CuS Microspheres as High-Performance Anode Material for Na-ion Batteries

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In this work, CuS microspheres are synthesized by a facile microwave synthesis without any template or additive. As-prepared CuS microspheres display steady reversibility by adopting triethylene glycol dimethyl ether (TEGDME) as the electrolyte solvent and adjusting cut-off voltage to 0.6 – 3.0 V. The discharge capacity stands at 162 mAh g⁻¹ after 200 cycles with the capacity retention of 95.8%. Electrochemical kinetics of CuS electrodes is investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT) tests. Beyond that, electrochemical reactions of CuS electrodes are explored using ex-situ X-ray diffraction (XRD). As far as we know, it is not only the best performance of CuS electrodes in Na-ion batteries (NIBs) but also the first time that the kinetics and reaction mechanism of CuS in NIBs are investigated.

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1. Introduction

With the rapid consumption of non-renewable fossil fuels and the issue of environmental pollution, renewable and clean energy such as wind and solar energy has gained much attention [1]. Large scale energy storage systems are required to store the electricity generated from wind turbines and solar cells, which can be used as green and renewable energy resources [2,3]. Although lithium-ion batteries (LIBs) can be regarded as a solution to meet these challenges theoretically, yet the insufficiency (the content of lithium in the earth’s crust is only about 20 ppm), maldistribution (lithium is mainly distributed in South America in the earth’s crust) and high price of lithium are blocking LIBs to be used in large scale energy storage [4]. Sodium is one of the most abundant elements in the earth’s crust (over 23 000 ppm) and sodium resources are unlimited everywhere in the earth’s crust [5]. Sodium is the second lightest alkali metal next to lithium. On the other hand, the standard electrode potential of Na/Na⁺ (-2.71 V vs SHE) is close to that of Li/Li⁺ (-3.04 V vs SHE) [6]. Due to its abundance and impressive properties, rechargeable Na-ion batteries (NIBs) are ideal substitutes for LIBs [7].

Finding suitable electrode materials for NIBs, especially anode materials, has always been an important issue for the development of NIBs, and a lot of work have been done on this issue [8–12]. Natural graphite, which is the most commonly used anode material for LIBs, fails to match NIBs on account of the larger size of sodium ion as well as the thermodynamic factors and the higher plating potential of sodium ion[13,14]. Although disordered carbon (hard carbon) is investigated as the anode material for NIBs, the cyclability is unsatisfying for commercial use [15,16]. It remains vital and challenging to find proper anode materials for NIBs.

Owing to their low cost and high theoretical capacities, metallic sulfides have been widely studied as anode materials for NIBs [17–20]. For example, Zhu et al. applied MoS₂ nanoneedles as the anode material for NIBs [21]. Hu et al. prepared long-life NIBs by using pyrite FeS₂ as the anode material [22]. Kim et al. studied the sodium storage property of Cu₃S at room temperature [23]. By adopting ether based electrolyte, the capacity stood at 220 mAh g⁻¹ after 20 cycles and the reaction mechanism was preliminarily investigated. CuS has been widely explored as the anode material for LIBs, it shows high discharge capacity and outstanding cycle life [24–28]. CuS could also be one of the potential anode material candidates for NIBs. Klein et al. successfully assembled CuS/Na battery whose initial discharge capacity could reach up to 750 mAh g⁻¹ [29]. However, the capacity faded quickly, the discharge capacity dropped to 85 mAh g⁻¹ after 5 cycles which may be caused by the use of carbonate based electrolyte and side reactions due to the low cut-off voltage (0.01 – 3.0 V). More efforts should be paid to fulfill the application of CuS in NIBs.
Herein we report a facile way to synthesize CuS microspheres with simple raw materials under microwave irradiation. By adopting triethylene glycol dimethyl ether (TEGDME) as the electrolyte solvent and adjusting cut-off voltage to 0.6 – 3.0 V, the discharge capacity of as-prepared CuS microspheres stands at 162 mAh g⁻¹ after 200 cycles with the capacity retention of 95.8%. Synthetic CuS shows outstanding cycle performance which surpasses previous work by Klein et al. greatly. In addition, the electrochemical kinetics of the batteries are investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT) tests. Beyond that, the electrochemical reactions of CuS electrodes are primarily investigated by ex-situ X-ray diffraction (XRD).

