward and ultrafast and did not require additional reagents, high temperature, or long processing time and can be considered as a facile one-step method. Copper sulfide materials with different stoichiometry ( $x = 1.8, 1.96$ ) were obtained by changing the temperature and the residence time of the copper foam in the DMSO solution. The effects of the temperature and time on phase and morphology of Cu<sub>x</sub>S were characterized by X-ray diffraction and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. Electrochemical tests resulted in a stable cyclability of Cu<sub>1.8</sub>S cathode with 100% Coulombic efficiency and capacity of approximately 250 mAh g<sup>-1</sup>.

**Keywords:** lithium-ion batteries, copper foam, sulfur, one-step method, copper sulfide

## INTRODUCTION

Currently, primary energy sources (i.e., fossil fuels such as oil, coal, and natural gas) are depleting at an increasing rate; thus, energy storage devices that suggest offering both rate performance and greater capacity are always of high interest. In addition to this, non-renewable energy sources are responsible for environmental hazards such as “greenhouse gas” emissions and contamination (Armaroli and Balzani, 2007). For the last three decades, lithium-ion batteries (LIBs) have been known as one of the superior technologies to store energy and are already used in portable electronics. Recently, LIBs made its progressive way into the field of electric vehicles, grid energy storage, and plug-in hybrid vehicles (Chung and Sohn, 2002). However, traditional LIBs are still not satisfying the needs for the high capacity, energy density, and, most importantly, safety aspects. For instance, a traditional LIB cell consists of a transition metal oxide (e.g., LiCoO<sub>2</sub>) as the cathode material and graphite as the anode material. Today, their energy density has reached its limits of <260 Wh kg<sup>-1</sup> and is not able to cope with the required energy demands of modern society

(Meng et al., 2012; Manthiram et al., 2017). Furthermore, inherent defects of LIBs such as safety concerns limit their development, with incidents ranging from Hewlett Packard's recall of hundreds of thousands of laptop batteries in 2009 due to overheating and fire, to the Samsung Galaxy Note 7 explosion in 2017 (Liu et al., 2018). Additionally, LiCoO<sub>2</sub> is expensive as well as toxic (Blomgren, 2017).

Alternatively, scholars have been investigating new electrode materials to solve these issues. Compared to conventional candidate materials, conversion-based materials [e.g., metal fluorides (Cabana et al., 2010; Wang et al., 2011), sulfides (Meng et al., 2014; Lu et al., 2017), phosphides, and nitrides (Cabana et al., 2010)] present an essential class that has not been well researched. Conversion-based materials have been suggested for LIBs because of their higher specific capacities and preferably cost-effectiveness. Over the past decades, copper sulfides (Cu<sub>x</sub>S) have attracted considerable attention in the field of LIBs because of their different valence states and stoichiometric compositions (Chung and Sohn, 2002). The latest studies have shown that Cu<sub>x</sub>S ( $1 \leq x \leq 2$ ) are an upcoming cathode candidate for interaction with lithium metal (i.e., Li-Cu<sub>x</sub>S,  $1 \leq x \leq 2$ ) with long cyclic performance and high rate capability.

Copper sulfide is known to have five stable phases starting from chalcocite "copper-rich" Cu<sub>2</sub>S to the covellite "copper-deficient" CuS. The excellent properties such as high electronic conductivity of  $10^{-3}$  S cm<sup>-1</sup> and theoretical capacities of 337–560 mAh g<sup>-1</sup> make them attractive electrode material for large-scale applications in secondary lithium, magnesium, and sodium batteries because of their abundance and inexpensiveness (Lu et al., 2017; Xiao et al., 2018; Wang et al., 2019). It has been reported that the electrochemical and electronic properties of the Cu<sub>x</sub>S system depend greatly on both the Cu/S ratios and crystalline structures. An increase in the bandgap occurs with an increase in the  $x$  value in bulk Cu<sub>x</sub>S (i.e., 1.2 eV for Cu<sub>2</sub>S, 1.5 eV for Cu<sub>1.8</sub>S, and 2.0 eV for CuS). This implied that Cu<sub>x</sub>S with the composition closer to Cu<sub>2</sub>S will demonstrate higher electronic conductivity than that of CuS electrodes (Grozdanov and Najdoski, 1995; Zhao et al., 2009).

