Interfacial Stabilization of a Graphene-Wrapped Cu$_2$S Anode for High-Performance Sodium-Ion Batteries via Atomic Layer Deposition

Jiyu Cai $^{1,2}$, Zonghai Chen $^2$,* and Xiangbo Meng $^{1,*}$

1 Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701, USA; jiyucai@uark.edu
2 Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA
* Correspondence: Zonghai.chen@anl.gov (Z.C.); xbmeng@uark.edu (X.M.)

Received: 20 November 2020; Accepted: 7 December 2020; Published: 8 December 2020

Abstract: Sodium-ion batteries (SIBs) have attracted increasing attention for storing renewable clean energy, owing to their cost-effectiveness. Nonetheless, SIBs still remain significant challenges in terms of the availability of suitable anode materials with high capacities and good rate capabilities. Our previous work has developed and verified that Cu$_2$S wrapped by nitrogen-doped graphene (i.e., Cu$_2$S@NG composite), as an anode in SIBs, could exhibit a superior performance with ultralong cyclability and excellent rate capability, mainly due to the multifunctional roles of NG. However, the Cu$_2$S@NG anode still suffers from continuous parasitic reactions at low potentials, causing a rapid performance deterioration. In this study, we investigated the effects of a conformal Al$_2$O$_3$ coating via atomic layer deposition (ALD) on the interfacial stability of the Cu$_2$S@NG anode. As a consequence, the ALD-coated Cu$_2$S@NG electrode can deliver a high capacity of 374 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$ and achieve a capacity retention of ~100% at different rates. This work verified that surface modification via ALD is a viable route for improving SIBs’ performances.

Keywords: sodium-ion batteries; atomic layer deposition; copper (I) sulfide; anode; surface coating

1. Introduction

Sodium-ion batteries (SIBs) have been highly regarded as a promising technology to constitute large stationary electrical energy storage (EES) systems for renewable clean energies (e.g., solar and wind power), featuring their low cost and the natural abundance of sodium [1,2]. Due to the larger radius (1.02 Å) of the Na-ions than that (0.76 Å) of the Li-ions [3], SIBs have experienced more difficulties in the search for a suitable anode material [4–9]. Among potential candidates, the conversion-type copper(I) sulfide (Cu$_2$S) has attracted much interest, owing to its high theoretical capacity of 337 mAh g$^{-1}$, outstanding rate capability over 10 C (1 C = 337 mA g$^{-1}$), and natural abundance [10–12].

It has been witnessed that Cu$_2$S and its analogs (e.g., Cu$_9$S$_5$ and Cu$_{1.8}$S) suffer from performance degradation, due to continuous parasitic reactions at their interfaces [13,14]. It has been demonstrated that, to deal with these kinds of issues, a physical encapsulation over Cu$_2$S is effective. In this regard, a variety of different coverings have been reported, such as carbon materials, amino-ended hyperbranched polyamide (AHP), and nitrogen-doped graphene (NG) [14–19]. For example, Cu$_9$S$_5$ nanoparticles embedded in N,S-doped carbon realized a capacity of 344.3 mAh g$^{-1}$ at 100 mA g$^{-1}$ for 200 cycles, but showed a low rate performance—i.e., a capacity of 138.2 mAh g$^{-1}$ at 1600 mA g$^{-1$} [18]. Chen et al. [14] applied an N,S dual-doped carbon to encapsulate Cu$_2$S, leading to a capacity of 182.3 mAh g$^{-1}$ for 50 cycles. Due to low electron conductivity in N,S dual-doped carbon, the addition of some extra conductive agent led to a 51.5 wt% content of the active material and a low electrode...
capacity of 93.9 mAh g\(^{-1}\) (which was based on all the electrode materials, including the active material, the conductive agent, and the binder) [14]. In this regard, we developed a superior Cu\(_2\)S@NG composite anode for SIBs in our previous work [19]. In the work, we demonstrated that the NG exhibited multifunctional roles in the anode [20,21] and contributed to a significant improvement in performance. Our Cu\(_2\)S@NG composite anode exhibited the highest electrode capacity (252 mAh g\(^{-1}\)) among all the Cu\(_2\)S-related electrodes reported to date. Nonetheless, we also noticed that there were still some parasitic reactions occurring at low potentials (e.g., <0.15 V), which deteriorated the performance of the Cu\(_2\)S@NG composite anode. The parasitic reaction might be exhibited as continuing electrolyte decomposition [22,23], which consumes part of the charge and even hinders the active capacity of electrode materials. To this end, we have adopted a higher discharge cutoff voltage of 0.2 V to mitigate the parasitic reactions for achieving a more stable performance—e.g., a sustainable capacity of 270 mAh g\(^{-1}\) for 1000 cycles at 5 C (1 C = 337 mAh g\(^{-1}\)) [19]. However, the higher cutoff potential of 0.2 V compromised the capacity of the Cu\(_2\)S anode to some extent.

