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Interface Optimization of Cu$_2$S Nanoparticles by Loading N-Doped Carbon for Efficient Sodium-Ion Storage

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Abstract: Rapid capacity fading and sluggish diffusion kinetics resulting from crystal conversion/powder pulverization hinder practical energy storage application of conversion-type electrodes. To address this issue, we prepared a Cu$_2$S/polyelectrolyte/graphene composite (denoted as Cu$_2$S/PG) through interfacial optimization by incorporating a polyelectrolyte to enhance the connection between Cu$_2$S powders and N-doped graphene. In comparison to CuS and Cu$_2$S, the electrochemical performance of Cu$_2$S/PG was significantly improved by nanocrystallization and carbon-coating, which delivers a capacity of 317 mAh g$^{-1}$ at 0.1 A g$^{-1}$ after 200 cycles. Moreover, we performed real-time analysis of the phase conversion and resistance evolution of the Cu$_2$S/PG electrode during Na$^+$ insertion/desertion using in situ X-ray diffraction (XRD) and in operando electrochemical impedance spectroscopy (EIS). Thus, the formation of the intermediate phase (Na$_2$S$_2$) was firstly discovered, which finally converts to Na$_2$S by the end of the sodiation process. In sum, the N-doped carbon/graphene wrapping acts as a protective barrier against electrolyte side reactions, thereby effectively improving the cyclability of the conversion-type Cu$_2$S electrodes.

Keywords: conversion anode; sodium-ion batteries; in situ X-ray diffraction; N-doped carbon compositing

1. Introduction
In recent decades, the extensive application of lithium-ion batteries in consumer electronics and electric vehicles has been notable, but has finally been constrained due to the limited availability and uneven distribution of lithium [1–4]. Consequently, there exists a pressing necessity for low-cost energy storage systems in renewable grids and power plants that has propelled escalated research into affordable sodium-ion batteries (SIBs), because they have been considered as potential alternatives due to the significantly high natural availability of sodium (2.75%) [5,6]. However, some issues for commercial usage of SIBs should be addressed, chiefly due to prevailing challenges such as their low energy density and subpar cycle lifespan. Therefore, there is much attention given to high-performance electrode materials for SIBs. Here, three types of SIB anode materials are generally recognized: intercalation type (such as hard carbon and Na$_2$Ti$_3$O$_7$), alloying type (including Sn and Sb), and conversion type (such as CuO and SnS) [7,8]. Moreover, transition metal sulfides (TMSs, like FeS$_2$, SnS$_2$, NiS, MnS, CuS, CoS, and ZnS) have attracted significant attention as conversion-type anodes for SIBs due to their high theoretical capacities and the low cost of materials [9–15]. Among them, copper sulfides (Cu$_x$S, $x = 1$–2) demonstrate relatively high theoretical capacities, ranging from 564 to 337 mAh g$^{-1}$ [16]. For
instance, the Cu_{1.8}S electrode displays a capacity of approximately 420 mAh g^{-1} due to the occurrence of both of Cu^{0}/Cu^{1+} and Cu^{1+}/Cu^{2+} redox couples [17]. Furthermore, Cu_{2}S exhibits enhanced conductivity attributed to its smaller bandgap (1.21 eV) [18] and larger Cu-S bond length (2.25–2.35 Å) when compared to CuS (~2.19 Å) [7,19]. Consequently, Cu_{2}S has demonstrated better electrochemical performance, characterized by long potential plateaus and high initial Coulombic efficiency [20,21].

Despite possessing the aforementioned advantages, Cu_{2}S faces critical challenges in electrochemical cycling, including electrode pulverization, capacity fading, and polysulfide formation [14]. In order to overcome these issues, two strategies have been widely applied: the first strategy involves the synthesis of TMS nanoparticles, while the second strategy is surface modification through carbon coating. In detail, TMS nanoscaling can mitigate internal stress induced by volume changes during cycling, thus relieving the occurrence of microcracks. Furthermore, surface coating not only preserves particle integrity but also hinders side reaction with liquid electrolyte, thereby promoting the formation of a stable solid electrolyte interphase (SEI) film [10,22]. Additionally, the introduction of a heteroatom-doped carbon layer serves as a physical barrier to inhibit polysulfide shuttling. Finally, it enhances wettability and compatibility between electrodes and electrolytes, resulting in improved electronic conductivity and ionic transferability [7,19,23,24].