Thus far, many studies have been devoted to the synthesis of 1–3D structured CuS and Cu<sub>2</sub>S electrodes by hydrothermal (Tao et al., 2014), solvothermal (Han et al., 2011; Liu and Xue, 2011), microwave (Xiao et al., 2016; Yuan et al., 2016; Wang et al., 2019), spray pyrolysis (Madarasz et al., 2001; Kalimuldina and Taniguchi, 2016a,b), and other methods. However, only a few have focused on the preparation of freestanding 3D structured Cu<sub>x</sub>S electrodes (Ni et al., 2013; Tang et al., 2017). In this research, we investigate a facile way to prepare a 3D structured freestanding cathode material at a low temperature via a straightforward one-step method that does not require expensive apparatus and additional chemical agents compared to the conventional and complex ways of cathode preparation.

To develop a better battery with sufficient volumetric and power densities, the fabrication of freestanding cathodes is being considered as a reasonable approach. Therefore, the preparation of freestanding Cu<sub>x</sub>S with high active mass loading by an ultrafast and low-cost method could benefit the simplification of cell

packaging configurations as binders, and current collectors can be omitted (Zeng et al., 2015).

## MATERIALS AND METHODS

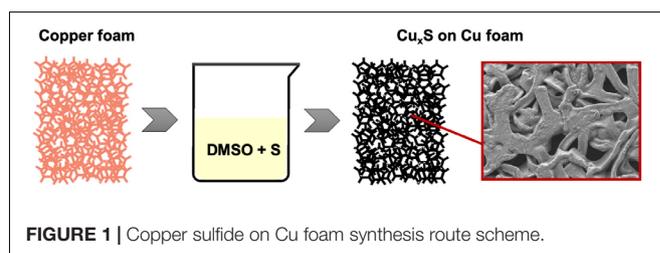
### Synthesis Procedure

The materials utilized in this work were commercialized copper foam (Cu foam; MTI Corp., United States), sulfur powder (S, LenReaktiv), and dimethyl sulfoxide (C<sub>2</sub>H<sub>6</sub>OS, DMSO; Sigma–Aldrich, Germany). Materials were analytical grade and were used as received without further purification. First, to assess the solubility of S powder in DMSO, different amounts of S powder were dissolved in 20 mL DMSO at a heating temperature of 80°C. It was found that more than 0.1 g of powder cannot be fully dissolved in the solution. Afterward, an optimized amount of 0.1 g was used in further experiments. The effect of temperature on the formation of Cu<sub>x</sub>S phases was investigated by varying the reaction temperature from 80°C to 110°C with the help of a heater while keeping the time constant at 30 s. After finding the desired favorable temperature for the synthesis, time was varied from 10 s to 1 min to optimize the reaction time.

In a typical synthesis procedure, 0.1 g of S powder was weighed and added into 20 mL of DMSO solution under vigorous stirring with a magnetic stirrer at the above-stated temperatures. For the preparation of the copper foam, it was cut into small rectangular pieces, washed with acetone, and dried in a vacuum oven at 60°C for 1 h. After the total dissolution of S powder, the prepared copper foam pieces were soaked into the solution as seen in **Figure 1**. Subsequently, blackened copper foam pieces were then dried in a vacuum oven at 60°C for 24 h. The masses of the obtained Cu<sub>x</sub>S active materials were calculated based on the fact that the Cu element from the Cu foam directly reacts with the S in the solution. First, the mass of the deposited S was calculated by subtracting the pristine Cu foam mass from the obtained Cu/Cu<sub>x</sub>S material mass. After, the electrode's mass was calculated considering the molar masses of Cu<sub>x</sub>S by the cross-multiplying method.

### Physical and Electrochemical Characterizations of Cu<sub>x</sub>S

Obtained Cu<sub>x</sub>S materials were characterized by X-ray powder diffraction (XRD; Rigaku SmartLab<sup>®</sup> X-ray diffraction system, Japan) to investigate the phases of Cu<sub>x</sub>S. The scanning electron microscope Crossbeam 540 coupled with energy-dispersive X-ray spectroscopy (SEM-EDS; Zeiss, Germany) was employed to observe the morphologies and distribution of separate



**FIGURE 1** | Copper sulfide on Cu foam synthesis route scheme.

components of obtained materials. CR2032 type coin cells were assembled and tested to assess the electrochemical performances of the synthesized electrodes. Copper foam pieces were cut into 16 mm in diameter disks and were used as cathodes without any binders and additives in half-cells with Li metal. The mass loading of Cu<sub>x</sub>S active material varied between 8.7 and 10.4 mg cm<sup>-2</sup>, depending on the synthesis time. Glovebox (MBraun, Germany) was used to assemble the half-cells, where the role of the separator was served by the Celgard 2400, and 1 M LiTFSI in DOL/DME was utilized as an electrolyte. The cells were then tested in the multichannel battery test system Arbin in the voltage range between 1.0 and 3.0 V with a constant current in the form of a C/5 rate (1C = 7–7.3 mAh).

