Li$_2$S-Incorporated Separator for Achieving High-Energy-Density Li-S Batteries

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ABSTRACT

We present a new and facile design of a high-performance Li-S cell by integrating a Li$_2$S-impregnated glass fiber separator together with a common sulfur cathode. We find that a considerable amount of Li$_2$S is consumed amidst the first charge, and most of Li$_2$S disappears at the end of the second charge. During the charge process, additional sulfur material is formed and contributes to a significant enhancement of the discharge capacity (~1400 mAh/g), compared with a control cell (~1260 mAh/g) without Li$_2$S. Moreover, the Li$_2$S containing cell exhibits much higher cycling stability (a 31% increase from ~840 to ~1100 mAh/g in the 100th cycle) and rate capability (a 30% increase from ~580 to ~750 mAh/g at 2 C) than the control cell. Our results indicate that adopting Li$_2$S-containing separator is highly effective to improving the electrochemical performances of Li-S cells.

Keywords: Li-S Battery, Li$_2$S-Incorporated Separator, High Energy Density, High Capacity

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1. Introduction

Excessive use of fossil fuels is without a doubt the main cause of current climate change and ever-increasing air pollution. There is an urgent need today to reduce carbon dioxide emissions in order to tackle upcoming environmental crisis. High energy density rechargeable batteries have drawn large attention as key devices for large-scale energy storage systems and electric transportation [1,2].

Recently, lithium-sulfur (Li-S) batteries have been highlighted as one of highly efficient and innovative battery systems due to the attractive features of sulfur: environmentally friendliness, low cost and high abundance in nature, and high theoretical capacity [3]. Significant efforts have been made to develop high performance and sustainable Li-S batteries in the past two decades [4-6]. Despite remarkable improvements, mass commercialization has been hampered by their low performance (e.g., practical energy density, cycle life, and sulfur utilization) and safety issues [4-6]. The insufficient performance of Li-S batteries is closely associated with the dissolution and diffusion of polysulfides [7].

Diverse strategies have been proposed to block the migration of polysulfides, including a carbon-sulfur composite, a porous carbon interlayer, and a modified separator with a protective coating [8-13]. These approaches have been shown to be highly effective for improving cycling stability and sulfur utilization. Substantially enhanced performance was obtained mostly with low sulfur loading (less than 2 mg/cm$^2$) [14,15]. As a results the merit of sulfur and its high theoretical capacity are overshadowed, which makes the realization of competitive Li-S batteries impossible when compared to present lithium-ion batteries [15]. To address this issue, efforts toward increasing sulfur loading in the Li-S cells have focused on fabricating highly porous carbons such as graphene foam, free-standing carbon film and carbon nanotubes [16-21]. These carbon materials were found to be highly beneficial for making high-loading sulfur cathodes with high performance [19-22]. However, most of materials reported in the literature have been obtained through complex and expensive synthesis...
methods, which make their practical application difficult. Previously, we found that Li$_2$S particles electrically isolated from the carbon cathode can be converted to elemental sulfur via the electrochemical reaction of medium order polysulfides that are generated by the chemical reactions between solid Li$_2$S and polysulfides [23]. Based on this finding, we expected that additional active materials can be supplied to the cathode during charge process by including Li$_2$S particles between a conventional sulfur cathode and a lithium metal anode. To achieve a high areal capacity, we suggest a new design of Li-S cell, composed of a sulfur cathode, lithium anode, and Li$_2$S-impregnated glass fiber separator fabricated via a simple solution-based method.