2. Experimental

2.1. Raw materials and synthesis

Cu(NO₃)₂·H₂O (AR) and Na₂S₂O₃·5H₂O (AR) were purchased from Shanghai Chemical Co. Ltd. Sodium metal (99%) and NaClO₄ (99.99%, water free) were purchased from Aladdin Industrial Corporation. Acetylene black (battery grade), polypropylene fluorides (PVDF, battery grade) and N-methyl-2-pyrrolidene (NMP, battery grade) were purchased from Guangzhou Songbai Chemical Industrial Co. Ltd. Ethylene carbonate (EC, battery grade), diethyl carbonate (DEC, battery grade) and TEGDME (battery grade) were bought from Zhejiang Guotai-Huaron New Chemical Materials Co. Ltd. All the chemicals were used without further purification.

CuS microspheres were prepared under microwave irradiation in this work, where Cu(NO₃)₂ was operated as copper source, Na₂S₂O₃ was used as sulfur source and deionized water was used as the solvent. 25 mL 2.0 M Cu(NO₃)₂ solution and 25 mL 2.0 M Na₂S₂O₃ solution were mixed together in a 100 mL flat-bottomed flask to form a transparent emerald solution. This solution was placed into domestic microwave reactor (microwave frequency: 2450 MHz, output power: 650 W), treated with microwave pulse for 30 minutes where duty ratio was set to 6/30 (6 seconds on, 24 seconds off). Black powders were collected afterwards, washed by deionized water and dehydrate ethanol for several times, then dried overnight in vacuum oven at 60°C.

2.2. Characterization

The XRD patterns were recorded with Rigaku Ultima IV (Rigaku Corporation, Japan) with CuKα radiation operated at 40 kV, 30 mA. Scanning rate was set to 2° min⁻¹ (2θ). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrum (EDS) were performed on Hitachi S-4800 (Hitachi Corporation, Japan). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern were tested with the JEM-2100 (JEOL, Japan) at 200 kV. The surface area and pore volume were measured using a micromeritics ASAP 2020 surface and porosity analyzer at 77 K. Surface areas was calculated using the Brunauer–Emmett–Teller method.

2.3. Electrochemical studies

The electrochemical characteristics were tested using CR2032-type coin cells. The active materials, acetylene black, and PVDF were mixed in a weight ratio of 70: 15: 15 in NMP. The slurry was coated on copper foil and dried in vacuum oven at 60°C for 12 hours. The electrode sheet was punched into 12 mm discs, and pressed at 16 MPa to make the active materials contact tighter with the current collector. The loading mass of active material is 1.82 – 2.10 mg per electrode (1.61 – 1.86 mg cm⁻²). Half cells were assembled using the prepared electrodes as positive electrode and sodium metal as negative electrode. The electrolyte was prepared by dissolving NaClO₄ (1 mol L⁻¹) in the mixture solvent of EC and DEC (1:1, V/V), or dissolving NaClO₄ (1 mol L⁻¹) in TEGDME. Celgard 2400 (Celgard, LLC, US) was used as separator. All cells were fabricated in an argon-filled glove box (Mbraun, Germany). The cyclic voltammograms were tested on the CHI 1030C multi-potentiostat (Shanghai Chenhua Electrochemical Instruments, Shanghai, P. R. China). The galvanostatically charge-discharge tests and GITT test were carried out on the Neware CT-3008W battery test system (Neware Battery Testing Instruments, Shenzhen, P. R. China). The EIS tests were performed on the Solarton 1260A and 1287A impedance/Gain-phase Analyzer (AMETEK, UK) with sodium metal as the reference and counter electrode. All the electrochemical tests were carried out at room temperature (25°C).