As mentioned above, a composite electrode material consisting of Cu_{2}S nanoparticles embedded in N-doped graphene was designed, achieving high capacity and cycling stability as an SIB anode. In this study, a simple precipitation and thermal reduction method was employed to synthesize CuS nanoparticles and a Cu_{2}S/polyelectrolyte/graphene composite (denoted as Cu_{2}S/PG), respectively. The influence of N-doping carbon on the electrochemical performance of the Cu_{2}S/PG composite was systematically assessed. Additionally, in situ XRD was utilized to uncover the phase transition of Cu_{2}S during sodiation/desodiation processes, while in operando EIS was conducted to analyze the evolution of resistance. The results could suggest that Cu_{2}S/PG provides a short ionic pathway for Na^{+} ions and exhibits remarkable cycling stability, making it a promising candidate for anode materials in SIBs.

2. Materials and Methods

2.1. Materials and Reagents

Firstly, Copper Sulfide (CuS) nanoparticles were fabricated utilizing the precipitation technique inspired by the previous report [25], as illustrated in Figure 1a. Copper nitrate trihydrate (Cu(NO_{3})_{2}-3H_{2}O) with purity ≥98.0% and thioacetamide (C_{2}H_{5}NS) with purity ≥99.0% were obtained from Sigma-Aldrich (St. Louis, MO, USA). The reactants were used in a S:Cu molar ratio of 1.1:1.0. A 10 wt.% aqueous solution of thioacetamide was incrementally added to a boiling solution containing 0.5M Cu^{2+}. Following 15 min of vigorous agitation, the resulting precipitate was repeatedly washed and centrifuged using both deionized water and ethanol. The precipitate material was then dried at 80 °C in a vacuum oven for 12 h to obtain the black CuS precursor.

The Cu_{2}S/graphene composite was prepared utilizing electrostatic attraction and thermal reduction methods [26]. A total of 0.50 g of CuS precursor and 1.25 g of poly(diallyldimethylammonium chloride) (PDDA) with 20 wt.% concentration from Aldrich were dispersed in 100 mL of deionized water by vigorous stirring, forming suspension A. Simultaneously, 0.10 g of graphene from Inner Mongolia Dasheng Co., Ltd. (Hohhot, China) and 0.84 g of poly(sodium-4-styrenesulfonate) (PSS) with 30 wt.% concentration from Aldrich were dispersed in 20 mL of deionized water to form suspension B. Suspensions A and B were thoroughly mixed by vigorous stirring again. The obtained sediment was washed and dried at 80 °C for 12 h. After carbonization under argon flow at 500 °C for 3 h, the final obtained composite sample was denoted as Cu_{2}S/PG.

For the control group, Cu_{2}S nanoparticles were prepared using a precipitation reaction between Cu(NO_{3})_{2}, thiosemicarbazide (>99%, Sigma-Aldrich), and Na_{2}SO_{3} (>98.0%, Sigma-Aldrich) employed as a mild reducing agent [27]. The solutions with a Cu^{2+}:S^{2–}...
ratio of 2.0:1.1 (molar ratio) were mixed using ultrasonic irradiation at 100 °C for 10 min. Subsequently, the resulting black precipitate was separated through centrifugation, washed several times with deionized water and ethanol, and finally collected as Cu$_2$S particles after drying at 80 °C in a vacuum oven for 12 h.

![Figure 1. (a) Preparation illustration of the Cu$_2$S/PG; (b–e) SEM images of (b) graphene, (c) CuS, (d) Cu$_2$S/PG, (e) Cu$_2$S; and EDS elemental mapping (f–j) of the Cu$_2$S/PG (Cu, S, C and N).](image)

2.2. General Characterization

The morphology of the prepared samples was characterized using a Hitachi SU1510 Scanning Electron Microscope (SEM, Tokyo, Japan). Quantitative elemental analysis was identified with Energy-Dispersive X-ray Spectroscopy (EDS) by Bruker. Raman measurements were obtained using a 523 nm laser with a Horiba JY HR-800 Raman spectrometer (Longjumeau, France). Crystallographic data were acquired with a Bruker D8 Venture X-ray Powder Diffraction (Karlsruhe, Germany) using Mo K$_\alpha1$ radiation ($\lambda = 0.70932$ Å), covering a 2θ range of 10° to 50°. Analytical assessment of the acquired diffraction patterns was carried out using the Rietveld refinement method utilizing FullProf software (Version 1.2.4) [28]. X-ray Photoelectron Spectroscopy (XPS) was conducted using a Thermo ESCALAB XI+ XPS spectrometer (Waltham, MA, USA).