2. Experimental

Li$_2$S particles were incorporated into a glass fiber separator (Advantec, GC-50) by a solution-based infiltration method (Fig. 1a). Commercial Li$_2$S powders (Aldrich) were dissolved in anhydrous ethanol (Aldrich) and stirred for 6 h to obtain a 0.80 M Li$_2$S solution. The separator was submerged in a sealed vessel containing the Li$_2$S solution for 5 h to ensure that Li$_2$S penetrates deep into the separator. The obtained separator was dried at room temperature and then left at 40°C under vacuum for a day to completely evaporate ethanol. All the fabrication processes involving Li$_2$S were performed in an argon-filled glovebox if to avoid harmful reactions of Li$_2$S with moisture and oxygen. The loading level of Li$_2$S in the separator was ~2.3 mg/cm$^2$. The surface morphologies of the pristine separator and the Li$_2$S-embedded separator were analyzed by scanning electron microscopy (FIB-SEM, Helios Nanolab 600i, FEI). The distribution and crystallinity of Li$_2$S were investigated by energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD), respectively.

The sulfur electrode consists of sulfur powder (Miwon chemicals, Korea), a conducting agent (Ketjenblack, International Co.) and a polyethylene oxide (Alfa Aesar) binder with a 6:2:2 weight ratio. It was fabricated by a slurry-casting method as described in our previous work [24]. On average, the sulfur loading on the cathode was ~2.0 mg/cm$^2$.

Coin cells containing the Li$_2$S-impergnated separator was assembled using 1.0 M LiN(CF$_3$SO$_2$)$_2$ solution in dimethoxyethane (DME) : diglyme (DG) : 1,3-dioxolane (DOL) (6:2:2 in volume) with 0.3 M LiNO$_3$ as an electrolyte. The sulfur electrode was used as a cathode and pure lithium metal as an anode. For comparison, a control cell was prepared following the same procedures, except for using a pristine glass fiber separator without Li$_2$S. The Li-S cells with the Li$_2$S-impregnated separator were charged to 4.0 V at 0.05 C in the first cycle after cell assembly. Subsequently, the Li-S cells were discharged and charged in the potential range between 1.8 V and 2.7 V at 0.05 C (vs. Li/Li$^+$) for the initial two cycles. Thereafter, cycling stability and rate capability were tested with cut-off voltages of 1.8 V and 2.7 V. Cycling performance was evaluated at 0.25 C, and rate property at various current densities from 0.1 C to 2 C. The current density values are based on the

![Fig. 1. Schematic illustrations of (a) the fabrication of a Li$_2$S-incorporated glass fiber separator and (b) the proposed oxidation route of solid Li$_2$S particles electrically isolated from the sulfur cathode in the early period of the first charge.](image-url)
sulfur mass within the cathode (1 C = 1675 mAh/g-S). Note that all specific capacity values were recorded with respect to the sulfur mass within the cathode, except for the first charge, in which case the specific capacity was evaluated by the Li$_2$S mass in the glass fiber separator. The control cell was tested using the same charge/discharge protocol, except that it was discharged to 1.8 V in the first cycle.

Moreover, the Li-S cells with Li$_2$S-containing separator were disassembled in the end of first and second charge cycles to determine the amount of unreacted Li$_2$S in the separator. The collected separators were cut into two pieces. One piece was washed several times with distilled DME solvent to remove lithium polysulfides and LiTFSI in the separator, followed by drying at 50°C for 6 hours. The resulting separators were investigated using a FIB-SEM. The other piece was washed several times with distilled DME and subsequently rinsed with CS$_2$ to eliminate sulfur precipitates that were formed in the separator during charging. The separator treated with CS$_2$ was dried at 40°C for 2 hours and examined by a FIB-SEM and EDS.

3. Results and Discussion

Electrically and ionically insulating Li$_2$S has been considered electrochemically inactive for a long time. However, Yang et al. reported that even micrometer-sized Li$_2$S particles can be utilized as a cathode material for Li-S batteries [25]. There, the authors suggested that the electrochemical reactions of Li$_2$S particles would proceed over charge transfer between carbon and solid Li$_2$S and the extraction of lithium ions from solid Li$_2$S particles at the beginning of the first charging cycle [25].