2.4. Calculation procedure

All calculations reported herein were performed using the Gaussian 09 computational package. All geometries were fully optimized at the B3PW91 level of DFT. There is no imaginary frequency when frequency calculations were performed at the B3PW91. The lanL2DZ basis set was used to describe S, and the standard 6-311G+(d, p) basis set was used for H, C, and O.

3. Results and discussions

In a typical microwave synthesis process, CuS nanoparticles are formed under microwave irradiation firstly, then the nanoparticles
aggregate into microspheres. According to the work by Nafees et al. [30], the chemical equations taken place in this reaction are:

\[ \text{Cu(NO}_3\text{)}_2 \rightarrow \text{Cu}^{2+} + 2\text{NO}_3^- \]  
\[ \text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{Na}^+ + \text{S}_2\text{O}_3^{2-} \]  
\[ \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HS}^- + \text{HSO}_4^- \]  
\[ \text{Cu}^{2+} + \text{HS}^- \rightarrow \text{CuS} \_\text{(nanoparticles)} + \text{H}^+ \]  
\[ \text{CuS} \_\text{(nanoparticles)} \rightarrow \text{CuS} \_\text{(microspheres)} \]

The structure and morphology information were characterized by XRD, SEM and TEM. The XRD pattern of as-prepared material is shown in Fig. 1. The diffraction lines correspond well with the standard PDF card of hexagonal CuS (JCPDS No. 78-0876), indicating pure phase of synthetic CuS. Fig. 2a, 2b display the low and high magnification SEM images. The particle size of as-prepared CuS microspheres is around 2 μm. The CuS microspheres are assembled by nano-sized primary particles, which also can be demonstrated from the TEM image (Fig. 2c). The HR-TEM image and SAED pattern (inset) are shown in Fig. 2d. The SAED pattern with clear rings indicates the polycrystalline structure of CuS microspheres formed by nanoparticles. The d-spacing of 0.281 and 0.305 nm correspond with the (103) and (102) lattice planes of CuS, respectively. Energy-dispersive X-ray spectrum (EDS) and elemental mapping images of as-prepared CuS are shown in Fig. 3, demonstrating the uniform distribution of Cu and S in the CuS microspheres, the elemental ratio of Cu to S is 1.04, close to theoretical ratio 1.

According to former work by Klein et al., CuS shows high initial discharge capacity, yet the capacity fades quickly. We have noticed that in their work, carbonate based electrolyte is used and the cut-off voltage is set to 0.01 – 3.0 V. As is often the case, the mismatch of electrolyte and inappropriate cut-off voltage may cause side reactions between electrolyte and active materials, further lead to poor battery performance. To optimize the electrochemical performance of CuS electrodes, a series of experiments were carried out. Firstly, batteries with various cut-off voltage were tested using CR-2032 coin-type batteries with the current density of 50 mA g⁻¹. When the cut-off voltage is adjusted to 0.1 – 3.0 V, the battery shows high capacity, yet the capacity fades quickly in 30 cycles and fails after 40 cycles (Fig. 4a). This can be ascribed to the decomposition of electrolyte and other side reactions like the formation of solid electrolyte interface (SEI) etc. [29]. By discharging the battery to 1.0 V and charging to 3.0 V, the battery shows much better cycle stability, yet the capacity is much lower (Fig. 4b), which can be owed to insufficient electrochemical reactions. When the cut-off voltage is set to 0.6 – 3.0 V, a relatively high capacity and outstanding cycle performance can be obtained (Fig. 4c). The illustrative comparison of CuS electrodes discharged to different voltage is shown in Fig. 4d.

Different types of electrolytes were tested with the current density of 50 mA g⁻¹ between 0.6 – 3.0 V. Fig. 4e exhibits the charge and discharge curves of CuS/Na battery using the carbonate based electrolyte, where NaClO₄ is dissolved in the mixture solvent of EC and DEC. The initial cycle shows good electrochemical activity, yet the capacity declines quickly after several cycles. This phenomenon matches with the results of Klein et al. [29]. Fig. 4b displays the charge and discharge curves of CuS/Na battery in ether-based electrolyte, where NaClO₄ is dissolved in TEGDME.

