Author's Accepted Manuscript

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 PII:
 S2211-2855(18)30128-9

 DOI:
 https://doi.org/10.1016/j.nanoen.2018.02.060

 Reference:
 NANOEN2547

To appear in: Nano Energy

Received date: 29 January 2018 Revised date: 28 February 2018 Accepted date: 28 February 2018

Cite this article as: Fangyu Xiong, Yuqi Fan, Shuangshuang Tan, Limin Zhou, Yanan Xu, Cunyuan Pei, Qinyou An and Liqiang Mai, Magnesium Storage Performance and Mechanism of CuS Cathode, *Nano Energy*, https://doi.org/10.1016/j.nanoen.2018.02.060

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Magnesium Storage Performance and Mechanism of CuS Cathode

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Abstract

The exploration of cathode materials with high energy density has been considered as one key for the development of magnesium batteries. The high magnesium storage capacity of CuS has been demonstrated at high temperature (over 100 °C), but its electrochemical performance at lower temperature still needed to be improved largely. Herein, we realize the high magnesium storage activity (over 300 mAh g⁻¹) of CuS cathode at room temperature via adjusting electrode-electrolyte interface. In the full magnesium battery, CuS cathode achieves a high capacity of 119 mAh g⁻¹ after 30 cycles at 50 mA g⁻¹. Besides, the conversion-type storage mechanism has been certified via *ex-situ* XRD and so on. This work demonstrated CuS is a promising cathode material for magnesium battery.

¹ These authors contributed equally to this work.

Graphical abstract



Keywords: Magnesium battery, copper sulfide, cathode, storage mechanism

1. Introduction

Magnesium batteries (MBs) have attracted many attentions due to the high capacity (2205 mAh g⁻¹ and 3833 mAh cm⁻³), low reduction potential (-2.37 V *vs.* SHE), abundant reserve and dendritic-free nature of magnesium metal anode[1-5]. However, the high charge/radius ration of Mg²⁺ ions leads to a strong interaction between ions and host, which puts forward higher requirements for cathode materials[6-9]. Chevrel phase compound (Mo₆S₈) presented by Aurbach *et al.* achieves sufficient magnesium storage reversibility[10]. But, its low capacity (122 mAh g⁻¹, theoretically) and operating potential (1.1 V *vs.* Mg²⁺/Mg) result in a limited energy density (lower than 140 Wh kg⁻¹), which restrains the application of MBs[8, 10, 11]. Thus, exploiting suitable cathode material is still a great challenge for the development of MBs.

Recently, many materials have been investigated as cathode materials for MBs, including transition-metal oxides[7, 12, 13], transition-metal sulfides[14-17], and polyanionic compounds[18-21]. Among those, transition-metal sulfides exhibit

excellent lithium/sodium storage performance and usually display favorable Mg mobility due to that the lower polarizability of S^{2-} than $O^{2-}[1, 22-25]$. For CuS, the high theoretical capacity (560 mAh g⁻¹) gives the great prospect to realize high energy density in MBs[26, 27]. Duffort *et al.*[28] reported the high magnesium storage capacity (over 200 mAh g⁻¹) of CuS in MBs with all-phenyl complex (APC, 2PhMgCl–AlCl₃) in tetraglyme (G4) as electrolyte at 150 °C. Unfortunately, just a negligible electrochemical activity could be obtained at room temperature (25 °C), impeding the application of CuS cathode in MBs. Thus, realizing high magnesium storage activity of CuS at room temperature is important for its further development and practical application.

Herein, we realize high magnesium storage capacity of CuS (361 mAh g⁻¹) at room temperature via changing electrode-electrolyte interface and the capacity remains at 153 mAh g⁻¹ after 20 cycles. Considering the application in MBs, the full MBs based on CuS cathode also have been assembled, which displays high capacity (183 mAh g⁻¹) with flat discharge plateau and good cycling stability at elevated temperature. Moreover, in order to further understand the magnesium storage behavior of CuS, the magnesium storage mechanism has been explored via ex-situ X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) technologies.