Motivated to further improve the electrochemical performance of our previously developed Cu\(_2\)S@NG electrode in the voltage window of 0.01–3.0 V, herein we demonstrate a design philosophy using a surface modification via atomic layer deposition (ALD) to suppress parasitic reactions. The ALD thin film technique has emerged as a promising approach for stabilizing lithium-ion batteries (LIBs) and SIB performance, featuring its capabilities for growing a large range of inorganic materials and forming an ultrathin, uniform, and conformal coatings [24–26]. It has been demonstrated that the inorganic oxide materials (i.e., Al\(_2\)O\(_3\), ZrO\(_2\), and TiO\(_2\)) coated on electrodes via ALD have remarkably improved the interfacial stability and thereby elongated the electrodes’ cycling life [27–29]. Particularly, Al\(_2\)O\(_3\) coating via ALD has been widely employed in SIBs, featuring its good protective effects against HF corrosion and mechanical reinforcement on electrodes [24]. In this study, we applied an ultrathin Al\(_2\)O\(_3\) coating via ALD on Cu\(_2\)S@NG electrode as a model system for investigating its effect on the interfacial stability of SIBs. Compared with the bare electrode, the ALD-coated electrode (i.e., ALD-Cu\(_2\)S@NG) could enable a more stable electrochemical performance, accounting for a capacity of 374 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) for 100 cycles versus a capacity of 304 mAh g\(^{-1}\) for the bare electrode at the same testing conditions and an exceptional capacity retention of ~100% at different current rates (up to 10 C). The electrochemical impedance spectroscopy (EIS) measurements confirmed that the ALD coating has dramatically reduced the interfacial resistance. Consequently, our study revealed that surface modification via ALD is an important strategy to enhance interfacial stability of sodium-ion batteries for better performances.