![Fig. 2. (a)&(b) low and high magnification SEM images of as-prepared CuS microspheres, (c) TEM image, (d) HR-TEM image and SAED pattern (inset) of as-prepared CuS microspheres.](image-url)
Battery shows impressive reversibility where discharge capacity of 168 mAh g⁻¹ can be maintained after 50 cycles. The distinct difference of cycle performances (Fig. 4f) demonstrates that TEGDME is a more suitable electrolyte solvent for CuS. We conjecture that the tremendous difference of cycle performance is related to the compatibility of CuS with electrolytes. According to the research by Klein et al. and our ex-situ XRD results below, conversion reactions take place when CuS is applied in NIBs, thus, sodium sulfide/polysulfide would be generated during electrochemical reactions [29]. Generated $S^{2-}/S_n^{2-}$ ($2 \leq n \leq 8$) tends to react with carbonate solvent, resulting in the poor cyclic performance of CuS/Na batteries [31,32]. On the contrary, these anionic groups would not react with TEGDME (Scheme S1). On the other hand, CuS microspheres are packed by nano-sized primary particles as we have mentioned. The surface is determined to be 7.876 m² g⁻¹, and porous structure can be deduced from the adsorption/desorption isotherm (Fig. S1). According to Z. Hu et al., TEGDME with 1D structure would boost the performance of anode materials because of lower reaction energy barrier [22]. These may explain why CuS shows much better electrochemical performance in ether based electrolyte than carbonate based electrolyte.

Ex-situ XRD tests were carried out to investigate the electrochemical reactions of the CuS electrodes. Fig. 5a shows the XRD patterns of CuS electrodes at different charge-discharge state, which corresponds with the discharge-charge capacity-voltage curve in Fig. 5b. XRD pattern 1 represents the pristine CuS electrode, where only diffraction lines correspond with hexagonal CuS can be observed, the slope from 20 – 30° (2 theta) is the XRD signals of conductive carbon black and binder added in the electrode. Pattern 2 corresponds the CuS sample discharged to 1.5 V, where diffraction lines attributed to Cu₂-S (0 ≤ x ≤ 0.2) can be detected, which means CuS may firstly converts into non-stoichiometric Cu₃₂-S. Pattern 3 is the diffraction pattern of fully discharged CuS electrode, where diffraction lines attributed to Na₂S and some intermediates (marked with *), mainly composed by NaₓCuₙS₋ₓ, where α, β, γ represent integers can be observed, diffraction lines corresponded with metallic Cu also can be seen. It is highly possible that Na⁺ would react with Cu₂-S to form the intermediary NaₓCuₙS₋ₓ firstly, then NaₓCuₙS₋ₓ converts into Na₂S and Cu. Possible electrochemical reactions during discharge process are shown below:

\[(2-x)\text{CuS} + (2x-2)\text{Na}^+ + (2x-2)e^- \rightarrow \text{Cu}_{2-x}\text{S} + (1-x)\text{Na}_2\text{S}\]  
\[\text{Cu}_{2-x}\text{S} + \text{Na}^+ + e^- \rightarrow \text{Cu} + 0.5\text{Na}_2\text{S}\]  
the overall reaction is:
\[\text{CuS} + 2\text{Na}^+ + 2e^- \rightarrow \text{Cu} + \text{Na}_2\text{S}\]

this conjecture matches with the CV curves below. Pattern 4 shows the electrode charged to 2.0 V after fully discharge, where we can tell that intermediates and some Cu₃₂-S were formed during the charge process. Pattern 5 is the diffraction pattern of the CuS electrode charged to 3.0 V, the main diffraction lines can be attributed to Cu₃₂-S. The possible electrochemical reactions in the charge process are listed below:

\[(2-x)\text{Cu} + \text{Na}_2\text{S} \rightarrow \text{intermediates} \rightarrow \text{Cu}_{2-x}\text{S} + 2\text{Na}^+ + 2e^-\]  
instead of CuS, Cu₃₂-S are generated after charging. The initial discharge process can be decomposed into irreversible part (CuS to Cu₃₂-S) and reversible part (Cu₃₂-S to CuS), the transformation from CuS to Cu₃₂-S is irreversible, which mainly leads to the low initial columbic efficiency [26]. The second and subsequent cycles are primarily the reversible transition between Cu₃₂-S and Cu (Fig. S2). This property is similar with CuO, which has been reported by Wang et al. [33].