2. Experimental Section

2.1 Material Synthesis

CuSO₄ · 5H₂O, Na₂S₂O₃, of analytical grade, were all purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Firstly, CuSO₄ · 5H₂O and Na₂S₂O₃ with molar ratio of 1:1 were dissolved into deionized water. Then, the solution was transferred into Teflon-lined stainless-steel autoclave and kept at 160 °C for 24 h, and then allowed to cool to room temperature. Finally, the as-synthesized sample was washed several times with deionized water and ethanol alternately, and dried at 70 °C under vacuum overnight.

2.2 Material Characterizations

XRD measurements were performed to investigate the crystallographic structure using a D8 Advance X-ray diffractometer with a nonmonochromated Cu Kα X-ray source. The field emission scanning electron microscopy (FESEM) images and energy dispersive spectrometry (EDS) elemental mappings were collected with a JEOL-7100F microscope. TEM and high resolution TEM (HRTEM) images were recorded by using a JEM-2100F STEM/EDS microscope. Raman spectra were obtained using a Renishaw INVIA micro-Raman spectroscopy system. XPS measurements were obtained using a VG MultiLab 2000 instrument.

2.3 Electrochemical Measurements

The electrochemical properties were characterized by assembling 2016 coin cells in a glove box ($O_2 \le 1$ ppm and $H_2O \le 1$ ppm), which used glass fiber as separator. Cathodes were obtained with 60% as-synthesized active materials, 30% acetylene black and 10% PTFE. The loading of the active material was about 5-7 mg cm⁻². With 0.5 M Mg(ClO₄)₂ dissolved in acetonitrile (Mg(ClO₄)₂/AN) as electrolyte, AC clothes

were utilized as anode and the potential of AC cloth is ~2.4 V vs. Mg^{2+}/Mg . While with 0.25 M 2PhMgCl-AlCl₃ dissolved in THF (APC/THF) and 2MgCl₂-AlCl₃ dissolved in DME (MACC) as electrolyte, magnesium foils were employed as anode. All the electrochemical performance was obtained after a discharge as conditioning. The main galvanostatic charge/discharge test and galvanostatic intermittent titration technique (GITT) test were performed with a multichannel battery testing system (LAND CT2001A) in the potential range of -1.65-0 V vs. AC or 0.2-1.9 V vs. Mg²⁺/Mg. Cyclic voltammetry (CV) curves were acquired with an electrochemical NUSCR workstation (CHI 760D).

3. Results and Discussion

In the Fig. 1a, all the diffraction peaks of as-synthesized sample were readily indexed to covellite CuS (JCPDS No. 01-078-0877, Hexagonal, space group: P63/mmc, a = 3.7938 Å, c = 16.341 Å) and no impurity was detected. In the Raman spectrum of as-synthesized sample (Fig. 1b), the sharp peaks located at about 268 and 477 cm⁻¹ were from covellite CuS and the peak located at about 477 cm^{-1} was identified as the S-S stretching mode at 4e sites [29, 30]. The as-synthesized CuS are composed of nanoshperes with diameter of 300-800 nm (Fig. 1c). From the high magnification FESEM image (Fig. 1d), the irregularity surface of CuS nanospheres was observed. Besides, the EDS elemental mappings show that the Cu and S elements are homogeneously distributed in the CuS nanospheres. The interior structure of CuS nanospheres have been characterized by TEM technology and the solid nature was

observed (Fig. 1e). In addition, the clear lattice fringes with distance of 0.328 nm were shown in the HRTEM image (Fig. 1f), corresponding to the d-space of (100) planes in covellite CuS. All the above results demonstrated that the pure CuS has been synthesized successfully.



Fig. 1. The structural characterizations for CuS. (a) The XRD pattern, (b) the Raman spectrum, (c) the SEM image, (d) the EDS elemental mappings, (e) the TEM image and (f) HRTEM image of as-synthesized CuS.