2.3. Electrochemical Characterization

In this study, the working electrodes were fabricated using an active material (80 wt.%), carbon black (10 wt.%, super P Li, Timcal, Willebroek, Belgium), and PVDF binder (10 wt.%, R6020/1001, Solvay, Brussels, Belgium). The slurry was then doctor bladed onto a copper foil. Afterward, the coated foil underwent initial drying at room temperature for 2 h, followed by further drying at 80 °C for 12 h. Subsequently, the coated foil was punched into discs with a diameter of φ12 mm to serve as working electrodes. Coin cells of CR2032 type were assembled within an argon-filled glovebox (Super, Mikrouna Mech, Beijing, China). Each coin cell consisted of a working electrode, a Whatman® separator (φ17 mm), a sodium foil (φ15 mm, Alfa Aesar, Ward Hill, MA, USA), and 200 μL of 1 M NaClO$_4$ in EC/PC electrolyte. Galvanostatic cycling with potential limitation (GCPL) and cyclic voltammetry (CV) techniques were employed using a Bio-Logic potentiostat (Seyssinet-Pariset, France), utilizing a potential range of 3.0 to 0.01 V vs. Na+/Na$^+$ to investigate the electrochemical performance. To analyze the Na$^+$ storage mechanism of the Cu$_2$S/PG electrode, a coin cell
with a Kapton foil window was assembled for an in situ XRD experiment. The cell was cycled at 80 mA g$^{-1}$ within a potential range of 0.01 to 3.0 V vs. Na/Na$^+$ during the XRD testing. Furthermore, a three-electrode EL-cell$^9$ was assembled to conduct in operando EIS tests, with the cell cycled over a potential interval of 0.185 V within a voltage range from the open-circuit voltage to 0.01 V.

3. Results and Discussion

3.1. Synthesis and Characterization of Copper Sulfide Composites

As depicted in Figure 1a, the CuS precursor was prepared by mixing C$_2$H$_5$NS (as a sulfur source, S$^{2-}$) and Cu$^{2+}$ in a weak alkaline environment. The Cu$_2$S/PG precursor was obtained through the electrostatic attraction of the CuS precursor, graphene, and polyelectrolytes, followed by thermal reduction during the carbonization process. SEM was conducted to examine the surface morphology of the samples. The graphene exhibits two-dimensional sheets with a wrinkled structure, where the sheet sizes reached at least 20 µm (Figure 1b). Figure 1c shows the stacking of CuS clusters composed of numerous primary nanoparticles (~90 nm). After carbonization, the Cu$_2$S/PG composites display a microstructure consisting of carbon-coated Cu$_2$S nanoparticles loaded onto graphene sheets (Figure 1d). Despite a rougher surface resulting from carbonization, the Cu$_2$S/PG composites maintain the original size of the CuS particles. Figure 1e shows Cu$_2$S nanoparticles prepared through ultrasonic stirring and precipitation reactions, showcasing an average diameter of approximately 60 nm. Additionally, EDS mapping in Figure 1f−j demonstrates the homogeneous distribution of Cu, S, C, and N throughout the Cu$_2$S/PG sample.

XRD analysis (see Figure 2a) reveals that hexagonal CuS belongs to space group $P6_3/mmc$ (registry no.: ICSD 41911), while the CuS undergoes reduction to Cu$_2$S by the loaded carbon, resulting in the formation of a tetragonal phase (registry no.: ICSD 95398, space group: $P4_32_12$, as shown in Figure 2b) [25,26]. Additionally, bare Cu$_2$S exhibits the same tetragonal phase as Cu$_2$S/PG, as evident from Figure 2c. The use of carbon modification strategies has been extensively adopted to address inherent issues associated with conversion-type anodes for SIBs [29]. However, the XRD reflections of polyelectrolyte and graphene-coated carbon in Cu$_2$S/PG cannot be observed due to their amorphous structure.