2. Results and Discussion

The as-received Cu\(_2\)S powders show a particle size distribution between 10 and 50 µm (Figure 1a), observed using a scanning electron microscopy (SEM). To facilitate Na\(^+\) diffusion, a high-energy planetary ball milling was used to grind the Cu\(_2\)S particles in the mixture of NG conductive agent and polyvinylidene (PVDF) binder. After ball milling, the Cu\(_2\)S particle size was significantly reduced to <2 µm (Figure 1b). The electrode active material consisted of NG-encapsulated Cu\(_2\)S particles. Because the parasitic reactions occurred at the low potential of ~0.13 V deteriorate the electrochemical performance of Cu\(_2\)S@NG electrode, in this work, we applied a surface coating of Al\(_2\)O\(_3\) on the electrodes to achieve a stable interface and thereby suppress the parasitic reactions. The ALD Al\(_2\)O\(_3\) coating on the electrode surface was used as a model system to demonstrate our design philosophy. Various thicknesses (2, 4, 6, and 8 nm) of the Al\(_2\)O\(_3\) coating were deposited on the Cu\(_2\)S@NG electrode to examine the effectiveness of Al\(_2\)O\(_3\) coating. Synchrotron-based XRD characterization was performed to investigate the crystallographic structure of the pristine Cu\(_2\)S powder and ALD-Cu\(_2\)S@NG electrode. Figure 1c reveals that both materials contained the mixed phases of Cu\(_2\)S and Cu\(_{1.8}\)S (both denoted as Cu\(_2\)S in this work), while the amorphous Al\(_2\)O\(_3\) nanocoating could not be identified by XRD. Figure 2 presents the energy-dispersive X-ray (EDX) mapping of element distribution on the electrode. The homogeneity of the Al element on the electrode reveals that Al\(_2\)O\(_3\) coating uniformly covers
both active Cu\textsubscript{2}S material and other inactive materials (e.g., PVDF and carbon additives). To further verify the coating uniformity on electrode materials, we also conducted an 80-cycle (~8 nm) Al\textsubscript{2}O\textsubscript{3} coating via ALD on either NG or Cu\textsubscript{2}S. SEM images of NG wrinkles (Figure S1a,b) and the Cu\textsubscript{2}S particle surface (Figure S1c,d) before and after ALD deposition both illustrate the superior uniformity and conformality of the Al\textsubscript{2}O\textsubscript{3} coating. EDX spectra of both materials (Figure S1e,f) also confirm the existence of Al\textsubscript{2}O\textsubscript{3} coating.

![Figure 1](image1.png)

**Figure 1.** SEM images of (a) the as-received Cu\textsubscript{2}S powder and (b) Atomic Layer deposition (ALD)-coated Cu\textsubscript{2}S@NG electrode. (c) XRD characterizations of the as-received Cu\textsubscript{2}S powder and ALD-coated Cu\textsubscript{2}S@NG electrode.

![Figure 2](image2.png)

**Figure 2.** (a) SEM image of ALD-coated Cu\textsubscript{2}S@NG electrode with energy-dispersive X-ray (EDX) mapping of (b) Al, (c) F, (d) Cu, (e) S, and (f) C elements, exhibiting the uniformity of Al\textsubscript{2}O\textsubscript{3} coating.

The electrochemical behavior of the ALD-Cu\textsubscript{2}S@NG electrode was investigated using SIB half-cells within a voltage range of 0.01–3 V. The cycling performance tests of the bare Cu\textsubscript{2}S@NG electrode and the ALD-coated electrodes, with 2, 4, 6, and 8 nm Al\textsubscript{2}O\textsubscript{3} coatings, were conducted with a constant current charging/discharging at 100 mA g\textsuperscript{-1} (Figure 3a). For the bare electrode, the discharge capacity at the first cycle was ~450 mAh g\textsuperscript{-1}, which is much higher than the theoretical capacity of Cu\textsubscript{2}S (337 mAh g\textsuperscript{-1}), and then decreased to ~350 mAh g\textsuperscript{-1} at the second cycle. The initially irreversible
capacity loss resulted from the formation of some solid electrolyte interphase (SEI) due to electrolyte decomposition. Starting from ~50 cycles, the bare Cu$_2$S@NG electrode suffered some capacity fading with a decreased capacity of 302 mAh g$^{-1}$ at the 100th cycle, probably due to some continued parasitic reactions. In comparison, all the ALD-coated electrodes showed some mitigation on capacity fading after 50 cycles and exhibited much better capacity retention. Among all electrodes, the electrode with a 6 nm Al$_2$O$_3$ coating showed the highest capacity (374 mAh g$^{-1}$) at the 100th cycle. Yet, a thicker coating (e.g., 8-nm Al$_2$O$_3$ coating) led to a relatively lower capacity (355 mAh g$^{-1}$), probably because of a lower Na ion diffusion. Compared with Cu$_2$S’s theoretical capacity of 337 mAh g$^{-1}$, the excessive capacity in the Cu$_2$S@NG electrode was attributed to the contribution from the sodiation into NG, because NG itself could deliver an initial capacity of ~290 mAh g$^{-1}$ and sustain a capacity of 84 mAh g$^{-1}$ at the 100th cycle (as shown in Figure S2). However, the irreversible capacity loss of the initial discharge can still be witnessed in the ALD-coated electrodes. This is probably related to the Al$_2$O$_3$ coating layer, which is covered by -OH functional groups. The -OH groups may cause some electrolyte decomposition but can be removed completely after the first discharge cycle. Figure 3b exhibits the nearly identical discharge/charge profiles between the bare and the ALD-coated (6 nm Al$_2$O$_3$) electrodes at the first cycle, revealing the electrochemically inactive nature of the Al$_2$O$_3$ coating. Hence, the improved capacity retention of all the ALD-coated electrodes (Figure 3a) indicates that Al$_2$O$_3$ coating can significantly enhance the interfacial stability after the first discharge–charge cycle and suppress the parasitic reactions during cycling. Because of the outstanding rate capability of Cu$_2$S, the ALD-Cu$_2$S@NG electrode with the 6 nm Al$_2$O$_3$ coating was also tested at various rates—i.e., 100 mA g$^{-1}$, 0.5 C, 1 C, 2 C, 5 C, and 10 C. The ALD-coated electrode showed an excellent rate capability, accounting for a capacity of ~250 mAh g$^{-1}$ at 10 C and a capacity retention of ~100% (363 mA g$^{-1}$ at 2nd cycle and 361 mA g$^{-1}$ at 110th cycle). It is apparent that the ALD-coated electrode outperforms the bare electrode (Figure 3c).