## RESULTS AND DISCUSSION

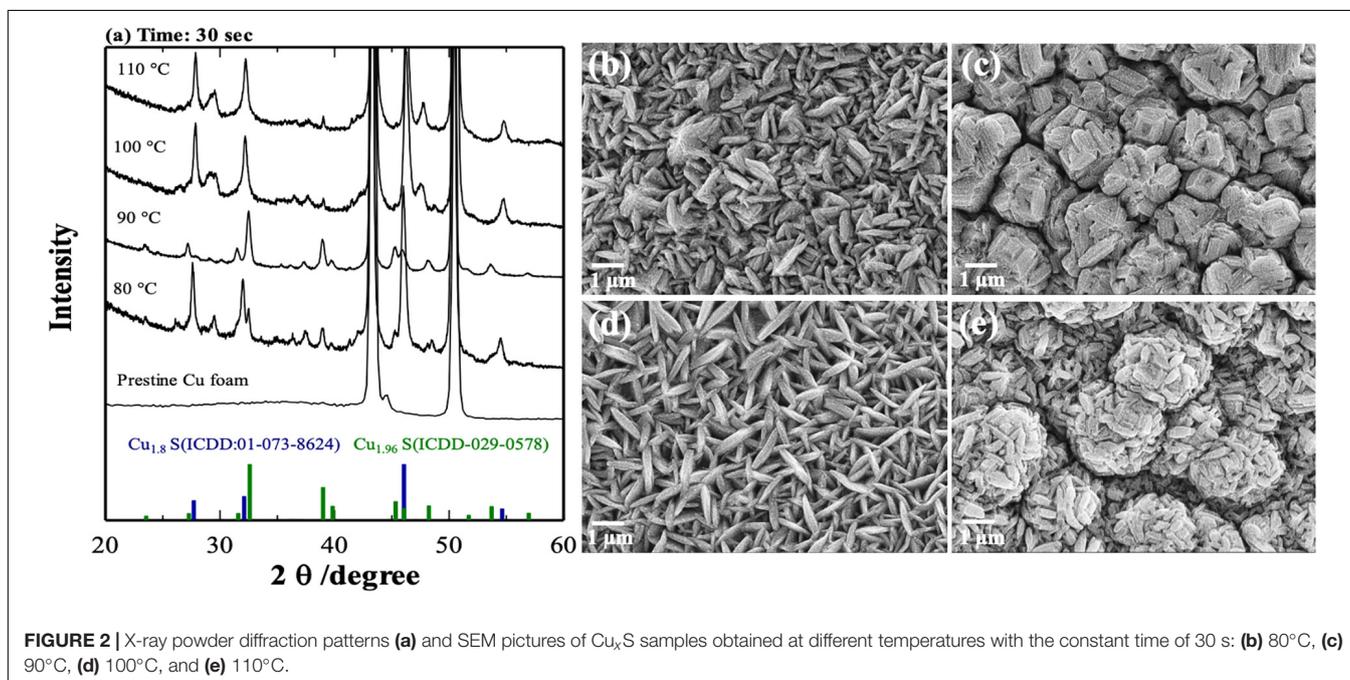
X-ray powder diffraction patterns and SEM pictures of Cu<sub>x</sub>S samples obtained at different temperatures with a constant time of 30 s are shown in **Figure 2**. The main diffraction peaks located at 43.5° and 50.7° for all samples can be assigned to the (1 1 1) and (2 0 0) crystal faces of the Cu foam, respectively. All other peaks could be indexed to Cu<sub>1.8</sub>S and Cu<sub>1.96</sub>S phases with the trace of very weak peaks (35°–38°) that could correspond to monoclinic Cu<sub>2</sub>S (Potter and Evans, 1976). At lower temperatures of 80 and 90°C, phases of Cu<sub>1.96</sub>S prevail, whereas at slightly higher temperatures of 100 and 110°C, formation of more Cu<sub>1.8</sub>S can be noticed. Also, one can observe from the SEM results (**Figures 2b–e**) that the temperature had a considerable effect on the morphologies and structures of the Cu<sub>x</sub>S phases. In essence, at 80°C, the only formation of two-dimensional irregular Cu<sub>x</sub>S plates can be observed, whereas increasing the temperature only by 10°C results in a surface with rough structures that resemble

