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New Insight into the Interaction between Carbonate-based Electrolyte and Cuprous Sulfide Electrode Material for Lithium Ion Batteries



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ABSTRACT

Cuprous sulfide (Cu₂S) is attractive electrode material for lithium-ion battery because of its high capacity and energy density. Interestingly, the cycling stability of cuprous sulfide is poor in the carbonate-based electrolytes used in lithium ion battery industry but excellent in ether-based electrolyte. In this study, we have compared the electrochemical performance of commercially available cuprous sulfide in various kinds of carbonate-based electrolytes. Our results show that the specific capacity of Cu₂S electrode fades quickly in cyclic carbonate-based electrolytes, but a much better electrochemical performance in linear carbonate-based electrolytes. In linear carbonate-based electrolyte (1 M LiPF₆ in EMC), it exhibits a specific discharge capacity of 242.8 mAh g^{-1} after 50 cycles with coulombic efficiency of 99.6%. Our study suggests that the poor cyclic carbonates with polysulfides on the surface of the electrode than linear carbonates, which was confirmed for the first time by our experiment studies and theoretical calculation. © 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Lithium-ion batteries have gained tremendous attentions as energy storage devices due to their high energy density, high operating voltage and longer cycle life [1–4]. However, the application of large-scale lithium-ion batteries in HEVs is significantly hindered by several major technological barriers, including insufficient cycle life, poor charge/discharge rate capability, and intrinsically poor safety [5,6].

Recently, transition-metal chalcogenides especially sulfides are widely studied because of their excellent chemical and physical properties [7–10]. Among these sulfides, cuprous sulfide (Cu₂S) has a higher theoretical specific capacity (about 335 mAh g⁻¹) with a flat discharge platform and better electronic conductivity (10^4 Scm^{-1}) compared with commercialized Li₄Ti₅O₁₂ anode [1,11]. Compared with the commonly-used graphitic carbon anode, Cu₂S exhibits a flat lithium insertion/extraction voltage platform at approximately 1.70 V (vs. Li/Li⁺), which is higher than the operating voltage of graphitic can be effectively reduced [12]. Moreover, the volumetric capacity of Cu₂S is much higher than graphite

http://dx.doi.org/10.1016/j.electacta.2015.06.109 0013-4686/© 2015 Elsevier Ltd. All rights reserved. (1876 Ah/L vs 830 Ah/L) [13]. Finally, cuprous sulfide is easily accessible and inexpensive, which makes it very attractive for commercialization. However, Cu₂S suffers from a rapid capacity decay during cycling [2,14,15], which is attributed to the high solubility (in organic solvent electrolytes) of the polysulfide ions formed during the charge/discharge processes. The dissolution of the polysulfides resulted in low active material utilization, low coulombic efficiency and poor cycle life of Cu₂S electrodes, thus the composition and polarity of the electrolyte can affect the cycling stability of Cu₂S or CuS dramatically [7,16,17]. For example, Cu₂S electrode exhibited a good cycling performance with capacity retained at about 200 mAh g⁻¹ after 150 cycles and coulombic efficiency of 98.4% in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1 M LiTFSI) electrolyte, on the other hand, its capacities rapidly dropped to 0 mAh g^{-1} after five cycles in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 M LiPF₆) electrolyte These results demonstrated that the conventional [7]. carbonate-based electrolyte is not suitable for the battery system of cuprous sulfide, however the exact reason of the poor cycling stability in carbonate-based electrolyte is not fully understood yet.

In this work, we chose dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), propylene carbonate (PC), vinylene carbonate (VC), fluoroethylene carbonate (FEC), and ethylene carbonate (EC) as the electrolytes to study the electrochemical performance of the Cu₂S electrode. The effect of linear carbonates (DMC, EMC) on Cu₂S performance is compared to that of cyclic carbonates (PC, VC, FEC,

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EC). Our study showed that the molecular structure of the carbonate electrolytes has a great influence on the cycle performance of Cu_2S electrodes.