Figure 3. (a) The cycling performance of Cu$_2$S@NG electrodes with different ALD coating thicknesses at 100 mA g$^{-1}$ in the potential range of 0.01–3.0 V. (b) Comparison of the 1st cycle discharge–charge profiles between the bare and ALD-modified Cu$_2$S@NG electrodes. (c) The comparison of rate performance between the bare and ALD-modified electrodes at 100 mA g$^{-1}$, 0.5, 1, 2, 5, and 10 C in 0.01–3.0 V.
To further investigate the effect of Al₂O₃ coating on the electrochemical performance of the ALD-Cu₂S@NG electrodes, we conducted a comparative study on the bare and ALD-coated electrodes to investigate their redox potentials during cyclic voltammetry (CV) and interfacial resistances using EIS. Figure 4a,b exhibit the CV profiles for the bare and ALD-coated electrodes within five cycles at a scan rate of 0.1 mV s⁻¹. Due to the electrochemically inactive nature of Al₂O₃ coatings, the redox potentials for the Cu₂S reaction in an ALD-coated electrode are identical to those of the bare electrode, accounting for five cathodic peaks (at 1.89, 1.47, 1.13, 0.80, and 0.41 V) and three anodic peaks (at 1.59, 1.88, and 2.13 V). Our previous study unveiled the electrochemical mechanism ascribed to the complex intercalation and conversion reactions using two synchrotron-based X-ray diffraction and absorption techniques [20]. Briefly, Na ions first enter the Cu₂S lattice via intercalation when discharged to 1.6 V. Then, the intercalation proceeds together with some conversion between 1.6 and 0.8 V. Afterwards, the conversion reaction completes while Cu₂S is fully discharged. On the other hand, two additional cathodic peaks at lower potentials of 0.13 and 0.016 V are due to SEI formation [30] and the Na-NG electrochemical reaction [19], respectively. To provide a better understanding of the specific capacity due to these two additional reactions, we integrated their areal CV profiles between 0.01 and 0.2 V (as shown in Figure 4c). The results reveal that the 6 nm Al₂O₃ coating could suppress side reactions in the initial three cycles. Moreover, the interfacial resistances of the bare and ALD-coated (2, 4, 6, 8 nm Al₂O₃) electrodes were examined after the first, second, and fifth cycle via EIS measurements (the Nyquist plots in Figure 4d,e and Figure S3a–e). EIS data fitting was conducted using an equivalent circuit model (Figure S3f). In comparison to the bare electrode, apparently, the interfacial resistance drastically decreased for the ALD-coated electrodes (Figure 4f and Table S2). This indicates that the interfacial stability is significantly enhanced by the ALD Al₂O₃ coating. Furthermore, Figure 5 also corroborates that there was little change observed on the ALD-coated Cu₂S@NG electrode using SEM images, accounting for a stable interface established by the ALD coating of Al₂O₃.