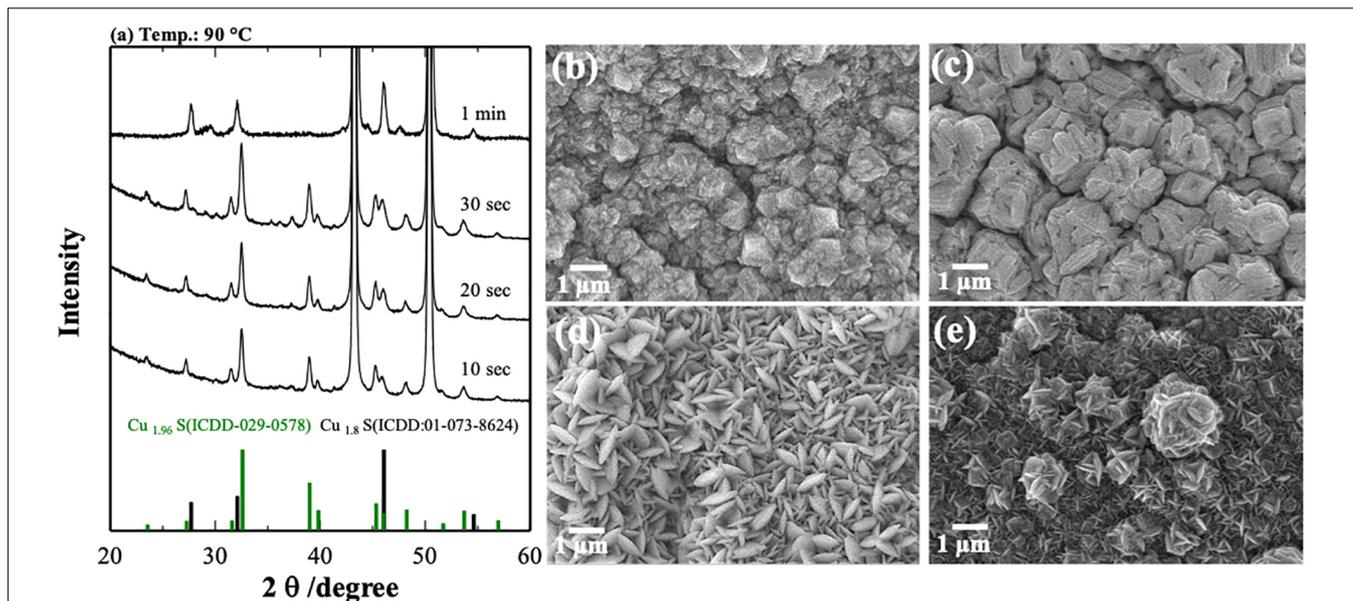
flowers-like humps. Going up to 100°C leads to the formation of homogenous hierarchical petals. Eventually, at 110°C, petals assemble themselves in flower-like spherical structures.

**Figure 3** represents the XRD results and SEM images of Cu<sub>x</sub>S on Cu foam obtained at 90°C at different times. The time had a significant influence on the phases and morphologies of the formed material as well. The samples prepared at the time of 10, 20, and 30 s showed a similar tendency of Cu<sub>1.96</sub>S formation. However, material obtained at 10 s showed the purest phase of Cu<sub>1.96</sub>S among them.