2. Experimental

2.1. Preparation

Cu₂S (Aldrich, 99.5%) and Li₄Ti₅O₁₂ (Battery, Shenzhen, China) were used without further treatment. The liquid electrolytes were made of LiPF₆ (1 M) dissolved in the solvent of DMC, EMC, FEC, PC, VC and EC, respectively, prepared in argon-filled glove box. All the solvents and lithium salt, purchased from Zhangjiagang Guotai Huarong Chemical New Material Co., Ltd., were of battery grade in purity and used as received. The electrode slurry was prepared with N-methyl pyrrolidinone (NMP) as solvent and polyvinylidene fluoride (PVDF) as binder, and the mass ratio of solid materials was: 70 wt% active materials, 15 wt% carbon black and 15 wt% PVDF. The working electrode was prepared by casting the slurry onto copper foil with the mass loading of 1.435 mg/cm² of Cu₂S. The CR2016-type coin cells were assembled by sandwiching a separator between the as-prepared electrode and Li metal foil with 100 μ L electrolyte.

2.2. Characterization

The structures of the active material powder and the composite electrode were characterized by field emission scanning electron microscope (SEM, S-4800, Hitachi, Japan) and X-ray diffraction (XRD, MiniFlex600 X'pert, Rigaku, Japan). XRD measurements were performed by using the Cu K α radiation and a graphite monochromator with steps of 0.02° and an integration time of 20 s. The operating voltage and current were 40 kV and 15 mA, respectively. The X-ray photoelectron spectroscopy (XPS) analysis

was performed with a QUANTUM 2000 spectrometer using focused monochromatized Al Ka radiation (1486.6 eV). The pass energy was 60 eV for the survey spectra and 20 eV for the paticular elements.

2.3. Electrochemical measurements

Galvanostatic charge/discharge experiments were performed at different current densities between 1.0 V and 3.0 V (vs Li/Li⁺) using a CT2001A cell testing instrument (LAND Electronic Co.,Wuhan, China). The cyclic voltammetry was performed by using a coin cell on the CHI1030C Electrochemical Work-station (Chenghua, Shanghai, China) with a voltage sweep rate of 0.1 mV s⁻¹ for 5 cycles.

2.4. Calculation procedure

All the calculations reported in this paper were performed using the Gaussian 09 computational package [18]. The HOMO and LUMO energies of ionic solvents were calculated with respect to the vacuum level using the density-functional theory (DFT). The Kohn–Sham equation was calculated with the B3PW91 functional and 6-311G+(d, p) basis sets. The functional included a three-parameter adiabatic connection exchange term [19]: a linear combination of the exact Hartree–Fock exchange, Slater exchange [20], and B88 gradient corrected exchange [21]. Frequency analyses were done with the same basis sets as those for the geometry optimization and Gibbs free energies are calculated at 298.15 K to examine the reaction path.

3. Results and Discussion

The SEM images of commercial cuprous sulfide powder and the prepared Cu_2S cathode are presented in Fig. 1 (**a**, **b**), respectively. As



Fig. 1. SEM images of (a) commercial Cu₂S powder (b) Cu₂S cathode (c) X-ray diffraction patterns of commercial Cu₂S powder.

shown in Fig. 1a, the cuprous sulfide powder shows irregular particle shape and wide size distribution. After milling with acetylene black, the cuprous sulfide has a better uniformity in particle size distribution (Fig. 1b), which could result in a good electrochemical performance [22]. Besides, the image (Fig. 1b) shows that Cu_2S particles are uniformly dispersed in homogenous matrix composed of binder (PVDF) and conducting agent (acetylene black).

The XRD pattern as shown in Fig. 1c can be indexed to orthorhombic Cu_2S phase (JCPDS Card No. 003-1071). Trace amounts of CuS (JCPDS 006-0464) and Cu (JCPDS 085-1326), however, were observed.