The electrode-electrolyte interface is important for magnesium storage performance, which decides the compatibility between electrolyte and cathode material[3, 31]. The electrode-electrolyte interface not only is affected by the electrode, but also depends on the components of electrolyte, including solvent and solute. In order to realize the high magnesium storage activity of CuS cathode, different electrolytes have been employed to adjust the electrode-electrolyte. Firstly, Mg(ClO₄)₂/AN has been selected due to its good compatibility for most kinds of

cathode material[1, 13, 21, 31, 32]. Considering the poor compatibility with magnesium metal of Mg(ClO₄)₂/AN electrolyte, the coin-type cells with AC clothes as anode have been assembled[3, 12, 31, 33]. Excitingly, the high magnesium storage capacity has been achieved at the room temperature. The CuS cathode displays a high initial discharge capacity of 361 mAh g⁻¹ with slope potential plateau at around 1.2 V (*vs.* Mg²⁺/Mg) (Fig. 2a, b). The gap between the discharge capacity and the charge capacity in first cycle may be attributed to the incomplete transformation and the side-reaction. After 20 cycles, the capacity of 153 mAh g⁻¹ was still obtained, indicating the good cycling stability. Moreover, during the conditioning, CuS displays a magnesium storage performance as high as 546 mAh g⁻¹, which is close to the theoretical capacity (560 mAh g⁻¹) (Fig. S1a). Although the Mg(ClO₄)₂/AN electrolyte is incompatible with magnesium metal anode, the excellent magnesium storage performance of CuS in this system demonstrated the possibility for it as cathode material in MBs with high capacity at room temperature.

For the application in MBs, the electrochemical performance of CuS in electrolytes possessed excellent compatibility with magnesium metal is important. Thus, APC/THF electrolytes also have been employed as electrolytes. The APC/THF electrolytes were prepared according to Mizrahi *et al.*[34] The electrochemical properties of as-prepared electrolyte were characterized via CV and galvanostatic charge/discharge tests (Fig. S2). The CV curve of Mg|APC|Mo cell at the scan rate of 100 mV s⁻¹ in the potential window of -1.0-2.0 V (vs. Mg²⁺/Mg) was shown in Fig. S2a. The reversible magnesium deposition/dissolution with efficiency of about 99%

was realized. The stability and polarization of magnesium deposition/dissolution have been evaluated by galvanostatic charge/discharge test at the current of 20 μ A cm⁻² (Fig. S2b). After the first few cycles, the overpotential stabilize at about 0.035 V. Compared to system with Mg(ClO₄)₂/AN electrolyte, CuS cathode with APC/THF electrolyte displays lower capacity, which may be attributed to the different electrode-electrolyte interfaces. At the current density of 20 mA g⁻¹, an initial discharge capacity of 138 mAh g⁻¹ was obtained (Fig. 2c and Fig. S3). During 12 to 15 cycles, the efficient capacity of about 80 mAh g⁻¹ with slope plateau at about 1.0 V was obtained (Fig. 2d). Although the capacity of CuS with APC electrolyte is lower than its theoretical capacity, which demonstrates the magnesium storage activity at room temperature and is higher than the reported highest capacity of CuS cathode with temperature below 100 °C (about 60 mAh g⁻¹)[28].



Fig. 2. The magnesium storage performance of CuS cathode at room temperature (25 °C). (a) The cycling performance of CuS cathode with $Mg(ClO_4)_2/AN$ as

electrolyte at 50 mA g^{-1} and (b) the corresponded charge/discharge curves. (c) The cycling performance of CuS cathode in full MBs with APC/THF as electrolyte at 20 mA g^{-1} and (d) the corresponded charge/discharge curves.

Working temperature has been considered as an important influence factor for magnesium storage performance[8, 12, 28]. And increasing working temperature appropriately is one efficient way to enhance the electrochemical performance. The charge/discharge curves of CuS cathode in full MBs at 20 mA g⁻¹ with different working temperature are shown in Fig. 3a. At 50 °C, CuS cathode exhibits a high capacity of 148 mAh g^{-1} with stable potential plateau at ~1.15 V. As temperature further increasing to 55 °C, the discharge capacity of CuS cathode at 20 mA g^{-1} increased to 164 mAh g^{-1} . But the low Coulombic efficiency (68.6%) was displayed, which may be attributed to the side reaction (e.g. the corrosion of stainless steel current collector) due to the over-high temperature.[28, 35] After adjusting the cut-off potential from 1.9 to 1.8 V, the Coulombic efficiency increased to 92.2% while the discharge capacity decreased to 53.2 mAh g^{-1} (Fig. S4). Thus, the working temperature of 50 °C was chosen during the subsequent electrochemical performance test. The rate performance of CuS cathode was shown in Fig. 3b and S5. At the current density of 5 mA g⁻¹, CuS cathode exhibited a high reversible capacity of 165 mAh g^{-1} with a short and a long discharge plateaus at ~1.55 V and ~1.15 V, respectively (Fig. S5). Compared with Mo₆S₈, the most successful cathode material for MBs, CuS cathode delivers higher capacity and higher operating voltage, which