Figure 4. Cyclic voltammetry profiles of (a) the bare Cu₂S@NG and (b) the ALD-modified Cu₂S@NG electrodes in the first 5 discharge–charge cycles. (c) Comparison of the discharged capacities in the range of 0.01–0.2 V for the first 5 cycles between the bare and ALD-modified electrodes. Nyquist plots with the fitting curves of electrochemical impedance spectroscopy (EIS) measurements of (d) bare and (e) ALD-modified electrodes in initial 3 cycles. (f) Comparison of the solid electrolyte interphase (SEI) film resistance between bare and ALD-modified electrodes.
Figure 5. SEM images of the ALD-coated Cu$_2$S@NG electrode (a) before cycling and after (b) 1st discharge and (c) 1st charge.

### 3. Conclusions

In this study, we investigated the surface modification strategy via ALD to stabilize the high-performance Cu$_2$S@NG anode in the full voltage range of 0.01–3 V. An ultrathin (6 nm) Al$_2$O$_3$ coating was coated homogeneously on a Cu$_2$S@NG electrode via ALD. Compared to the bare electrode, the ALD-coated Cu$_2$S@NG electrode sustains high capacity of 374 mAh g$^{-1}$ at 100 mA g$^{-1}$ for 100 cycles and exhibits ~100% retention in rate capability (up to 10 C). The stable performance of the ALD-coated Cu$_2$S@NG electrode is mainly ascribed to the significantly enhanced interfacial stability by the ALD Al$_2$O$_3$ coating. Our study revealed that the ALD Al$_2$O$_3$ coating can suppress the parasitic reactions at low potentials. As a consequence, the ALD-coated Cu$_2$S@NG electrode enabled the highest electrode capacity of ~300 mAh g$^{-1}$, much higher than the capacity of 252 mAh g$^{-1}$ of the bare Cu$_2$S@NG electrode (Table S1). This work demonstrates that surface modification via ALD is a key strategy to enhance interfacial stability and improve electrochemical cyclability for the Cu$_2$S@NG electrode. We expect that this work will shed light on development of high-performance SIBs using ALD modification.

### 4. Experimental Section

Preparation of electrode materials: The as-received copper(I) sulfide (Cu$_2$S) powder (Sigma-Aldrich) was mixed with a conductive additive (NG, ACS Material) and polyvinylidene fluoride (PVDF) binder (MTI Corporation) in a weight ratio of 8:1:1 in 1-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich) solvent. The mixture was ball-milled in a high-energy planetary system (MSE 0.4L Bench Top Vertical Planetary Ball Milling machine) at a speed of 870 rpm for 6 h, leading to a homogeneous slurry. Subsequently, the received slurry was cast onto a Cu foil with a 200 µm doctor blade. The resultant laminates were dried in air overnight and then further dried at 100 °C in a vacuum for 8 h. The surface modification with an Al$_2$O$_3$ coating was performed on the dried electrode laminates in a commercial ALD (Savannah 200, Veeco) system at 100 °C, using trimethylaluminum (TMA) and H$_2$O as precursors.