To evaluate the performance of Cu₂S cathode indifferent electrolyte systems we studied the charge/discharge profiles of the Cu₂S electrodes with 1 M LiPF₆ dissolved in different solvents at room temperature. Fig. 2a shows the charge/discharge curves of the Cu₂S electrodes in the different electrolytes. During the first discharge, the Cu₂S electrodes show a quite similar discharge behavior in all electrolytes with two flat discharge plateaus at around 2.0 V and 1.6 V (Fig. 2a), respectively. The ideal discharge characteristics of Cu₂S would exhibit only one defined discharge plateau at 1.7 V [7], the presence of two discharge plateaus for the commercial copper sulfides indicates the existence of CuS. The content of CuS is about 7.0 wt% and more information about evaluating the CuS content is shown in the supporting information (Fig. S1). The specific capacities of Cu₂S electrodes in VC-based, FEC-based, and DMC-based electrolytes are about 400 mAh g^{-1} , 370 mAh g^{-1} , and 353 mAh g^{-1} , respectively. These numbers are slightly higher than the theoretical capacity of Cu_2S (335 mAh g⁻¹), further indicating the presence of CuS (560 mAh g^{-1}). The much higher capacity of Cu₂S in VC-based electrolyte may be due to a side reaction as reported [23,24]. The voltage plateaus can be explained by a two-step discharge mechanism [7,25]: the upper plateau is from the formation of polymorphic $Cu_{2-x}S$ and the lower one, Li_2S . The reactions can be summarized as follow:

$$CuS + Li \rightarrow 0.5Cu_2S + 0.5Li_2S (2.0 - 2.2V)$$
(1)

$$0.5Cu_2S + Li \rightarrow Cu + 0.5Li_2S (1.6 - 1.7 V)$$
⁽²⁾

As a result of this mechanism, there are two defined plateaus for the first charging process. From the charge profiles of Cu₂S electrodes as shown in Fig. 2a, a two-step behavior is observed in all electrolytes, which is consistent well with the mechanism. Fig. 2b presents the cycling performances of the Cu₂S electrodes in different electrolytes. As can be seen, the Cu₂S electrodes in the linear carbonate-based electrolytes exhibit better cycle stabilities with smaller capacity fading rates than those in cyclic carbonate-based electrolytes. The coulombic efficiencies related to the electrochemical reversibility in different electrolytes are shown in Fig. 2c and 2d. As Fig. 2c shown, the initial coulombic efficiency of the Cu₂S electrode is 92.6% in the DMC-based electrolyte and 95.2% in the EMC-based electrolyte, and both increase quickly to about 100% in the subsequent charge/discharge cyclings. On the contrary, the initial coulombic efficiencies of Cu₂S in cyclic carbonate-based electrolytes are all much lower than that in linear carbonate-based electrolytes (Fig. 2d). Based on these data, electrolytes with linear carbonates should be better for Cu₂S electrodes (More electrochemical data has shown in the Fig. S2, and the related capacity retention is presented in Table S1 as well).

The phase changes of the active electrode material during cycling were examined by *ex-situ* XRD, as shown in Fig. 3 (taken the



Fig. 2. (a) Discharge–charge profiles of the Cu₂S electrode at first cycle in different electrolytes, (b) cycle performance of the Cu₂S electrode in different electrolytes, (c) (d) the coulombic efficiency of the Cu₂S electrode in different electrolytes. All the experiments were tested between 1.0 and 3.0 V vs. Li/Li^{*} at a rate of 0.5 C (1 C = 335 mA g⁻¹, 0.21 mA cm⁻²).



Fig. 3. The ex-situ XRD patterns of the Cu₂S electrodes in EC and DMC-based electrolytes (1 M LiPF6) during the second cycle.