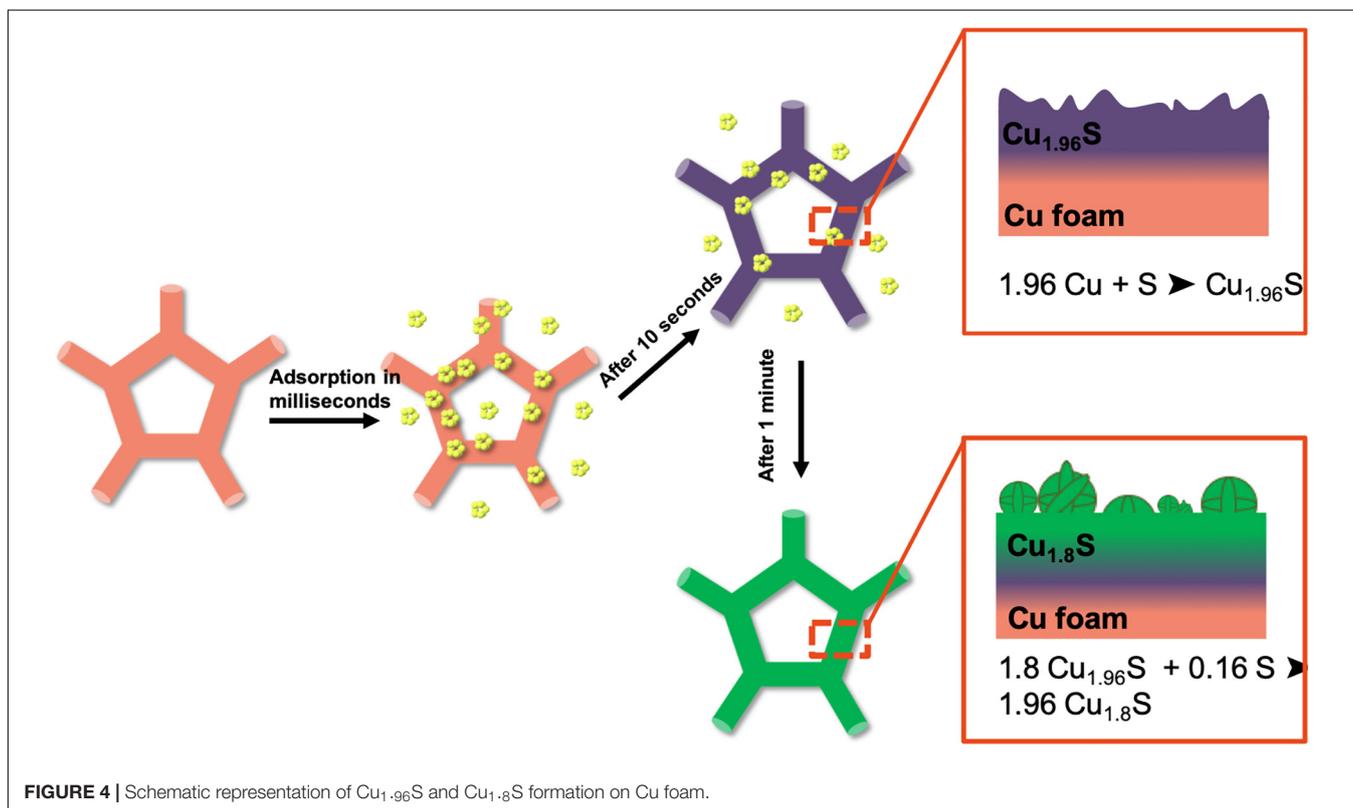
On the other hand, 1-min synthesis triggered the formation of a flower-like Cu<sub>1.8</sub>S phase. As shown in **Figures 3b–e**, the morphology evolution of CuS from irregular form to the flower-like structure can be seen, involving several growth stages. The introduction of copper foam into a sulfur solution for 10 s resulted in the formation of irregular pieces (**Figure 3b**), whereas changing the time for 20 s enhanced the size of that particle (**Figure 3c**). After 30 s, pieces transformed into the sheets, and they became geometrically regular (**Figure 3d**). The time increase to 1 min affected significantly the structure of composites, forming a flower-like structure of Cu<sub>x</sub>S (mainly Cu<sub>1.8</sub>S) (**Figure 3e**).

The phase evolution of Cu<sub>x</sub>S is depicted in **Figure 4**, and several steps are suggested: first, after the Cu foam is soaked in the solution, instant adsorption of sulfur molecules takes place on the surface of the foam. Then, after several seconds, the adsorbed sulfur molecules react with the copper molecules in the surface of the Cu foam, resulting in a copper-rich Cu<sub>1.96</sub>S phase. Subsequently, increasing the reaction time leads to the reaction of the Cu<sub>1.96</sub>S phase with the sulfur again causing the formation of sulfur-rich Cu<sub>1.8</sub>S phase. Also, it is worth to mention that the main transformation of Cu<sub>1.96</sub>S to the Cu<sub>1.8</sub>S phase is due to the large surface area of the nanocrystals (**Figures 3b–d**), which





**FIGURE 3** | X-ray powder diffraction patterns (a) and SEM pictures of Cu<sub>x</sub>S samples obtained at different times with the constant temperature of 90°C: (b) 10 s, (c) 20 s, (d) 30 s, and (e) 1 min.