Electrochemical measurements: The CR2032 coin cells were used to evaluate the electrochemical performance of ALD-coated Cu$_2$S electrodes, using sodium metal as the counter electrode. The electrode laminates and sodium metal were punched into discs (7/16 inches in diameter), having an active loading range of 1.5–2 mg cm$^{-2}$. The separators used were polypropylene/polyethylene membranes (25 µm thick, Celgard MTI Corporation). The liquid electrolyte was 1 M NaPF$_6$ (Sigma-Aldrich) in diethylene glycol dimethyl ether solvent (DEGDME or diglyme, Sigma-Aldrich). The coin cells were assembled in an Ar-filled glove box with H$_2$O and O$_2$ levels of <0.01 ppm. Galvanostatic charge/discharge tests were conducted on a Neware Battery Testing System at room temperature (~25 °C). Cyclic voltammetry (CV) tests were performed using an SP-200 potentiostat (Bio-logic) at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.01–3.0 V versus Na/Na$^+$. The EIS measurements were carried out using the SP-200 potentiostat at the frequency range from 0.01 Hz to 100 kHz with an AC signal amplitude of 5 mV.
Material characterizations: The microscopic images of the electrodes were obtained using a NanoSEM 450, which was coupled with an EDX spectroscopy. The synchrotron-based ex situ X-ray diffraction (XRD) was carried out at APS 11 ID-C (0.1173 Å wavelength) at Argonne National Laboratory.

Supplementary Materials: The following are available online at [http://www.mdpi.com/2504-777X/4/4/184/s1](http://www.mdpi.com/2504-777X/4/4/184/s1), Figure S1: High-magnification SEM images of (a) bare and (b) Al₂O₃-coated (80 cycles) NG and (c) bare and (d) Al₂O₃-coated (80 cycles) Cu₂S demonstrate the uniformity and conformity of ALD coating on electrode materials. EDX element mapping of Al₂O₃-coated (e) NG and (f) Cu₂S reveals the contents of Al as the Al₂O₃ coating, Figure S2: Cycling performance of a Na-NG half-cell, delivering 84 mAh g⁻¹ capacity at 100th cycle. Figure S3: Nyquist plots from EIS measurements of ALD-coated Cu₂S@NG electrodes with (a) 1, (b) 2, (c) 4, (d) 6, and (e) 8 nm Al₂O₃ coatings during 5 cycles. (f) The physical model used for fitting EIS data, Table S1: Summary of electrode loading and battery performance in all previously reported literature and this study, Table S2: The fitted EIS data for Cu₂S@NG and ALD-coated Cu₂S@NG at 0.01–3V.

Author Contributions: Conceptualization, X.M.; methodology, X.M.; validation, X.M. and J.C.; formal analysis, J.C.; investigation, J.C.; resources, X.X.; data curation, X.X.; writing—Review and editing, X.M. and Z.C.; supervision, X.M. and J.C.; project administration, X.M.; funding acquisition, X.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the University of Arkansas. X.M. acknowledges the partial support from the Center for Advanced Surface Engineering, under the National Science Foundation Grant No. OIA-1457888 and the Arkansas EPSCoR Program.