Raman spectra of the prepared samples are presented in Figure 2d. The band observed at approximately 261 cm$^{-1}$ corresponds to the Cu–S lattice vibration [30], while the band at 466 cm$^{-1}$ is attributed to S–S stretching (A1g mode), indicating the high crystallinity of CuS and Cu$_2$S [31]. Conversely, in the Cu$_2$S/PG spectrum, the dominant D band and G band associated with carbon are observed at approximately 1321 and 1583 cm$^{-1}$, respectively. Moreover, the bands related to Cu-S vibration and S-S stretching disappear, suggesting complete coverage of Cu$_2$S particles by loaded carbon [32,33]. Peak fitting analysis of the Cu$_2$S/PG spectrum (Figure S1) indicates a high ratio of G to D bands ($I_G/I_D = 0.88$), signifying a substantial proportion of sp$^2$-conjugated carbon. This value exceeds the threshold value for electron-conductive carbon ($I_G/I_D \geq 0.52$) [34]. Consequently, it can be inferred that the carbon layer coating is beneficial to electronic conductivity.

Additionally, X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical composition of Cu$_2$S/PG. Figure S2a indicates two distinct peaks at 952.6 eV and 932.5 eV, attributed to Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ bands, correspondingly. In conjunction with a Cu LMM peak at 917.1 eV, it confirms a +1-valence state of copper within Cu$_2$S/PG, as depicted in Figure S2b [20]. As shown in Figure S2c, the S 2p spectral data have been deconvoluted to six peaks of varying binding energy. They signify the existence of S$^{2-}$, along with detected impurities such as (S$_2$)$^{2-}$ on the sample’s surface. Figure S2d presents the deconvolution of the C 1s peak into two peaks, ascribed to the preponderance of C-C bonds and the minor presence of C–N bonds. This implies a successful introduction of N atoms into the carbon lattice. Figure S2e shows the N 1s peak deconvoluted into two peaks at 398.9 eV and 400.4 eV, corresponding respectively to pyridinic N and pyrrolic N. This corroborates the successful doping of the N atom from PDDA amine functional groups.
Predictably, N-doping aids the electron transfer and electrolyte infiltration in a Cu$_2$S/PG electrode, thereby enhancing the electrochemical performance of Na$^+$ storage [24,35].

![Figure 2](image_url)

**Figure 2.** (a–c) XRD patterns of (a) CuS, (b) Cu$_2$S/PG, and (c) Cu$_2$S; (d) Raman spectra of CuS, Cu$_2$S/PG, and Cu$_2$S.

### 3.2. Electrochemical Test

In this study, the as-prepared electrodes were tested in half cells with Na metal serving as the counter electrode. Figure 3a,b illustrate the CV curves of CuS and Cu$_2$S at a scan rate of 0.1 mV s$^{-1}$. During the initial cycles, multiple electrochemical reactions are evident by several redox peaks. In both samples, the cathodic scan of the first cycle exhibits peaks at 1.7 V and 1.5 V, which are attributed to the Na$^+$ insertion into CuS and Cu$_2$S, respectively [10,36]. Subsequently, the broad peak at approximately 1.1 V is associated with the formation of a solid–electrolyte interphase (SEI) layer [37,38]. The sharp peak around 0.3 V in the CuS sample and peaks below 1.0 V in the Cu$_2$S sample correspond to the conversion reaction to Na$_2$S and Cu. In the subsequent anodic process, the relatively weak peak at around 1.2 V corresponds to Na$^+$ extraction from the loaded carbon. The subsequent anodic peaks at 1.5 V, 1.8 V, and 2.2 V are assigned to the conversion process from Na$_2$S+Cu to CuS during Na$^+$ extraction [37,39]. However, the redox pairs for both samples disappear after five cycles due to the rapid structural failure of the sulfur skeleton and irreversible conversion process [40]. In contrast, the Cu$_2$S/PG sample, which exhibits similar redox peak potentials, demonstrates a relatively stable cycling process. The CV curves in Figure 3c clearly reveal two repeatable redox pairs at 1.5 V vs. 1.6 V and 1.8 V vs. 2.2 V. This stability can be attributed to the modification of Cu$_2$S with N-doped carbon, which suppresses polysulfide shuttling and side reactions with the electrolyte, thus stabilizing the electrode’s surface [7]. Moreover, the incorporation of graphene efficiently enhances the electronic conductivity of the composite Cu$_2$S/PG. Additionally, the surface-controlled charge storage below 0.8 V further contributes to more Na$^+$ storage [41].
2.6 V is illustrated in Figure 4a. The corresponding XRD patterns (scan 1−103) are presented in Figure 4b. Based on the transformation of the XRD patterns, the entire process can be roughly divided into four steps (referred to as step I−IV).