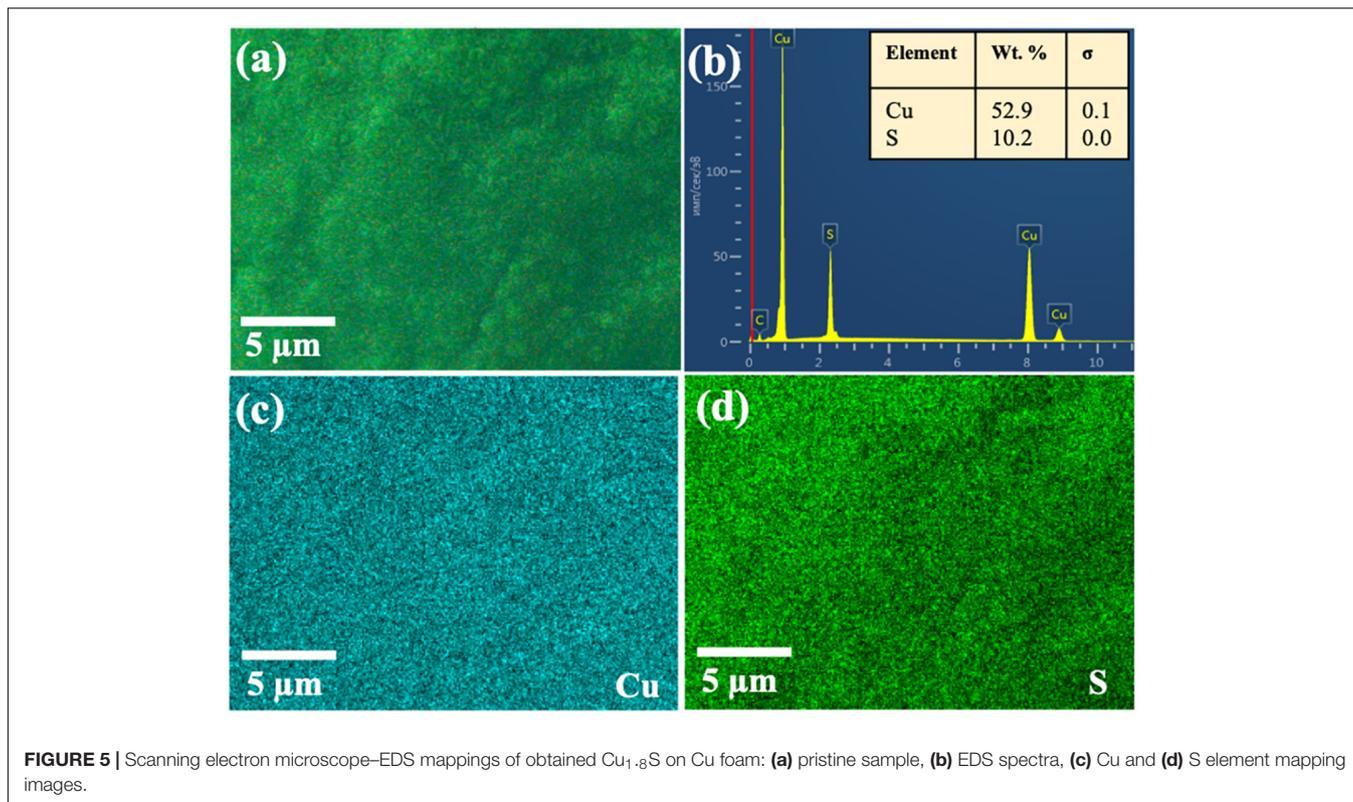


**FIGURE 4** | Schematic representation of Cu<sub>1.96</sub>S and Cu<sub>1.8</sub>S formation on Cu foam.

allowed the rapid diffusion of Cu ions out of the crystal, thereby increasing the surface oxidation which possibly accelerated the djurleite formation (Green et al., 2012).

The scanning electron microscope–EDS images of Cu<sub>1.8</sub>S (Figure 5) indicated that the distribution of Cu and S elements

on the copper foam’s surface was uniform, and the coverage was even. Although the reaction between Cu<sub>1.96</sub>S and S continues on the surface of the Cu foam in a gradient pattern, the composition distribution of the main elements is homogenous throughout the 3D material.



