



High capacity of lithium-sulfur batteries at low electrolyte/sulfur ratio enabled by an organosulfide containing electrolyte



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ARTICLE INFO

Keywords:

Batteries
Dimethyl disulfide
Lithium-sulfur
Electrolyte/sulfur ratio
High sulfur loading

ABSTRACT

Lithium-sulfur (Li-S) battery is a promising energy storage technology to replace lithium ion batteries for higher energy density and lower cost. Dissolution of lithium polysulfide intermediates in conventional Li-S electrolytes is known as one of the key technical barriers to the development of Li-S, because it promotes redistribution and irreversible deposition of Li_2S , and also forces large amounts of electrolyte to be used, shortening cycling life and driving down cell energy density. Recently, dimethyl disulfide as a functional co-solvent has been demonstrated to show an alternate electrochemical reaction pathway for sulfur cathodes by the formation of dimethyl polysulfides and lithium organosulfides as intermediates and reduction products. In this work, comprehensive studies show that this new pathway not only provides high capacity but also enables excellent capacity retention through a built-in automatic discharge shutoff mechanism by tuning carbon/sulfur ratio in sulfur cathodes to reduce unfavorable Li_2S formation. Furthermore, this new electrolyte system is also found to enable high capacity of high-sulfur-loading cathodes with low electrolyte/sulfur (E/S) ratios, such as a stable specific capacity of around 1000 mAh g^{-1} using a low electrolyte amount (i.e. E/S ratio of 5 mL g^{-1}) and high-sulfur-loading (4 mg cm^{-2}) cathodes. This electrolyte system almost doubles the capacity obtained with conventional electrolytes under the same harsh conditions. These results highlight the practical potential of this electrolyte system to enable high-energy-density Li-S batteries.

1. Introduction

Rechargeable Li-S batteries are considered as a promising next-generation energy storage system and have received increasing attention in recent years due to their high theoretical energy density, and the use of low-cost, naturally abundant and non-toxic sulfur cathodes [1]. Despite the considerable advantages, the applications of Li-S batteries remain hindered by critical performance drawbacks such as low practical energy density, low Coulombic efficiency, fast capacity degradation, and severe self-discharge. The major reasons for these issues have long been ascribed to several fundamental challenges, such as the poor conductivity of sulfur and its reduction products, the dissolution and side-reactions of lithium polysulfide intermediates, and the irreversible deposition of Li_2S on the cathode [2,3].

To address these challenges, great efforts have been made focusing on the design of advanced porous carbon-sulfur (C-S) composites cathodes, which enhance the overall conductivity and help to trap the active materials within the porous carbon matrix [4–11]. However, this approach does not solve the issues intrinsically, especially for dissolution and diffusion of lithium polysulfides out of cathode that is

inevitable in liquid electrolytes [12]. Additional approaches have thus been developed, in parallel to the development of the advanced sulfur cathodes, to effectively mitigate polysulfide loss and lead to improved cycling performance. The approaches include electrolyte additives [13–15], optimized electrolytes with low polysulfides solubility [16,17], new cell configurations with polysulfides blocking interlayers or separators [18–20], protected lithium anodes [21–23], and new recharge technique with constrained charge capacity [24].

Despite significant process, it has been pointed out that specific capacity or sulfur utilization, cycle stability and energy density of Li-S batteries can be significantly influenced by many parameters like the sulfur content/areal loading in the cathode, amount of electrolyte, lithium excess and cycling rate [25]. To obtain a high energy density, both the sulfur content/loading and sulfur utilization should be as high as possible [26], along with a low electrolyte/sulfur (E/S in mL g^{-1}) ratio [27]. Recently, some efforts have been made to use more realistic sulfur loadings and demonstrate a few approaches to achieve high areal capacity with acceptable cycle life [28–31]. Unfortunately, much more electrolyte is still required in Li-S batteries compared to conventional LIBs (over 30% of the cell's weight vs. below 10%, respectively), as demonstrated in Li-S

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<http://dx.doi.org/10.1016/j.nanoen.2016.11.057>

Received 3 September 2016; Received in revised form 18 November 2016; Accepted 29 November 2016