means higher energy density (Fig. 3c). As the current density increasing to 50 mA g⁻¹, the capacity of 117 mAh g⁻¹ was still achieved (Fig. 3b). Meanwhile, with MACC electrolyte, CuS cathode also displays a high reversible capacity (over 100 mAh g⁻¹) at 50 mA g⁻¹ (Fig. S6). In the CV curve of CuS (Fig. 3d), two reduced peaks at 1.49 and 1.08 V and one oxidant peak located at 1.74 V were observed, corresponding well to the charge/discharge curves (Fig. S5). Besides, the cycling stability of CuS cathode also has been evaluated (Fig. 3e, f). After charging/discharging at 50 mA g⁻¹ for 30 cycles, the capacity of CuS cathode still remains at 119 mAh g⁻¹ (Fig. 3e). The high reversible capacity and excellent cycling performance make CuS become a promising cathode material for MBs.



Fig. 3. The electrochemical performance of CuS cathode in full MBs at elevated temperature. (a) The charge/discharge curves of CuS at 20 mA g⁻¹ at different temperatures. (b) The rate performance of CuS cathode at 50 °C; (c) the charge/discharge curves of CuS and Mo₆S₈; (d) the CV curve of CuS at 0.02 mV s⁻¹ in 0.2-1.9 V at 50 °C; (e) the cycling performance of CuS at 50 mA g⁻¹ at 50 °C and (f)

the corresponding charge/discharge curves.

In order to further understand the magnesium-ion storage behavior of CuS cathode, the reaction mechanism has been investigated via ex-situ XRD, XPS and HETEM technologies (Fig. 4). The ex-situ XRD patterns of CuS at different stages and the corresponded charge/discharge curves are shown in Fig. 4a, b, respectively. In conditioning process, after discharging to 1.25 V (stage b), the peaks of Cu_2S and MgS appear and the peaks of CuS weaken, indicating that the conversion reaction between CuS and Mg^{2+} was occurred. When further discharge to 0.2 V (stage c), the peaks of CuS disappear, demonstrating the complete conversion of CuS. In the subsequent charge process, the peaks of CuS appear again. However, after charging to 1.9 V (stage e), the peaks of CuS still are weaker than that of fresh electrode, which is attributed to the irreversible capacity. Moreover, the incomplete transformation from Cu₂S to CuS is one of the main reasons for the gap between theoretical capacity and practical capacity. Enhancing the reversibility of transition between Cu₂S to CuS may be an efficient way to further improve the magnesium storage performance of CuS. In the subsequent discharge process, the peaks of CuS disappear again, and the peaks of Cu₂S first strengthen and then disappear, indicating that Cu₂S has been further reduced during the magnesium storage process. The ex-situ XPS spectra have been utilized to investigate the valence state change of Cu element during the charge/discharge process (Fig. 4c). For fresh CuS cathode (stage a), most Cu element is +2 valence, while after discharging to 0.2 V in the first cycle (stage c), Cu^{2+} is