Fig. 4. Cycle voltammetry measurements of Cu_2S electrodes at a rate of 0.1 mV s⁻¹ in different electrolytes: (a) the DMC with 1 M LiPF6, (b) the EMC with 1 M LiPF6, (c) the FEC with 1 M LiPF6, (d) the PC with 1 M LiPF6, (e) the VC with 1 M LiPF6, (f) the EC with 1 M LiPF6.

Table 1

The redox potentials of Cu_2S electrode in different electrolytes measured by cyclic voltammetry in the first cycle.

Solvent	Oxidation peak/V		Reduction peak/V
DMC	1.90, 2.15	2.32	2.00, 1.62
EMC	1.90, 2.09	2.35	2.08, 1.58
FEC	1.93, 2.23	2.43	1.84, 1.58
PC	1.91, 2.19	2.42	2.00, 1.58
VC	1.92, 2.20	2.47	2.00, 1.42
EC	1.90, 2.24	2.38	2.05, 1.53

electrodes cycled in EC-based and DMC-based electrolytes as examples). Both electrodes show that during the lithiation processes, Cu₂S peak gradually disappears, and Li₂S and Cu peaks appear; during the delithiation processes, Li₂S and Cu peaks disappear and Cu₂S peak regenerates. These data agrees well with the above proposed reaction mechanism.

To further understand the electrochemical reactions of Cu_2S electrodes, these electrodes in different electrolytes were investigated by cyclic voltammogram (CV) mearsurements, as shown in Fig. 4. All cyclic voltammogram curves are composed of more than two couples of oxidation-reduction peaks,which are attritubed to the electrochemical reactions of Cu_2S electrodes as shown in the Table 1. All the CVs show two well-defined reduction peaks at the voltage of around 2.0 and 1.6 V, and two oxidation peaks at around 2.1 and 1.9 V. The reduction peaks at 2.0 V and 1.6 V during the discharge processes are attributed to the insertion of lithium as shown in the above reaction (1) and (2). The oxidation peaks at 2.1 V and 1.9 V are accounted for the inverse lithiation reactions of CuS and Cu₂S, respectively. The transient oxidation peak at 2.3 V is due to the poor contact between Li₂S particles and electrolyte [26], which gradually disappears with cycling.

In order to investigate the oxidation peak at 2.3 V, the cycled electrode was taken out and reassembled into a new cell with fresh DMC-based electrolyte in an argon-filled glove box. It is surprising that the disappeared voltage platform reappears immediately, then disappears slowly with the increased cycle numbers (as shown in Fig. 5). It can be concluded that the transient voltage peak at 2.3 V is primarily related to the side reaction occurred at the interface between the active material and the electrolyte. More detailed investigation is needed to analyze its origin.

The peaks with weak intensities in CV curves of Cu_2S in the cyclic carbonate-based electrolyte are similar to those in the linear carbonate-based electrolyte in the first cycle. However, the reduction and oxidation peaks in the cyclic carbonate-based electrolyte fade quickly since the second cycle. It is highly consistent with the charge/discharge curves. These results have further confirmed that the linear carbonate are better electrolytes for Cu_2S electrodes, compared to the cyclic carbonate.

To further investigate the negative impact of cyclic carbonatebased electrolyte on Cu₂S cycling performance, galvanostatic



Fig. 5. Voltage profiles of the reassembling cell with the used Cu_2S electrode and fresh DMC-based (1 M LiPF₆) electrolyte.

charge/discharge measurements were carried out (as shown in **Fig. S3**). The most commonly used linear carbonate (DMC, EMC) and cyclic carbonate (EC) are chosen as electrolytes. We find that even a small portion of EC in electrolyte, the capacities of Cu_2S fade rapidly, which further confirms that the cyclic carbonate-based electrolyte is detrimental to the cycle performance of Cu_2S electrodes.