The evaluation of the rate capability of prospective electrode materials is significantly crucial for SIBs. This work represents the specific capacities recorded at escalating current densities, which include 0.1, 0.2, 0.5, 1.0, and 2.0 A g\(^{-1}\) (see Figure 3d). When compared to the CuS and Cu\(_2\)S electrodes, the Cu\(_2\)S/PG electrode exhibits an enhanced specific capacity. It presents average capacities of 468, 347, 240, 181, and 133 mAh g\(^{-1}\) at ascending current densities. When setting current to its initial density (0.1 A g\(^{-1}\)), the Cu\(_2\)S/PG electrode shows a superior capacity of approximately 491 mAh g\(^{-1}\). Continuously, the Cu\(_2\)S/PG electrode was studied using a long-term cyclic test, as displayed in Figure 3e. In the initial twenty cycles, a decrease in the specific capacity is found in the Cu\(_2\)S/PG electrode, which then becomes a stable capacity within 200 cycles. Herein, the Cu\(_2\)S/PG electrode exhibits specific capacities of 151 mAh g\(^{-1}\) at 1 A g\(^{-1}\) and 317 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), respectively. Concurrently, a Coulombic efficiency of over 98% is achieved after fifty cycles. In relation to Table S1, the initial capacity of the Cu\(_2\)S/PG electrode is not the most impressive among recent Cu\(_2\)S composite anodes for SIBs, while it denotes exceptional potential concerning outstanding cycling stability.

3.3. Mechanism Study for Initial Na\(^+\) Storage

In the CV test (see Figure 3c), the Cu\(_2\)S/PG exhibits a reversible electrochemical process. Previous studies have indicated that the initial cathodic peak in the CV curve was ascribed to the intercalation process of Na\(^+\) ions, which was revealed through ex situ XRD analysis [7,42]. Additionally, in situ XRD is a powerful technique for unravelling the phase evolution and electrochemical mechanism during sodiation/desodiation processes. To gain further insights into the Na\(^+\) storage mechanism, this work employs in situ XRD measurements with high resolutions for the Cu\(_2\)S electrode for the first time. The first galvanostatic cycling profile in the potential range of open circuit voltage (OCV)→0.01 V→2.6 V is illustrated in Figure 4a. The corresponding XRD patterns (scan 1−103) are presented in Figure 4b. Based on the transformation of the XRD patterns, the entire process can be roughly divided into four steps (referred to as step I−IV).
In the initial sodiation (OCV-1.4 V, Step I), the XRD diffractions of the Cu$_2$S exhibit a slight left shift, with a gradual intensity decline, and finally disappear by the sixth scan at 1.4 V (Figures 4c–e and S3a). Also, this process shows no emergence of any other new phase. It indicates that Na$^+$ intercalation in the Cu$_2$S structure leads to the expansion and disordering of the Cu$_2$S lattice. Subsequent scans between 1.4 V and 0.9 V (Step II) gradually exhibit new reflections at 7.6°, 9.4°, 10.3°, 13.5°, and 17.1° from the sixth to the thirteenth scan. This evidence hints at the formation of cubic Na$_2$S$_2$ (COD #96-901-6082, see Figure S3b), accompanied by a quick disappearance of residual Cu$_2$S. Concurrently, the reflections at 13.2° and 18.6° become more intense, corresponding to the formation of metallic Cu (see Figure 4d,e). It can be inferred that Na$^+$ prefers to first intercalate into the Cu$_2$S, followed by the conversion process [43]. As such, the preliminary intercalation process plays a vital role in the nanostructural conversion of the Cu$_2$S/PG electrode.