reduced to Cu^+ completely[36, 37]. After charging back to 1.9 V (stage *e*), part Cu^+ is oxidized to Cu^{2+} . After second discharge process, the peak of Cu^{0} has been observed, demonstrating the further reduction of Cu⁺ was occurred although the peaks of Cu metal is not detected in the XRD pattern[36]. Moreover, the ex-situ HRTEM also has been performed to demonstrate the component of cathode at different stages (Fig. 4d-g). The ex-situ HRTEM images are corresponded well with ex-situ XRD patterns. Besides, Cu metal nanoparticle with diameter below 5 nm has been observed (Fig. 4f), which coincides with XPS results, demonstrating that Cu₂S has been partly reduced to Cu metal. According to the above analysis, the theoretical magnesium storage mechanism of CuS is conversion reaction, which can be described as following equation (1) and (2). The theoretical specific capacity is as high as 560 mAh g^{-1} , ...paci ...o₆S₈ (122 mAh g⁻¹) $CuS + Mg^{2+} + 2 e^{-} \leftrightarrow Cu_2S + MgS$ 2 Cu₂S + Mg²⁺ + 2 e⁻ ↔ 2 Cu + MgS which is much higher than that of Mo_6S_8 (122 mAh g⁻¹).

$$2 \operatorname{CuS} + \operatorname{Mg}^{2+} + 2 e^{-} \leftrightarrow \operatorname{Cu}_2 S + \operatorname{MgS}$$
(1)

(2)



Fig. 4. The magnesium storage mechanism of CuS. (a) Ex-situ XRD patterns of CuS at different stages during first and second cycles and (b) the corresponding voltage-time curves; (c) The XPS spectra and (d-g) HRTEM images of CuS at different stages.

In addition, the micro/nanostructure change of CuS with APC electrolyte after magnesiation has been analyzed. The SEM image shows that the CuS nanospheres

after first discharge process are composed of nanoparticles with the size below 50 nm (Fig. S7). Besides, the TEM technology was utilized to further characterize the micro/nanostructure change of CuS (Fig. 5a). The solid nanospheres transform to hollow porous nanospheres, which may result from the large structural change of conversion-type reaction. The enhanced specific surface area of hollow porous structure may be responsible for the increase of discharge capacity of CuS cathode in the first several cycles. In addition, the EDS elemental mappings (Fig. 5b) show that Mg, Cu and S elements are uniform distribution in nanosphere, demonstrating the magnesiation of CuS was occurred during the discharge process. Magnesium-ion diffusivity $(D_{Mg2\scriptscriptstyle +})$ is one of the most important influence factors for magnesium storage performance. The galvanostatic intermittent titration technique (GITT) has been employed to analyze the D_{Mg2+} of CuS cathode (Fig. 5c and S6). In the GITT test of CuS, a high discharge capacity of 183 mAh g^{-1} was achieved. Moreover, the D_{Mg2+} of CuS cathode at different discharge stages was calculated from GITT curves (Fig. 5d, the detail of calculation is shown in Supporting Information) [12, 38]. In the first discharge plateau, CuS displays a high D_{Mg2+} about 1.6×10^{-11} cm² s⁻¹, while the D_{Mg2+} of CuS decreases to $1 \times 10^{-15} \sim 1 \times 10^{-13}$ in the second plateau. Different from the most reported results that D_{Mg2+} of cathode materials decreases as the discharge depth increasing, the D_{Mg2+} of CuS increases from 6.5×10^{-15} to 1.3×10^{-12} cm² s⁻¹ in the slope plateau at about 0.7 V. This result indicating that the D_{Mg2+} of cathode in this system is not only related to magnesium-ion concentration, but also affected by component.



Fig. 5. The magnesium storage behaviors of CuS. The characterizations for structural change after magnesiation: (a) The TEM image, (b) HAADF image and EDS elemental mappings of CuS after first discharged process. The analysis for magnesium storage dynamics: (c) the GITT curves at constant current pulse of 10 mA g^{-1} for 10 min followed by a relaxation period of 30 min (performed after conditioning); (d) the diffusivity of Mg²⁺ versus state of discharge calculated based on GITT curves.