Using a specially designed cell comprising an active material-free carbon cathode and commercial micro-sized Li$_2$S powder in the electrolyte region, we found that as-received Li$_2$S particles electrically isolated from a carbon cathode are completely consumed, thus exhibiting considerable capacities on charging [23]. We suggested following reaction routes: (1) a trace amount of medium order polysulfides (i.e., S$_3^{2-}$, S$_4^{2-}$), impurities in the commercial Li$_2$S powder, are oxidized to generate their mononians (S$_3^-$ and S$_4^-$) in the initial step; (2) mononians are converted to high order polysulfides through dimerization; and (3) the high order polysulfides diffuse towards the separator and react with solid Li$_2$S particles to produce medium-order polysulfides. Thus, Li$_2$S material does not require the presence of carbon to be oxidized, due to the presence of intermediate polysulfides that continuously consume Li$_2$S [23].

Based on this finding, it has been expected that the integration of a Li$_2$S-impregnated separator to a conventional Li-S battery would have following effects: (1) generation of a significant amount of medium order polysulfides via a well-known chemical reaction of solid Li$_2$S and sulfur molecules dissolved in the electrolyte solution (see Fig. 1b); (2) conversion of Li$_2$S particles into sulfur through the reaction routes mentioned above upon charging, and (3) improvement of the areal capacity by supplying additional sulfur to the cathode.

To verify this scenario, we constructed a new type of Li-S cell combining a Li$_2$S-infiltrated glass fiber separator with a conventional sulfur cathode. The Li$_2$S-infiltrated separator was prepared by soaking the pristine separator in the solution of Li$_2$S in anhydrous ethanol (Fig. 1a). Fig. 2a and 2b show the SEM images of the surface of a pristine separator and the Li$_2$S-incorporated separator. The pores of a glass fiber separator are observed to be uniformly filled with Li$_2$S. The EDS elemental mapping results for S clearly show that Li$_2$S is uniformly distributed in the micro-sized pores (Fig. 2c). To examine whether Li$_2$S was successfully incorporated into a separator with-

![Fig. 2.](image-url)
out exposure to moisture and oxygen, XRD analysis was carried out on the prepared Li$_2$S-embedded separator. Measured XRD pattern well agreed with that of pure Li$_2$S powder (Fig. 2d), indicating that the chemical nature of Li$_2$S remained intact. To provide additional active materials to the sulfur cathode by converting Li$_2$S to sulfur, Li-S cells with Li$_2$S-filled separator were charged to 4.0 V after cell fabrication. The cell delivered a considerable charge capacity of ~865 mAh/g-Li$_2$S with a distinctive charging profile (Fig. 3a). This confirms that a large portion of Li$_2$S within the separator was oxidized to sulfur during the first charge. The potential profile can be divided into two parts with a breakpoint at around 75% of the charging process: (1) a long flat plateau region at ~2.4 V, and (2) a sulfur formation region with extremely high overpotential. This feature is clearly distinguishable from those of previous works involving coarse Li$_2$S particles, where sharply rising potential curves were observed at the beginning of the first charge.

Yang et al. reported that the micro-sized Li$_2$S/carbon black cathode showed a high overpotential at the beginning of charging for Li$_2$S [25]. There, the authors explained that the large overpotential may arise from the strong bond between Li$^+$ and S$^{2-}$ ions [25].

In a previous study, we showed a Li-S cell composed of a sulfur-free carbon cathode, Li$_2$S placed between two separators and a lithium anode exhibits

![Fig. 3. Potential profiles for the first (—) and the second (―) cycles of (a) a Li-S cell containing Li$_2$S-impregnated separator and (b) a control Li-S cell without Li$_2$S. After cell assembly, the control cell was discharged to 1.8 V in the first cycle, whereas the Li-S cell with Li$_2$S was charged to 4.0 V.](image)

![Fig. 4. Schematic presentation of a proposed charging mechanism in the second part of the first charge of the Li-S cell with Li$_2$S: (a) in the voltage range of 2.5 ~ 3.5 V in the first charge, and (b) at the end of the first charge.](image)
a significant overpotential during the entire charging process [23]. This observation indicates that the reaction rate of the cell was significantly restricted. We suggest that the slow kinetics corresponds to the chemical reactions of Li$_2$S and high order polysulfides, and the long-distance mass transport of polysulfides between the carbon electrode surface and Li$_2$S particles [23]. In particular, the steeply rising potential at the onset of charging is attributed to the significantly low concentration of medium order polysulfides.