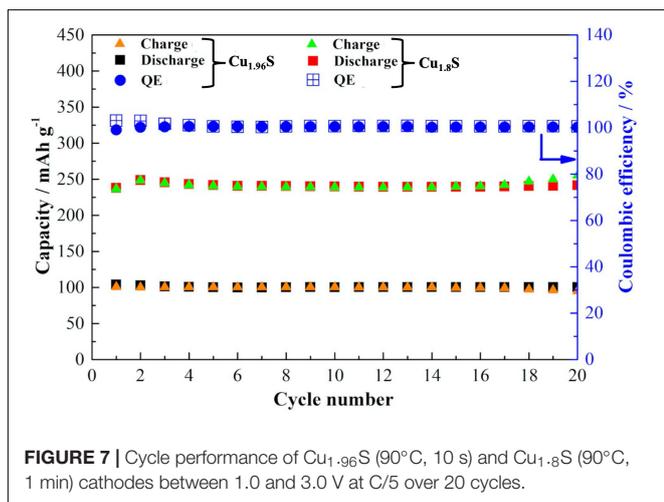
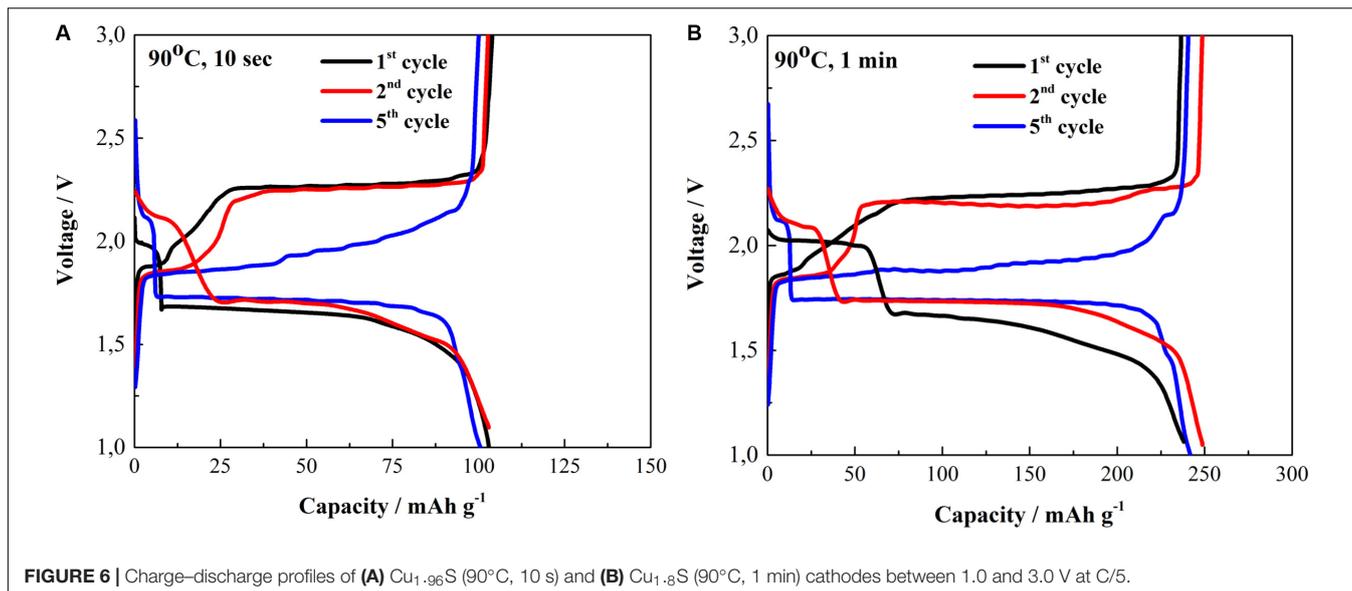
The electrochemical characterization of Cu<sub>1.96</sub>S and Cu<sub>1.8</sub>S as cathode materials in lithium half-cells is presented in **Figure 6**. Galvanostatic tests were carried out at a rate of C/5 based on the mass of Cu<sub>x</sub>S. **Figure 6A** shows charge–discharge profiles of Cu<sub>1.96</sub>S freestanding electrodes. It can be observed that the first discharge profile exhibits short and prolonged plateaus at 2.0 and 1.73 V, respectively. The reaction mechanism for Cu<sub>2</sub>S was reported as the initial discharge plateau should be at 1.73 V and corresponded to  $\text{Cu}_2\text{S} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{S} + 2\text{Cu}$  during the first cycle (Kalimuldina and Taniguchi, 2016b). However, for Cu<sub>1.96</sub>S, additional small peaks at 2.0 V can be seen, which is a more typical discharge plateau to CuS electrode (Kalimuldina and Taniguchi, 2017). That difference might come from some impurities residing in the obtained Cu<sub>1.96</sub>S electrode. After the fifth cycle, the discharge profile showed almost disappeared plateau at 2.2 V and much prolonged at 1.75 V with a capacity of 100 mAh g<sup>-1</sup>. Those changes might indicate the phase transformation of Cu<sub>1.96</sub>S with some impurities into pure Cu<sub>1.96</sub>S with the increase in the cycle number. The impurities could be the insignificant trace of copper-rich phases (Fu and Manthiram, 2013; Jache et al., 2014; Foley et al., 2018).