To explain the poor cycling performance of Cu₂S electrodes in cyclic carbonate-based electrolytes, theoretical calculations on the bond length and bond order of S_8 (Fig. 6) and the most possible reaction routes in the linear carbonate-based and cvclic carbonatebased electrolytes (Scheme 1) were performed. As far as we know, among the polysulfide ions formed during the cycling process for lithium-sulfur batteries, S_4^{2-} is the stablest form as an intermediate product [27]. It can be clearly seen from Fig. 6 that the bonds of S(2)-S(3) and S(6)-S(7) have the longest bond lengths and lowest bond orders, which means they are the most unstable bonds and most likely to involve in cleavage reaction during cycling process. Thus the major forms of polysulfide ions should be S_4^{2-} and S_2^{2-} . Based on the calculated results, two possible reaction routes of S_4^{2-} and S_2^{2-} were further investigated (shown in Scheme 1). Reactions (a) and (c) are based on nucleophilic attack reactions, which can be catalyzed by alkali metals, hydroxides, and carbonates [28]. Reactions (b) and (d) are based on nucleophilic attack, similarly to the methylation of DMC [29]. In lithium/sulfur battery system, a similar reaction is proposed based on GC-MS and NMR analysis [30], and X-ray spectroscopic studies [31]. Our theoretical results agree well with these experimental foundings.

The detailed information of geometry optimization and Gibbs free energies was listed in Table 2. From these data, we can draw a conclusion that nucleophilic attack reaction on linear carbonatebased electrolyteis more difficult due to the increase of the Gibbs



Fig. 6. The bond length and bond order of S₈.



Scheme 1. Proposed reactions between S_4^{2-} , S_2^{2-} and carbonates.

Table 2Gibbs free energies of the solvents and the changes of the Gibbs free energies for the proposed reactions.

Species	EC	DMC	S_4^{2-}	1	2	$\Delta G^{(a)}$	$\Delta G^{(b)}$
G(Hartree/Particle)	-342.35	-343.55	-1592.68 S ₂ ²⁻ -796.20	1935.09 3 1138.57	1935.67 4 1139.05	$-0.05 \ \Delta { m G}^{(c)} \ -0.12$	$\begin{array}{c} 0.56 \\ \Delta \mathrm{G}^{\mathrm{(d)}} \\ 0.58 \end{array}$

*1hartree/partical = 2624.20 kJ/mol; $\Delta G^{(a)}$ = -124.70 kJ/mol; $\Delta G^{(c)}$ = -314.90 kJ/mol.

free energies of reaction (b) and (d). This is consistent with other calculation results as shown in Table 3. The LUMO energies of the cyclic carbonate molecules are lower, compared with those of linear carbonate molecules [5,32]. Based on the molecular orbital

theory, the cyclic carbonate molecules can easily obtain electrons through an electrophilic reaction. At the same time, the total energy of the cyclic carbonate molecules is higher than that of linear carbonate molecules, thus the cyclic carbonate molecules

Table 3

Structures, molecular orbitals of organic solvents and their energies.

	DMC	EMC	FEC	РС	VC	EC
Structure	, 3 , 4, 3,	್ಮತ್ತಿ ವೈತ್ಯ				
номо	, 		}	鶨.	2	*
Е _{номо} (eV)	.7.8187	-7.7477	-8.8494	-7.9771	-7.0138	-8.0620
LUMO		., 53 .		,	3	2
E _{LUMO} (eV)	1.1279	1.1902	0.5135	1.0313	-0.0528	0.9355
ΔE_{g}^{a} (eV)	6.6908	6.5575	8.3359	6.9459	6.961	7.1265



Fig. 7. The electrochemical performance of the cycled electrodes (after 10 cycles) in EC-based electrolyte (1 M LiPF_6) with DMSO washing in new ether-based electrolyte.

are more unstable. All these results indicate that the electrolyte composed of cyclic structure (FEC, PC, VC and EC, etc) may react with nucleophilic anions readily, which results in poor electrochemical performance of Cu_2S .