In contrast, a long flat plateau (~2.4 V) without any potential spike was observed at the initial stage of charging in this work (Fig. 3a), even though large Li$_2$S particles electrically isolated from the sulfur cathode were included in the cell. This can be explained by the chemical reaction of Li$_2$S in separator and sulfur molecules in the electrolyte (see Fig. 1b). Due to the presence of molecular sulfur in the cell, considerable amount of medium-order polysulfides (e.g., Li$_2$S$_3$ and Li$_2$S$_5$) are produced and promote the electrochemical reactions.

In the second part of the first charge, the cell potential rose rapidly from 2.4 V to 4.0 V. This potential increase implies that the formation of sulfur induces a significantly higher overpotential (Fig. 3a). Since Li$_2$S materials are placed in the electrolyte region away from the cathode, most of polysulfides exist outside the cathode and undergo oxidation reactions preferentially at the outer surface of the cathode. As sulfur formed participates on the cathode surface, the active sites (i.e., the surfaces of carbon particles) are covered with insulating sulfur and electrolyte access is significantly restricted by sulfur deposition at the cathode surface (See Fig. 4a). Such sulfur precipitates make further oxidation of the high-order polysulfides to sulfur at the cathode surface difficult, thereby causing a large overpotential. We expect that most reaction sites near the outer surface of the cathode would be blocked against the further charge transfer reaction at the end of the charge process, as shown in Fig. 4b.

Subsequently, the cells were discharged to a lower cut-off voltage of 1.8 V at a current of 0.05 C. The cells with the Li$_2$S-incorporated separator delivered higher capacities than the control cell due to additional sulfur produced during the first charge (Fig. 3). However, the increase in the discharge capacities was found to be much lower than the charge capacities (~865 mAh/g) of Li$_2$S. This can be ascribed to the low utilization of the sulfur that was mainly formed at the sulfur cathode surface. We think that the long-chain polysulfides, resulting from deposited sulfur on the cathode surface upon discharge, may diffuse more easily towards the lithium anode, thus limiting their further reduction.

In the following cycles, the cell with the Li$_2$S-impregnated separator showed extra capacity with potential profiles similar to the control cell (Fig. 3a). This is in good agreement with previous results [23,25]. Above all, this demonstrates that by simple addition of the Li$_2$S-embedded separator, a high loading cathode can be achieved, resulting in improving the capacities of Li-S cells.

The electrochemical oxidation of the Li$_2$S materials in the separator was scrutinized by post-mortem analysis of the cells collected at the end of the first charge. The separator washed with DME clearly show that a substantial amount of sulfur precipitated on the surface of separator due to its poor solubility (Fig. 5a). Presumably, this is likely due to sulfur formed in the electrolyte region via the chemical reaction (4S$^2-$ → S$_8$ + 4S$^2-$) of polysulfides. To remove sulfur from the separator, it was rinsed several times with CS$_2$. SEM image of the as-prepared Li$_2$S-embedded separator shows that a large amount of Li$_2$S had been consumed during the first charge (Fig. 5b), which is in line with the electrochemical data obtained in the first charge. Although, EDS elemental mapping result reveals that a noticeable amount of Li$_2$S remained within the separator (Fig. 5c). We thus investigated the amount of unreacted Li$_2$S at end of the second charge. The fine structure of the glass fiber separator was clearly visible (Fig. 5d and 5e), and the number of sulfur agglomerates was significantly reduced (Fig. 5f), indicating that that most of the Li$_2$S materials had been consumed amidst the second charge.