The first charge voltage profiles are depicted at 1.85 and 2.25 V, respectively. Furthermore, after five cycles, we can observe previously reported flattening of the charge plateau to 1.85 V (Jache et al., 2014). Consequently, we can write the reversible electrochemical reaction accordingly from the obtained charge–discharge profiles as  $\text{Li}_2\text{S} + 2\text{Cu} \hat{=} \text{Cu}_{1.96}\text{S} + 0.04\text{Cu} + 2\text{Li}^+ + 2\text{e}^-$  (Debart et al., 2006;

Kalimuldina and Taniguchi, 2016b, 2017). The similar charge–discharge profile of Cu<sub>1.8</sub>S electrode is demonstrated in **Figure 6B**. However, the change in the discharge plateaus at 2.1 and 1.65 V can be seen as there longer 2.1 V discharge plateau than that of in **Figure 6A** for Cu<sub>1.96</sub>S. However, after the fifth cycle, both charge and discharge show single plateaus at 1.75 and 1.85 V with about 250 mAh g<sup>-1</sup>, respectively. This implies that the richer the sulfur content in the composition of Cu<sub>x</sub>S, the more its electrochemical properties get closer to the behavior of the covellite CuS electrode (Jianga et al., 2019).

Cycling performance of both Cu<sub>1.96</sub>S and Cu<sub>1.8</sub>S is demonstrated in **Figure 7**. The residue time of 10 s to obtain Cu<sub>1.96</sub>S at 90°C released a low but stable capacity of 100 mAh g<sup>-1</sup> for 20 cycles with 100% Coulombic efficiency. On the contrary, when the reaction residue time was increased up to 1 min to achieve Cu<sub>1.8</sub>S, the significant capacity increase was observed. The capacity of Cu<sub>1.8</sub>S electrode with a mass loading of 10.4 mg cm<sup>-2</sup> without any binders and additives achieved 250 mAh g<sup>-1</sup> for 20 cycles with 100% Coulombic efficiency. It is well known that CuS is more attractive in the term of theoretical capacity (560 mAh g<sup>-1</sup>); however, the electrode with higher copper content is more electrically conductive (Grozdanov and Najdoski, 1995). Based on the theoretical capacities of Cu<sub>1.96</sub>S and Cu<sub>1.8</sub>S, the latter will deliver higher value. That can be considered as one of the reasons for such differences in the capacity between those electrodes.

The ultrafast and straightforward method of preparation of 3D Cu<sub>x</sub>S electrodes on Cu foam showed very prospective



electrochemical properties as an applicable compartment in the future LIBs. The work confirms that other phases of  $\text{Cu}_x\text{S}$  are also electrochemically stable and have reversible charge–discharge processes even at high active mass loading conditions.

## CONCLUSION

Different phases of  $\text{Cu}_x\text{S}$  as  $\text{Cu}_{1.96}\text{S}$  and  $\text{Cu}_{1.8}\text{S}$  were successfully prepared by a simple method of soaking Cu foam in an S/DMSO solution for a short period of time. The effect of temperature and synthesis time on the tendency for the reaction between Cu foam and S were studied. The morphology of  $\text{Cu}_x\text{S}$  samples was cubic-type irregular shapes at  $80^\circ\text{C}$  and grew further to the nanoflower-like structures at  $110^\circ\text{C}$ . The reaction activity of formed  $\text{Cu}_x\text{S}$  on the surface of Cu foam with remaining S in the DMSO solution was enhanced with the increase in the soaking time.

Electrochemical properties of  $\text{Cu}_{1.96}\text{S}$  formed at  $90^\circ\text{C}$  and 10-s synthesis time showed only  $100 \text{ mAh g}^{-1}$  at 5/C rate, whereas the sample of  $\text{Cu}_{1.8}\text{S}$  that was obtained by holding Cu foam up to 1 min at  $90^\circ\text{C}$  in S/DMSO solution reached stable cycling performance at  $250 \text{ mAh g}^{-1}$  with extremely high mass loading. This allows us to study the phase change of  $\text{Cu}_x\text{S}$  materials, depending on the time and temperature and its influence on the electrochemical properties of the cathode material.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

## AUTHOR CONTRIBUTIONS

AA, AN, and GK contributed to the synthesis, characterization, and manuscript writing. GK, DA, ZB, and IT contributed to the characterization, interpretation, and discussion of obtained results. All authors contributed to the article and approved the submitted version.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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