Acknowledgments: ASSET III. XRD (beamlines 11 ID-C) measurements were performed at the Advanced Photon Source, a U.S. DOE Office of Science User facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Yang, Z.; Zhang, J.; Kintner-Meyer, M.C.; Lu, X.; Choi, D.; Lemmon, J.P.; Liu, J. Electrochemical energy storage for green grid. *Chem. Rev.* 2011, 111, 3577–3613. [CrossRef] [PubMed]
2. Deng, X.; Chen, Z.; Cao, Y. Transition metal oxides based on conversion reaction for sodium-ion battery anodes. *Mater. Today Chem.* 2018, 9, 114–132. [CrossRef]
3. Yabuuchi, N.; Kubota, K.; Dahbi, M.; Komaba, S. Research development on sodium-ion batteries. *Chem. Rev.* 2014, 114, 11636–11682. [CrossRef]
4. Metrot, A.; Guerard, D.; Billaud, D.; Herold, A. New results about the sodium-graphite system. *Synth. Met.* 1980, 1, 363–369. [CrossRef]
5. Jache, B.; Adelhelm, P. Use of Graphite as a Highly Reversible Electrode with Superior Cycle Life for Sodium-Ion Batteries by Making Use of Co-Intercalation Phenomena. *Angew. Chem. Int. Ed.* 2014, 53, 10169–10173. [CrossRef]
6. Stevens, D.; Dahn, J.J. The mechanisms of lithium and sodium insertion in carbon materials. *J. Electrochem. Soc.* 2001, 148, A803–A811. [CrossRef]
7. Tian, H.; Liang, Y.; Repac, J.; Zhang, S.; Luo, C.; Liou, S.; Wang, G.; Ehman, S.H.; Han, W. Rational design of core–shell-structured particles by a one-step and template-free process for high-performance lithium/sodium-ion batteries. *J. Phys. Chem. C* 2018, 122, 22232–22240. [CrossRef]
8. Lin, H.; Li, M.; Yang, X.; Yu, D.; Zeng, Y.; Wang, C.; Chen, G.; Du, F. Nanosheets-Assembled CuSe Crystal Pillar as a Stable and High-Power Anode for Sodium-Ion and Potassium-Ion Batteries. *Adv. Energy Mater.* 2019, 9, 1900323. [CrossRef]
9. Lu, S.; Wu, H.; Hou, J.; Liu, L.; Li, J.; Harris, C.J.; Lao, C.Y.; Guo, Y.; Xi, K.; Ding, S.; et al. Phase boundary engineering of metal-organic-framework-derived carbonaceous nickel selenides for sodium-ion batteries. *Nano Res.* 2020, 13, 2289–2298. [CrossRef]
10. Wueensch, B.J.; Buerger, M. The crystal structure of chalcocite, Cu₂S. *Miner. Soc. Am. Spec. Paper* 1963, 1, 164–170.
11. Putnis, A. Electron diffraction study of phase transformations in copper sulfides. *Am. Miner.* 1977, 62, 107–114.
12. Klein, F.; Jache, B.; Bhide, A.; Adelhelm, P. Conversion reactions for sodium-ion batteries. *Phys. Chem. Chem. Phys.* 2013, 15, 15876–15887. [CrossRef] [PubMed]
13. Boebinger, M.G.; Xu, M.; Ma, X.; Chen, H.; Unocic, R.R.; McDowell, M.T. Distinct nanoscale reaction pathways in a sulfide material for sodium and lithium batteries. *J. Mater. Chem. A* **2017**, *5*, 11701–11709. [CrossRef]

14. Chen, Q.; Ren, M.; Xu, H.; Liu, W.; Hei, J.; Su, L.; Wang, L. Cu$_2$S@N, S Dual-Doped Carbon Matrix Hybrid as Superior Anode Materials for Lithium/Sodium ion Batteries. *ChemElectroChem* **2018**, *5*, 2135–2141. [CrossRef]

15. Li, H.; Wang, K.; Cheng, S.; Jiang, K. Controllable electrochemical synthesis of copper sulfides as sodium-ion battery anodes with superior rate capability and ultralong cycle life. *ACS Appl. Mater. Interfaces* **2018**, *10*, 8016–8025. [CrossRef] [PubMed]

16. Qin, A.; Wu, H.; Chen, J.; Li, T.; Chen, S.; Zhang, D.; Xu, F. Constructing hyperbranched polymers as a stable elastic framework for copper sulfide nanoplates for enhancing sodium-storage performance. *Nanoscale* **2019**, *11*, 7188–7198. [CrossRef]

17. Fang, Y.; Yu, X.; Lou, X.W. Bullet-like Cu$_9$S$_5$ Hollow Particles Coated with Nitrogen-Doped Carbon for Sodium-Ion Batteries. *Angew. Chem.* **2019**, *131*, 7826–7830. [CrossRef]