4. Conclusions

The CuS cathode can achieve a high magnesium storage activity (361 mAh g⁻¹) at room temperature with Mg(ClO₄)₂/AN electrolyte. Moreover, it also displays excellent electrochemical performance in full MBs at elevated temperature. A high reversible capacity of 165 mAh g⁻¹ was obtained with main plateau at 1.15 V and excellent cycling stability (119 mAh g⁻¹ after 30 cycles at 50 mA g⁻¹). This electrochemical performance is better than the reported best result at similar

temperature. Besides, the magnesium storage mechanism of CuS cathode has been demonstrated as conversion reaction. Those results demonstrate that CuS is a promising cathode material for MBs with high capacity.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2016YFA0202603), the Programme of Introducing Talents of Discipline to Universities (B17034), the National Natural Science Foundation of China (51521001, 51602239), the National Natural Science Fund for Distinguished Young Scholars (51425204), the Hubei Provincial Natural Science Foundation of China (2016CFB267), and the Fundamental Research Funds for the Central Universities (WUT: 2017-YB-001).

Reference

- [1] P. Canepa, G. Sai Gautam, D.C. Hannah, R. Malik, M. Liu, K.G. Gallagher, K.A.Persson, G. Ceder, Chem. Rev. 117 (2017) 4287–4341.
- [2] J.W. Choi, D. Aurbach, Nat. Rev. Mater. 1 (2016) 16013.
- [3] J. Muldoon, C.B. Bucur, T. Gregory, Chem. Rev. 114 (2014) 11683–11720.
- [4] H.D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, D. Aurbach, Energy Environ. Sci. 6 (2013) 2265–2279.
- [5] J. Luo, S. He, T.L. Liu, ACS Energy Lett. 2 (2017) 1197–1202.
- [6] I. Shterenberg, M. Salama, Y. Gofer, E. Levi, D. Aurbach, MRS Bull. 39 (2014)453–460.
- [7] T. Koketsu, J. Ma, B.J. Morgan, M. Body, C. Legein, W. Dachraoui, M. Giannini,

- A. Demortiere, M. Salanne, F. Dardoize, H. Groult, O.J. Borkiewicz, K.W. Chapman,
- P. Strasser, D. Dambournet, Nat. Mater. 16 (2017) 1142–1148.
- [8] H.D. Yoo, Y. Liang, H. Dong, J. Lin, H. Wang, Y. Liu, L. Ma, T. Wu, Y. Li, Q. Ru,
- Y. Jing, Q. An, W. Zhou, J. Guo, J. Lu, S.T. Pantelides, X. Qian, Y. Yao, Nat. Commun. 8 (2017) 339.
- [9] I.A. Rodriguez-Perez, Y. Yuan, C. Bommier, X. Wang, L. Ma, D.P. Leonard, M.M.
- Lerner, R.G. Carter, T. Wu, P.A. Greaney, J. Lu, X. Ji, J. Am. Chem. Soc. 139 (2017) 13031–13037.
- [10] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, Nature 407 (2000) 724–727.
- [11] H.S. Kim, T.S. Arthur, G.D. Allred, J. Zajicek, J.G. Newman, A.E. Rodnyansky,A.G. Oliver, W.C. Boggess, J. Muldoon, Nat. Commun. 2 (2011) 427.
- [12] Q. An, Y. Li, H. Deog Yoo, S. Chen, Q. Ru, L. Mai, Y. Yao, Nano Energy, 18(2015) 265–272.
- [13] K.W. Nam, S. Kim, S. Lee, M. Salama, I. Shterenberg, Y. Gofer, J.S. Kim, E. Yang, C.S. Park, J.S. Kim, S.S. Lee, W.S. Chang, S.G. Doo, Y.N. Jo, Y. Jung, D. Aurbach, J.W. Choi, Nano Lett. 15 (2015) 4071–4079.
- [14] Y. Liang, H.D. Yoo, Y. Li, J. Shuai, H.A. Calderon, F.C. Robles Hernandez, L.C.Grabow, Y. Yao, Nano Lett. 15 (2015) 2194–2202.
- [15] X. Sun, P. Bonnick, L.F. Nazar, ACS Energy Lett. 1 (2016) 297–301.
- [16] Z.L. Tao, L.N. Xu, X.L. Gou, J. Chen, H.T. Yuan, Chem. Commun. (2004) 2080–2081.