To gain more insight into the rapid capacity decay of Cu_2S in cyclic-carbonate electrolytes, we designed experiments to clarify which is the major contributor: high polarity of cyclic carbonate or surface reaction on the electrode. The first experiment we designed was to rinsing the cycled electrode surface with DMSO. As shown in the Fig. 7, the specific capacity of the cycled electrodes (after 10 cycles), followed with rinsing of DMSO, can be recovered, indicating that the products generated from side reaction at the interface greatly hinders the lithiation/delithiation process of Cu_2S electrodes.

Cyclic carbonates generally have higher polarity than linear carbonate, thus it is possible that the polysulfides might have higher solubilities in cyclic carbonates, the dissolution and migration away from electrode of polysulfide will cause capacity decay. To investigate this possibility, we assembled a new cell with commercialized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as working electrodes, lithium as anode and EC-based electrolyte (after cycled in Cu₂S cell until the capacity is zero), and tested by galvanostatic charge/discharge measurements. As shown in Fig. 8, the electrochemical performance of the Li₄Ti₅O₁₂ electrode is not affected by the cycled EC electrolyte. Therefore, we believe that the surface side



Fig. 9. The XPS spectra of the pristine electrode and the cycled electrode after first cycling in EC and DMC-based electrolytes (1 M LiPF₆).

reaction between cyclic carbonate and polysulfides, not its polarity, is the major cause of rapid capacity decay.

XPS investigations of the electrodes in EC and DMC based electrolytes after the first charging process also demonstrated the surface chemical differences, as shown in Fig. 9. The S2p peak of the electrode charged in DMC-based electrolyte is similar to that of un-charged electrode with peak located at around 162 eV. However, for the electrode charged in EC-based electrolyte, the S2p peak shifts to a higher bound energy (163.4 eV), which may be assigned to C-S from the production of the proposed reactions between S_4^{2-} or S_2^{2-} anion and cyclic carbonates [33,34]. The SEI structure of the electrode is yet to be studied, but the generated chemicals with C-S bonds are unambiguously disastrous to Cu₂S cycling performance.

The related SEM images of Cu_2S electrodes under different measurement conditions also indicate that some side reactions happen on the interface of the Cu_2S electrodes in EC-based electrolyte. As shown in Fig. 10, the morphology of the electrode in EC-based electrolyte is different from the original Cu_2S electrode and a transparent film is formed after the charge/discharge process. However, the morphology of the electrode in DMC-based electrolyte remains smooth surfaces and similar as the original Cu_2S electrode.



Fig. 8. The electrochemical performance of the commercial $Li_4Ti_5O_{12}$ electrode in the EC-based electrolyte (after cycled in Cu_2S cell until the capacity is zero) (a) the discharge-charge profiles, (b) the cycle performance at first cycle.



Fig. 10. SEM images of Cu₂S electrode surface obtained (a) before cycling, (b) after ten cycles in DMC-based electrolyte (1 M LiPF₆), (c) after ten cycles in EC-based electrolyte (1 M LiPF₆).

4. Conclusions

The effects of the carbonate-based electrolyte on cuprous sulfide electrodes have been investigated in our study. It was found that the linear carbonate-based electrolytes can enable a much better cycling performance of Cu_2S than the cyclic carbonate-based electrolytes. The copper sulfide electrodes exhibit a discharge capacity of 200 mAh g⁻¹ after 50 cycles both for the DMC-based and EMC-based electrolytes. On the other hand, the capacities of the electrole in FEC-based, PC-based, VC-based, and EC-based electrolyte all decrease rapidly to 0 mAh g⁻¹ after 10 cycles. Based on the results from the paper, it would be fair to conclude that the cyclic carbonates have a higher tendency to react with polysulfides on the surface of the active materials than linear carbonates. The reaction leads to a surface film, which then blocks subsequent lithium insertion and extraction from the material, resulting in poor cycle performance.

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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. electacta.2015.06.109.