In Step III (Scans 14–52, ranging from 0.9 to 0.01 V), XRD reflections for Na$_2$S begin to emerge once the Na$_2$S$_2$ reflection diminishes, as shown in Figure S3c. Inspired by Bauer’s study [44], Na$_2$S can transition into longer polysulfides (Na$_2$S$_x$, 4 ≤ x ≤ 8) by a side reaction, which can be dissolved in the electrolyte. In the present research, the occurrence of Na$_2$S$_2$ signals the suppression of polysulfide shuttling, aided by N-doped carbon modification [45]. From the 14th to the 30th scan, no significant changes are witnessed, implying that no discernible transitions in crystalline phases took place. Also, peak diffraction of Cu is found in the entire sodiation process. During the initial desodiation process (Step IV, Scans 53–103, from 0.01 V to 2.6 V as shown in Figure S3d), the reflection intensities for both the generated cubic Cu and Na$_2$S diminish progressively, but they persist until the completion of the desodiation process. This indicates that the transformed metallic Cu particles do not entirely revert to Cu$_2$S, and the residual Cu nanoparticles are scattered in the electrode matrix, thereby enhancing the conductivity. In summary, the initial sodiation/desodiation process, as studied by in situ XRD, can be described in the following steps:
Step I (sodiation—intercalation, OCV~1.4 V):
\[ \text{tetragonal Cu}_2\text{S} + x\text{Na}^+ + xe^- \rightarrow \text{Na}_x\text{Cu}_2\text{S} \]

Step II (sodiation—conversion, 1.4 V~0.9 V):
\[ \text{Na}_x\text{Cu}_2\text{S} + y\text{Na}^+ + ye^- \rightarrow 0.5(x + y)\text{Na}_2\text{S}_2 + \text{Cu} \]

Step III (sodiation—conversion, 0.9 V~0.01 V):
\[ \text{Na}_2\text{S}_2 + 2\text{Na}^+ + 2e^- \rightarrow \text{cubic 2Na}_2\text{S} \]

Step IV (desodiation—conversion, 0.01 V~2.6 V):
\[ \text{cubic Na}_2\text{S} + \text{Cu} \rightarrow \text{CuS} + 2e^- + 2\text{Na}^+ \]

The discussion of the in situ XRD test indicates that the Na\(^+\) insertion/extraction in Cu\(_2\)S/PG is a multi-step process. To deeply view Na\(^+\) diffusion during the electrochemical cycle, *in operando* EIS data during the initial cycle were analyzed. As depicted in Figure S4, Nyquist plots are drawn based on a three-electrode EL-cell\(^\text{®}\), wherein a ring-shaped Na reference electrode closely envelopes both the working and counter electrodes. This test cell was (dis)charged at a potential interval of 0.185 V, followed by a stabilization period of 1 h, as seen in Figure S5.

The variation in resistance with the potential interval is primarily influenced by crystal phase transitions and the formation of surficial SEI. In order to elucidate the evolution of resistance during the initial cycle, *in operando* EIS plots and the corresponding fitted resistances are presented in Figure 5. The applied equivalent circuit used for fitting is illustrated in Figure S6. By analyzing the Nyquist plots in combination with the equivalent circuit, four distinct regions can be identified. The intersection of the plots with the x-axis corresponds to the resistance of the liquid electrolyte, denoted as R\(_{le}\). The semicircular curve observed in the high-frequency region signifies interface resistance (R\(_{int}\)), which can be further categorized into electrode surface resistance (R\(_{sur}\)) and SEI resistance (R\(_{SEI}\)). The semicircle observed in the medium-frequency region can be attributed to the charge transfer resistance (R\(_{ct}\)). Finally, the steeply inclined line in the low-frequency region is attributed to Warburg diffusion (W\(_a\)), specifically Na\(^+\) diffusion within the porous structure of the electrode.