18. Jing, M.; Li, F.; Chen, M.; Zhang, J.; Long, F.; Jing, L.; Li, X.; Ji, X.; Wu, T. Facile synthetic strategy to uniform Cu$_9$S$_5$ embedded into carbon: A novel anode for sodium-ion batteries. *J. Alloys Compd.* **2018**, *762*, 473–479. [CrossRef]

19. Cai, J.; Reinhart, B.; Eng, P.; Liu, Y.; Sun, C.; Zhou, H.; Ren, Y.; Meng, X. Nitrogen-doped graphene-wrapped Cu$_2$S as a superior anode in sodium-ion batteries. *Carbon* **2020**, *170*, 430–438. [CrossRef]

20. Lapteva, L.; Fedoseeva, Y.V.; Shlyakhova, E.; Makarova, A.; Bulusheva, L.; Okotrub, A.J. NEXAFS spectroscopy study of lithium interaction with nitrogen incorporated in porous graphitic material. *Mater. Sci.* **2019**, *54*, 11168–11178. [CrossRef]

21. Pu, N.; Peng, Y.; Wang, P.; Chen, C.; Shi, J.; Liu, Y.; Ger, M.; Chang, C. Application of nitrogen-doped graphene nanosheets in electrically conductive adhesives. *Carbon* **2014**, *67*, 449–456. [CrossRef]

22. Pham, D.T.; Sambandam, B.; Kim, S.; Jo, J.; Kim, S.; Park, S.; Mathew, V.; Sun, Y.K.; Kim, K.; Kim, J. Dandelion-shaped manganese sulfide in ether-based electrolyte for enhanced performance sodium-ion batteries. *Commun. Chem.* **2018**, *1*, 1–14. [CrossRef]

23. Smith, A.J.; Burns, J.C.; Dahn, J.R. A high precision study of the Coulombic efficiency of Li-ion batteries. *Electrochem. Solid State Lett.* **2010**, *13*, A177. [CrossRef]

24. Meng, X. Atomic-scale surface modifications and novel electrode designs for high-performance sodium-ion batteries via atomic layer deposition. *J. Mater. Chem. A* **2017**, *5*, 10127–10149. [CrossRef]

25. Sun, Q.; Lau, K.C.; Geng, D.; Meng, X. Atomic and Molecular Layer Deposition for Superior Lithium-Sulfur Batteries: Strategies, Performance, and Mechanisms. *Batter. Supercaps* **2018**, *1*, 41–68. [CrossRef]

26. Cai, J.; Sun, Q.; Meng, X. Novel nanostructured materials by atomic and molecular layer deposition. *AIMS Mater. Sci.* **2018**, *5*, 957. [CrossRef]

27. Liu, Y.; Wang, X.; Cai, J.; Han, X.; Geng, D.; Li, J.; Meng, X. Atomic-scale tuned interface of nickel-rich cathode for enhanced electrochemical performance in lithium-ion batteries. *J. Mater. Sci Technol.* **2020**, *54*, 77–86. [CrossRef]

28. Gao, H.; Cai, J.; Xu, G.; Li, L.; Ren, Y.; Meng, X.; Amine, K.; Chen, Z. Surface modification for suppressing interfacial parasitic reactions of a Nickel-Rich Lithium-Ion cathode. *Chem. Mater.* **2019**, *31*, 2723–2730. [CrossRef]

29. Luo, C.; Zhu, H.; Luo, W.; Shen, F.; Fan, X.; Dai, J.; Liang, Y.; Wang, C.; Hu, L. Atomic-layer-deposition functionalized carbonized mesoporous wood fiber for high sulfur loading lithium sulfur batteries. *ACS Appl. Mater. Interfaces* **2017**, *9*, 14801–14807. [CrossRef]

30. Hu, M.; Zhou, H.; Gan, X.; Yang, L.; Huang, Z.; Wang, D.; Kang, F.; Lv, R. Ultrahigh rate sodium ion storage with nitrogen-doped expanded graphite oxide in ether-based electrolyte. *J. Mater. Chem. A* **2018**, *6*, 1582–1589. [CrossRef]

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).