References

- [1] F. Han, W.C. Li, D. Li, A.H. Lu, In Situ Electrochemical Generation of Mesostructured Cu₂S/C Composite for Enhanced Lithium Storage: Mechanism and Material Properties, ChemElectroChem 1 (2014) 733–740.
- [2] M. Wang, W. Wang, A. Wang, K. Yuan, L. Miao, X. Zhang, Y. Huang, Z. Yu, J. Qiu, A multi-core-shell structured composite cathode material with a conductive

polymer network for Li–S batteries, Chemical Communications 49 (2013) 10263–10265.

- [3] Z. Yang, J. Guo, S.K. Das, Y. Yu, Z. Zhou, H.D. Abruña, L.A. Archer, In situ synthesis of lithium sulfide-carbon composites as cathode materials for rechargeable lithium batteries, Journal of Materials Chemistry A 1 (2013) 1433–1440.
- [4] A. Parasuraman, T.M. Lim, C. Menictas, M. Skyllas-Kazacos, Review of material research and development for vanadium redox flow battery applications, Electrochimica Acta 101 (2013) 27–40.
- [5] J.B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, Chemistry of Materials 22 (2009) 587–603.
- [6] G. Salitra, E. Markevich, A. Rosenman, Y. Talyosef, D. Aurbach, A. Garsuch, High-Performance Lithium–Sulfur Batteries Based on Ionic-Liquid Electrolytes with Bis (fluorolsufonyl) imide Anions and Sulfur-Encapsulated Highly Disordered Activated Carbon, ChemElectroChem 1 (2014) 1492–1496.
- [7] B. Jache, B. Mogwitz, F. Klein, P. Adelhelm, Copper sulfides for rechargeable lithium batteries: Linking cycling stability to electrolyte composition, Journal of Power Sources 247 (2014) 703–711.
- [8] Y. Chen, C. Davoisne, J. Tarascon, C. Guéry, Growth of single-crystal copper sulfide thin films via electrodeposition in ionic liquid media for lithium ion batteries, Journal of Materials Chemistry 22 (2012) 5295–5299.
- [9] K. Chang, W. Chen, L-cysteine-assisted synthesis of layered MoS₂/graphene composites with excellent electrochemical performances for lithium ion batteries, ACS nano 5 (2011) 4720–4728.
- [10] Y. Zhou, C. Wu, H. Zhang, X. Wu, Z. Fu, Electrochemical reactivity of Co-Li₂S nanocomposite for lithium-ion batteries, Electrochimica acta 52 (2007) 3130–3136.
- [11] X. Li, X. He, C. Shi, B. Liu, Y. Zhang, S. Wu, Z. Zhu, J. Zhao, Synthesis of One-Dimensional Copper Sulfide Nanorods as High-Performance Anode in Lithium Ion Batteries, ChemSusChem 7 (2014) 3328–3333.
- [12] X. Li, H. Lin, W. Cui, Q. Xiao, J. Zhao, Fast Solution-Combustion Synthesis of Nitrogen-Modified Li₄Ti₅O₁₂ Nanomaterials with Improved Electrochemical Performance, ACS applied materials & interfaces 6 (2014) 7895–7901.
- [13] I. Kim, P. Kumta, G. Blomgren, Si/TiN nanocomposites novel anode materials for Li-Ion batteries, Electrochemical and Solid-State Letters 3 (2000) 493–496.
- [14] Y. Wang, X. Zhang, P. Chen, H. Liao, S. Cheng, In situ preparation of CuS cathode with unique stability and high rate performance for lithium ion batteries, Electrochimica Acta 80 (2012) 264–268.
- [15] I. Exnar, J. Hep, Copper (II) sulfide as cathode active material in secondary lithium batteries, Journal of power sources 44 (1993) 701–705.
- [16] Y. Han, Y. Wang, W. Gao, Y. Wang, L. Jiao, H. Yuan, S. Liu, Synthesis of novel CuS with hierarchical structures and its application in lithium-ion batteries, Powder Technology 212 (2011) 64–68.
- [17] J.-S. Chung, H.-J. Sohn, Electrochemical behaviors of CuS as a cathode material for lithium secondary batteries, Journal of power sources 108 (2002) 226–231.
- [18] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery Jr., T. Vreven, K. Kudin, J. Burant, Gaussian 03, revision c. 02, Gaussian, Inc., Wallingford, CT, 20044.
- [19] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, The Journal of Chemical Physics 98 (1993) 5648–5652.