**Figure 5.** Analysis of Nyquist plots achieved from *in operando* EIS test in the 1st cycle: (a) discharge 2.50–1.39 V, (b) discharge 1.20–0.01 V, (c) resistances evolution in the 1st discharge process; (d) charge 0.09–1.20 V, (e) charge 1.39–2.50 V, (f) resistances evolution in the 1st charge process.
The evolution of fitted resistances is illustrated in Figures S5c and 5f. Initially, $R_{le}$ exhibits no significant change, suggesting that the electrolyte remains stable during cycling. Regarding $R_{int}$, it maintains a modest value of 1–2 Ω, with slight fluctuations during the discharge/charge cycle. Notably, the $R_{int}$ during the charging cycle is lower than during the discharge cycle. This can be attributed to the facilitation of Na$^+$ diffusion through the interface, due to a compatible SEI layer formed during the discharge cycle. According to a report by J. Zhang et al. [46], the solvated Na$^+$ structure in the NaClO$_4$-EC/PC possesses a high electron cloud density. Furthermore, the surface of N-doped carbon on the Cu$_2$S tends to repel Na$^+$ cations and absorb ClO$_4^-$ anions, which is conducive to promoting the formation of an inorganic-rich SEI (containing Na$_2$O and NaCl), thereby enhancing the interfacial compatibility of the Cu$_2$S/PG electrodes.

Moreover, $R_{ct}$ demonstrates several peak values at approximately 2.0 V, 1.4 V, and 0.6 V during discharge, coinciding with the reduction peaks observed in the CV curve (Figure 3c) and the Na$^+$ insertion processes identified through in situ XRD: Cu$_2$S $\rightarrow$ Na$_x$Cu$_2$S $\rightarrow$ Na$_2$S$_2$ $\rightarrow$ Na$_2$S, as also confirmed in previous reports [47]. Additionally, the $R_{ct}$ decreases to 0.7 V due to increased electrode conductivity resulting from the accumulation of metallic Cu grains [25]. During the charge process, $R_{ct}$ exhibits high resistance around 1.2 V, which can be attributed to the charge transfer involved in the reversed conversion reaction.

In sum, the proposed mechanism for the Na$^+$ insertion/extraction process in Cu$_2$S/PG is illustrated in Figure 6. In this study, the introduction of N-doped carbon modification assists in stabilizing the surface of the Cu$_x$S material, thereby inhibiting polysulfide shuttling between the electrodes and mitigating side reactions with the electrolyte [48]. Furthermore, the incorporation of graphene significantly enhances the electrode’s conductivity. Consequently, the Cu$_2$S/PG electrode exhibits excellent long-term cycling stability.

4. Conclusions

In this study, we successfully prepared a N-doped carbon/graphene-modified Cu$_2$S electrode material for SIBs by employing precipitation and thermal reduction methods. The incorporation of N-doped carbon and graphene layers effectively suppresses polysulfide shuttling, thereby preserving the structural integrity and enhancing the conductivity of the Cu$_2$S particles. Consequently, we observed improved cycling stability in the Cu$_2$S/PG sample compared to the bare Cu$_2$S, which exhibits a sustainable capacity of 257 mAh g$^{-1}$ after 200 cycles (at a current density of 0.1 A g$^{-1}$), demonstrating good cycling stability.
Furthermore, the Cu$_2$S/PG sample displayed superior rate performance compared to the bare CuS and Cu$_2$S. To gain a comprehensive understanding of the sodiation/desodiation mechanism during the first cycle, we analyzed the phase and structure transformation of Cu$_2$S/PG in SIBs using in situ XRD and in operando EIS techniques. The insights obtained from this analysis contribute to a deeper understanding of the working mechanism of TMS conversion-type materials. Overall, this work provides valuable insights into copper sulphide as a potential electrode material for Na$^+$ storage.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/su152416846/s1](https://www.mdpi.com/article/10.3390/su152416846/s1), Figure S1: Raman curve fitted with band combination for the first-order spectrum of the Cu$_2$S/PG; Figure S2: XPS spectra of pristine Cu$_2$S/PG: Cu 2p (a), Cu LMM-2 (b), S 2p (c), C 1s (d), and N 1s (e); Table S1: A review of preparation methods and electrochemical performance of Cu$_2$S composites as SIB electrodes; Figure S3: Analysis of typical phase change of the Cu$_2$S/PG electrode in the 1st (de)sodiation for Na$^+$ storage: (a) step I—scan2, (b) step II—scan7, (c) step III—scan50, and (d) step IV—scan70; Figure S4: Nyquist plots obtained from in operando EIS test in the first cycle: 1st discharge process (a) and 1st charge process; Figure S5: Setting potential steps in the EIS measurement for the 1st cycle; Figure S6: Illustration of equivalent circuit for fitting the Nyquist plots. References [49–51] are cited in the supplementary materials.

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