Furthermore, we evaluated the cycling stability and rate capability of the cell with the Li$_2$S impregnated separator. The cell with Li$_2$S exhibited significantly larger capacities of ~1100 mAh/g with an excellent capacity retention of 87% after 100 cycles than those (~840 mAh/g) of the control cell (Fig. 6a). This feature may stem from the change in utilization of extra active materials. The long-chain polysulfides generated from the reduction of extra S on the external surface of the cathode may migrate towards the
lithium anode during the first discharge. In result, considerable amount of active materials are present between the cathode and the anode. During subsequent cycling, however, active materials in the electrolyte region are gradually absorbed within the cathode, resulting in enhanced utilization of extra sulfur materials as evidenced by the slight capacity increase in the beginning of cycle test. In contrast, the control cell exhibited typical capacity fading due to the ongoing loss of active materials during cycling.

Fig. 5. Surface microstructural analysis of the separators collected in the end of charge process. In the first charge, (a) SEM image of the sample washed with DME, (b) SEM image and (c) corresponding EDS elemental mapping of the sample treated with CS$_2$. In the second charge, (d) SEM image of the sample washed with DME, (e) SEM image and (f) corresponding EDS elemental mapping of the sample treated with CS$_2$.

Fig. 6. (a) Cycling stability tests of the Li-S cell containing Li$_2$S with a sulfur cathode ($\Delta$) and the control cell without Li$_2$S (○). Rate performances of the prepared Li-S cells: (b) the Li-S cell with Li$_2$S and (c) the control cell at different current densities of 0.1 C (—), 0.2 C (—), 0.5 C (—), 1.0 C (—), and 2.0 C (—).
In addition, high capacity retention at high rates was observed in the cell. The discharge capacities were as high as 1220, 1162, 955, and 860 mAh/g at 0.1 C, 0.2 C, 0.5 C, and 1 C, respectively (Fig. 6b). In particular, the cell with Li$_2$S delivered a much higher capacity (751 mAh/g) at 2 C, compared with the control cell (Fig. 6b and 6c). This result can be explained by the same reason mentioned above: practical utilization of extra S increases for subsequent cycles as more active materials are involved in the electrochemical reactions. Overall the cell adopting the Li$_2$S-embedded separator along with the sulfur cathode outperforms the control cell in terms of cycle life and rate property. This unambiguously demonstrates that the simple addition of Li$_2$S-impregnated separator significantly improves the electrochemical performances of Li-S cells.

4. Conclusions

In this work, we present a new cell design for a high-performance Li-S battery. A Li$_2$S-impregnated separator was sandwiched between a common sulfur cathode and a lithium anode. Li$_2$S was found to be homogeneously distributed within the pores of the separator. The cell containing Li$_2$S exhibits a much larger discharge capacity (1402 mAh/g) compared with a control cell without Li$_2$S. SEM and EDS analysis of the separator after the second charge confirmed that most of Li$_2$S is consumed and finally oxidized to sulfur during the second charge. Although the micron-sized Li$_2$S particles are electrically isolated from the cathode, the Li-S cell was charged without an initial potential peak at the beginning of the first charge, as it had been observed in the cathode with micron-sized Li$_2$S particles. This is ascribed to the presence of a large amount of medium-order polysulfides, which are formed by the chemical reaction between solid Li$_2$S and dissolved molecular sulfur in the electrolyte. Moreover, the cell with Li$_2$S outperforms the control cell regarding cycling stability and rate performance. This confirms the validity of our cell design strategy. We expect the performances of the cell to be further improved by optimization of key design parameters (e.g., thickness and pore structure of a separator, the content of Li$_2$S in a separator, and the structure of a sulfur cathode). Owing to its simplicity, we believe that our design is suitable for the development of cost-effective and high-energy-density Li-S batteries.

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