- [17] Y. Liang, R. Feng, S. Yang, H. Ma, J. Liang, J. Chen, Adv. Mater. 23 (2011) 640–643.
- [18] Z.-D. Huang, T. Masese, Y. Orikasa, T. Mori, T. Minato, C. Tassel, Y. Kobayashi,
- H. Kageyama, Y. Uchimoto, J. Mater. Chem. A 2 (2014) 11578–11582.
- [19] Y. NuLi, Y. Zheng, F. Wang, J. Yang, A.I. Minett, J. Wang, J. Chen, Electrochem.
- Commun. 13 (2011) 1143–1146.
- [20] R. Zhang, C. Ling, ACS Appl. Mater. Interfaces 8 (2016) 18018–18026.
- [21] J. Zeng, Y. Yang, S.B. Lai, J.X. Huang, Y.Y. Zhang, J. Wang, J.B. Zhao,
- Chem.-Eur. J. 23 (2017) 16898–16905.
- [22] J. Ni, X. Bi, Y. Jiang, L. Li, J. Lu, Nano Energy 34 (2017) 356–366.
- [23] K. Zhang, M. Park, L. Zhou, G.-H. Lee, J. Shin, Z. Hu, S.-L. Chou, J. Chen,
- Y.-M. Kang, Angew. Chem. Int. Ed. 55 (2016) 12822-12826.
- [24] D. Kong, H. He, Q. Song, B. Wang, W. Lv, Q.-H. Yang, L. Zhi, Energy Environ.
- Sci. 7 (2014) 3320-3325.
- [25] H. Liang, J. Ni, L. Li, Nano Energy 33 (2017) 213-220
- [26] J.S. Chung, H.J. Sohn, J. Power Sources 108 (2002) 226–231.
- [27] Y. Wang, X. Zhang, P. Chen, H. Liao, S. Cheng, Electrochim. Acta 80 (2012) 264–268.
- [28] V. Duffort, X. Sun, L.F. Nazar, Chem. Commun. 52 (2016) 12458–12461.
- [29] M. Ishii, K. Shibata, H. Nozaki, J. Solid State Chem. 105 (1993) 504-511.
- [30] T. Hurma, S. Kose, Optik 127 (2016) 6000–6006.
- [31] H. Tang, N. Xu, C. Pei, F. Xiong, S. Tan, W. Luo, Q. An, L. Mai, ACS Appl.

Mater. Interfaces 9 (2017) 28667–28673.

- [32] P. Novák, R. Imhof, O. Haas, Electrochim. Acta 45 (1999) 351–367.
- [33] Y. Shao, M. Gu, X. Li, Z. Nie, P. Zuo, G. Li, T. Liu, J. Xiao, Y. Cheng, C. Wang,
- J.-G. Zhang, J. Liu, Nano Lett. 14 (2013) 255–260.
- [34] O. Mizrahi, N. Amir, E. Pollak, O. Chusid, V. Marks, H. Gottlieb, L. Larush, E.
- Zinigrad, D. Aurbach, J. Electrochem. Soc. 155 (2008) A103–A109.
- [35] Y. Cheng, T. Liu, Y. Shao, M.H. Engelhard, J. Liu, G. Li, J. Mater. Chem. A 2 (2014) 2473–2477.
- [36] S.K. Chawla, N. Sankarraman, J.H. Payer, J. Electron Spectrosc. Relat. Phenom.
- 61 (1992) 1–18.

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- [37] Y. Xie, A. Riedinger, M. Prato, A. Casu, A. Genovese, P. Guardia, S. Sottini, C.
- Sangregorio, K. Miszta, S. Ghosh, T. Pellegrino, L. Manna, J. Am. Chem. Soc. 135 (2013) 17630–17637.
- [38] C. Pei, F. Xiong, J. Sheng, Y. Yin, S. Tan, D. Wang, C. Han, Q. An, L. Mai, ACS Appl. Mater. Interfaces 9 (2017) 17060–17066.



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Highlights

- 1. The high magnesium storage capacity (over 300 mAh g⁻¹) of CuS has been realized.
- 2. The full magnesium metal battery displays excellent electrochemical performance.
- 3. The conversion-type magnesium storage mechanism of CuS has been demonstrated.