- [20] S. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis, Canadian Journal of physics 58 (1980) 1200–1211.
- [21] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Physical review A 38 (1988) 3098.
- [22] E. Strauss, D. Golodnitsky, E. Peled, Study of phase changes during 500 full cycles of Li/composite polymer electrolyte/FeS₂ battery, Electrochimica acta 45 (2000) 1519–1525.
- [23] H. Ota, K. Shima, M. Ue, J.-i. Yamaki, Effect of vinylene carbonate as additive to electrolyte for lithium metal anode, Electrochimica Acta 49 (2004) 565–572.
- [24] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, On the use of vinylene carbonate (VC) as an additive to electrolyte solutions for Li-ion batteries, Electrochimica Acta 47 (2002) 1423–1439.
- [25] X. Wang, Y. Wang, X. Li, B. Liu, J. Zhao, A facile synthesis of copper sulfides composite with lithium-storage properties, Journal of Power Sources 281 (2015) 185–191.
- [26] Y. Yang, G. Zheng, S. Misra, J. Nelson, M.F. Toney, Y. Cui, High-capacity micrometer-sized Li₂S particles as cathode materials for advanced rechargeable lithium-ion batteries, Journal of the American Chemical Society 134 (2012) 15387–15394.
- [27] M. Cuisinier, P.-E. Cabelguen, S. Evers, G. He, M. Kolbeck, A. Garsuch, T. Bolin, M. Balasubramanian, L.F. Nazar, Sulfur Speciation in Li–S Batteries Determined by Operando X-ray Absorption Spectroscopy, The Journal of Physical Chemistry Letters 4 (2013) 3227–3232.

- [28] J.H. Clements, Reactive applications of cyclic alkylene carbonates, Industrial & engineering chemistry research 42 (2003) 663–674.
- [29] Y. Ono, Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign building block, Applied Catalysis A: General 155 (1997) 133–166.
- [30] T. Yim, M. Park, J. Yu, K.J. Kim, K.Y. Im, J. Kim, G. Jeong, Y.N. Jo, S. Woo, K.S. Kang, Effect of chemical reactivity of polysulfide toward carbonate-based electrolyte on the electrochemical performance of Li–S batteries, Electrochimica Acta 107 (2013) 454–460.
- [31] J. Gao, M.A. Lowe, Y. Kiya, H.c.D. Abruña, Effects of liquid electrolytes on the charge-discharge performance of rechargeable lithium/sulfur batteries: electrochemical and in-situ X-ray absorption spectroscopic studies, The Journal of Physical Chemistry C 115 (2011) 25132–25137.
- [32] R. Chen, F. Wu, L. Li, Y. Guan, X. Qiu, S. Chen, Y. Li, S. Wu, Butylene sulfite as a film-forming additive to propylene carbonate-based electrolytes for lithium ion batteries, Journal of Power Sources 172 (2007) 395–403.
- [33] D.S. Jung, T.H. Hwang, J.H. Lee, H.Y. Koo, R.A. Shakoor, R. Kahraman, Y.N. Jo, M.S. Park, J.W. Choi, Hierarchical porous carbon by ultrasonic spray pyrolysis yields stable cycling in lithium-sulfur battery, Nano letters 14 (2014) 4418–4425.
- [34] S. Xin, L. Gu, N.H. Zhao, Y.X. Yin, LJ. Zhou, Y.G. Guo, LJ. Wan, Smaller sulfur molecules promise better lithium-sulfur batteries, Journal of the American Chemical Society 134 (2012) 18510–18513.