Available online 30 November 2016

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prototypes, which significantly reduces their practical energy densities [32]. Such a large electrolyte amount is used partially because the porosity of C-S cathodes is typically high to sustain active material volume change, resulting in a high electrolyte uptake [26]. In addition, excess of electrolyte is needed to avoid quick electrolyte depletion due to the unstable lithium anode/electrolyte interphase [33]. More importantly, it was found that dissolution of polysulfides can remarkably increase electrolyte viscosity and resistance, leading to poor redox kinetics and low utilization of sulfur cathodes at low E/S ratios [27]. Due to these factors, a high E/S is usually needed to maintain acceptable capacity/rate capability and cycling performance, and therefore most publications that report their E/S ratio used a value of 10 or higher [34–36]. High capacity with high-sulfur-loading cathodes and an E/S ratio of 5 or lower, to the best of our knowledge, is challenging to achieve.

Recently we reported a novel functional electrolyte system using dimethyl disulfide (DMDS) as a co-solvent to promote an alternate electrochemical reaction pathway for sulfur cathodes by formation of dimethyl polysulfide (DMPS) and lithium organosulfides as new redox intermediates and boost the capacity of Li-S cells [37]. However, there are still several important scientific questions on the new electrolyte system attractive to be answered for addressing key technical issues of Li-S batteries, such as, what are the key parameters of sulfur cathode on the effect of performance in this electrolyte, can this electrolyte promote using low amount of electrolyte to achieve high capacity, and how to optimize them to further improve its practical performance. In this paper, we comprehensively evaluate this new electrolyte, aiming to achieve high capacity of Li-S batteries, using different sulfur cathodes with various conditions such as C-S cathodes with various sulfur contents, high areal sulfur loading and low E/S ratio. Enabled by the new mechanism in DMDS-containing electrolyte, interestingly, it is found that the discharge process of sulfur cathodes can shut off by reaching the cut-off voltage at different degrees of depth of discharge by tuning sulfur content (i.e., C/S ratio) in the cathode, due to the conductive surface passivation by varied precipitates of reduction products of DMPS intermediates. The cathodes with high sulfur content (low C/S ratio) produce ultimately more lithium organosulfides with better redox kinetics and reversibility, creating an automatic shutoff mechanism for the discharge process to mitigate the detrimental irreversible formation of insoluble Li_2S . It not only allows for excellent cyclability of sulfur cathodes with high sulfur contents, but also shows a high capacity owing to the DMDS-induced capacity contribution. Moreover, the new reaction pathway in DMDS-containing electrolyte avoids the formation and dissolution of viscosity-raising long-chain lithium polysulfides and thus enables high capacity with less amount of electrolyte. For example, when a low E/S ratio of 5 and high-sulfur-loading (4 mg cm^{-2}) cathodes were used, cells with this new electrolyte system can achieve high stable sulfur-specific capacities of around 1000 mAh g^{-1} , which almost double the value obtained in conventional Li-S electrolyte under the same conditions. These findings demonstrate the great promise of this DMDS-containing electrolyte system for future practical applications.

2. Material and methods

Sulfur cathode materials were made by thermal treatment of elemental sulfur and carbon mixtures at 159°C in sealed vials for 10 h. Two types of carbon, ordered mesoporous carbon (OMC) synthesized according to a previous report [7] and commercial Ketjenblack EC-600JD (KB), were used as conductive frameworks. The composites were combined with Super P carbon and PVDF as a binder in a mass ratio of 80:10:10 or 70:20:10 for low- ($\sim 1 \text{ mg cm}^{-2}$) or high- ($\sim 4 \text{ mg cm}^{-2}$) sulfur-loading electrodes, respectively, and stirred into a slurry with *n*-methyl-2-pyrrolidone (NMP). The slurry was then blade cast onto carbon-coated aluminum foil and vacuum dried overnight at 55°C . After drying under vacuum, the electrodes were pressed at 15 MPa, punched into round pieces with diameter of 12 mm, and assembled into CR2016 coin cells with exactly controlled amount of electrolyte and lithium foil as anode in

an Ar-filled glove box with H_2O and O_2 level below 0.1 ppm. Cycling performance was carried out on an Arbin BT2000 or Land CT2001A battery tester from 1.6 to 2.6 V.