Cyclic voltammetry (CV) was carried out to investigate the sodium storage property of as-prepared CuS electrode. The optimized TEGDME was used as the electrolyte solvent. The CV curves at scan rate of 0.2 mV s⁻¹ in the voltage range of 0.6 – 3.0 V are shown in Fig. 6a. In the first cathodic scan, a small reduction peak at 1.85 V can be observed, which corresponds with the conversion from CuS to Cu₃₂-S. This reaction is irreversible, so the peak at 1.85 V disappears gradually in the subsequent scans. Two major peaks at 1.12 V and 0.84 V represent the reaction of Cu₃₂-S into intermediary NaₙCuₙS₋ₙ, and the reaction from intermediary NaₙCuₙS₋ₙ to Na₂S and Cu, respectively. In the anodic scan, two major oxidation peaks can be observed. The anodic peak at 1.60 V represents the conversion from Cu and Na₂S to the intermediary NaₙCuₙS₋ₙ, while the peak at 2.10 V corresponds with the conversion reaction from intermediary NaₙCuₙS₋ₙ to Cu₃₂-S. This reaction mechanism can also be supported by ex-situ XRD carried out.
In subsequent scans, reduction peaks shift to more positive potential while oxidation peaks shift to lower potential, which demonstrates smaller polarization of the electrode. The smaller polarization indicates better reversibility of the electrode. It is worth noting that a small peak at 1.65 V arouses in the subsequent anodic scans, which may correspond with the phase transition of various intermediaries. The dQ/dV curves of CuS electrode in the initial cycle and the 20th cycle show similar results (Fig. S3).

The electrochemical stability evaluation was carried out with the current density of 200 mA g⁻¹. The discharge capacity after 200 cycles remains at 162 mAh g⁻¹ with the capacity retention of 95.8% (which is compared with the 2nd discharge capacity, eliminating initial irreversible capacity), showing remarkable cyclic stability (Fig. 6b). The charge and discharge curves with different current densities are shown in Fig. 6c. The discharge capacities with current density of 50, 100, 200, 400, 800 and 1600 mA g⁻¹ are 180, 157, 140, 120, 100 and 90 mAh g⁻¹, respectively. The capacity can return to 177 mAh g⁻¹ when the current density is restored to 50 mA g⁻¹, indicating good reversibility of as-prepared CuS in the case of high current density (Fig. 6d). However, the capacity drops significantly when operated at high current density, this may be caused by insufficient electronic conductivity, which can be possibly improved by extra effort such as preparation of CuS/
carbon composites (like CuS/carbon nano tubes or CuS/graphene, etc.) [34,35].

To investigate the electrochemical reaction kinetics of the electrodes, electrochemical impedance spectroscopy (EIS) was carried out (Fig. 7a). The high frequency semicircle in the Nyquist plot is related with the charge transfer resistance of the electrode, while the spike at the low frequency is an indication of Warburg impedance of long-range Na-ion diffusion. The charge transfer resistance decreases from 425 to 289 Ω after 20 cycles (enlarged Fig. 7b). The reduced resistance can be ascribed to the activation of the electrode as well as the better filtration of the electrolyte.

To get further insights, CV test was carried out. Fig. 7c shows CV curves of CuS/Na battery with different scan rate from 0.2 – 1.5 mV s⁻¹. As the scan rate increases, the intensity and area of the redox peaks increases because the capacity equals the area divided by scan rate, and the capacity should be a constant. Furthermore, the cathodic peaks shift to lower potential while corresponding anodic peaks shift to higher potential, which demonstrates
enlarged polarization of CuS electrode. The Na-ion apparent diffusion coefficient \((D_{CV})\) can be calculated using Randles–Sevcik equation:

\[
i_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{1/2}\]

(10)

where \(n\) represents the number of electrons transferred in the redox event (for single redox peak, \(n\) is usually 1), \(F\) is Faraday Constant (96485 C mol\(^{-1}\)), \(A\) is the working electrode area (1.13 cm\(^2\)), \(C\) stands for sodium ion concentration in the electrode (0.048 mol cm\(^{-3}\)), \(v\) is the scan rate, \(R\) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \(T\) is the temperature in Kelvin (298.15 K).

Linear relationship lies between the peak current \(i_p\) and the square root of scan rate \(v^{1/2}\), the \(D_{CV}\) can be calculated making use of the slope of the linear fit (Fig. 7d). The \(D_{CV}\) calculated through peak C1, C2, A3, A4, A5 is \(1.20 \times 10^{-11}\), \(1.39 \times 10^{-11}\), \(1.53 \times 10^{-12}\), \(2.23 \times 10^{-11}\) and \(2.20 \times 10^{-12}\) cm\(^2\) s\(^{-1}\), respectively. It is obvious that peak A3 and A5 display much lower diffusion coefficient than
other peaks, which means the transition from Cu back to copper sulfide is more kinetically difficult in the electrochemical reactions [36]. On the contrary, larger D_{CV} derived from peak A4 indicating the transition between intermediaries is prone to taking place.

In a typical GITT measurement, the battery was discharged with a current impulse with the current density of 0.1C for an interval τ of 600 seconds followed by an open circuit standing for 3600 seconds, where 1C was taken as 200 mA g⁻¹ according to previous constant current discharge test. Fig. 7e exhibits the comparison of GITT and constant current (CC) measurement of the discharge process of the same CuS electrode. The GITT curve matches well with the CC curve, where two plateaus around 1.7V and 1.2V can be observed. According to equation (11), the Na-ion diffusion coefficients (D_{GITT}) in CuS at various voltages can be determined using GITT data:

\[
D_{GITT} = \frac{4}{\pi \tau} \left( \frac{mV_m}{MA} \right) \left( \frac{\Delta E_s}{\Delta E_s} \right)^2 \left( \tau = \frac{l^2}{D_{GITT}} \right) \tag{11}
\]

where m and M are the active material mass (1.96 mg) and molecular weight (96 g mol⁻¹) of CuS, respectively, V_m is the molar volume of CuS (20.83 cm³ mol⁻¹). A is the electrode surface area (1.13 cm²), and L is the thickness of the electrode (13 μm). ΔE_s is the change of steady-state potential after a discharge pulse and open circuit standing, while ΔE_p is the voltage change during a discharge pulse. The calculated D_{GITT} values are shown in Fig. 7f. The D_{GITT} values of CuS electrode lie in 4.26 × 10⁻¹⁴ – 1.42 × 10⁻¹⁰ cm² s⁻¹. We have noticed that the minimum value of D_{GITT} appears around 1.64 and 1.15 V, which coincides with the plateaus of the discharge curve. The smaller diffusion coefficient could be due to the phase transition during discharge process [37,38]. This result is comparable with the apparent diffusion coefficients obtained from CV test (Table 1).

4. Conclusions

In summary, CuS microspheres are synthesized rapidly by a facile microwave synthesis method. By adopting TEGDME as the electrolyte solvent and adjusting the cut-off voltage to 0.6 – 3.0 V, the cyclic stability of CuS electrodes improve significantly. When served as anode material for NIBs, the synthesized CuS can deliver a reversible discharge capacity of 162 mAh g⁻¹ after 200 cycles with the current density of 200 mA g⁻¹. It can still maintain the discharge capacity of 101 and 90 mAh g⁻¹ with the current density of 800 and 1600 mA g⁻¹, respectively. The electrochemical kinetics of CuS electrodes are investigated through EIS, CV and GITT tests. Moreover, the reaction mechanism of CuS in the electrode is preliminarily studied by ex-situ XRD. To the best of our knowledge, it is not only the first time that CuS is successfully applied in long-life rechargeable NIBs but also the first time that the kinetics and reaction mechanism of CuS/Na batteries are explored.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.lectacta.2017.07.018.

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