The conventional electrolyte was composed of 0.1 M LiNO_3 additive and 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (v/v, 1:1). The 50 vol% DMDS-containing electrolytes were prepared similarly by dissolving 0.1 M LiNO_3 and 1 M LiTFSI in a mixed solvent of DMDS, DME, and DOL (v/v/v, 2:1:1). The ionic conductivity of the conventional and 50 vol% DMDS-containing electrolyte is ~ 10 and 5 mS cm^{-1} at room temperature, respectively. To improve the cycling efficiency, 0.4 M LiNO_3 was added to the electrolytes used for high-areal-capacity cells. Note that 0.4 M LiNO_3 did not completely dissolve in the 50 vol% DMDS-containing electrolyte, so it actually contains the amount of LiNO_3 needed to achieve saturation.

3. Results and discussion

3.1. Effect of carbon/sulfur ratio on electrochemical performance and automatic shutoff mechanism

To study the influence of C/S ratio on electrochemical performance, three OMC-S composite cathodes with different sulfur fractions (40, 50 and 70 wt%), labeled as OMC-S40, -S50, and -S70 were tested in the 50 vol% DMDS-containing electrolyte. All of these cells again contained $\sim 1 \text{ mg}$ of sulfur and $10 \mu\text{L}$ of electrolyte, so only the ratio of carbon to sulfur and DMDS was changed. The OMC-S40, -S50 and -S70 cathodes show initial sulfur-specific capacities of 2485, 1950 and 1361 mAh g^{-1} (Fig. 1a). It is interesting that low C/S ratio (e.g., OMC-S70) allows for a moderate sulfur-specific capacity with excellent capacity retention while increasing carbon fraction (e.g., OMC-S40) greatly increases the sulfur-specific capacity but leads to much worse capacity retention (Fig. 1b). Since increasing C/S ratio results in more dead weight from inactive carbon, there should be a balance between C/S ratio and the sulfur-specific capacity. As shown in Fig. 1c and d, if the whole mass of OMC-S composite was used to re-calculate the specific capacity, the three cathodes show similar initial capacity of $\sim 1000 \text{ mAh g}^{-1}$ per composite and OMC-S70 delivers the best overall performance. In contrast, tuning the carbon fraction has little effect on the sulfur-specific capacity and capacity retention in conventional electrolyte, as all the cathodes show similar initial sulfur-specific capacities of $\sim 1200 \text{ mAh g}^{-1}$ (thus lower composite-specific capacity with increasing C/S ratio), have fast capacity fading during the first 1–10 cycles, and then stabilize at a low sulfur-specific capacity of $\sim 500\text{--}700 \text{ mAh g}^{-1}$ (Fig. 2).

This major difference in behavior between the conventional and DMDS-containing electrolyte systems stems from the new reduction pathway in DMDS-containing electrolyte, which proceeds mainly through the formation and subsequent multi-step reduction of DMPS species to lithium organosulfides, and ultimately forms CH_3SLi and Li_2S . According to our previous NMR results [37], the DMPS intermediates are mainly composed of DMTS and dimethyl tetrasulfide (DMTtS), which, upon complete reduction involve the transfer of 4 and 3 e^- per sulfur reacting with DMDS, or a maximum specific capacity of 3350 and 2515 mAh g^{-1} based on solid sulfur in the cathode, respectively.

Discharge of sulfur cathodes with low C/S ratio ends at a relatively low sulfur-specific capacity (i.e., $\sim 1400 \text{ mAh g}^{-1}$ per sulfur initially for OMC-S70, equaling to 42% or 56% utilization of DMTS or DMTtS, respectively), because lithium organosulfides (especially CH_3SSLi and CH_3SLi) show limited solubility only in the electrolyte (see Fig. S1) and thus deposit on and passivate the conductive surface, preventing further reduction of themselves to form insoluble Li_2S (schematically illustrated in Fig. 3b). Since increasing C/S ratio provides more conductive surface for the interfacial reactions of DMPS intermediates and also significantly enhances the electrical conductivity of the cathode, it is understandable that the use of sulfur cathodes with high

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