Cathode-Supported All-Solid-State Lithium–Sulfur Batteries with High Cell-Level Energy Density

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ABSTRACT: Bulk-type all-solid-state lithium batteries (ASSLBs) are being considered as a promising technology to improve the safety and energy density of today’s batteries. However, current bulk-type ASSLBs suffer from low cell-level energy density due to the challenges in reducing the electrolyte thickness. In this work, we report cathode-supported ASSLBs with a thin solid electrolyte layer. Starting from a stainless steel mesh-supported Li2S cathode, we are able to build an ASSLB with a ~100 μm thick Li3PS4 electrolyte reinforced by a Kevlar nonwoven scaffold and with Li metal as the anode. The ASSLB delivers a high capacity with high rate and cycling performances at room temperature. Moreover, the unique cell design also enabled utilization of a thick cathode with a Li2S loading of 7.64 mg cm−2, providing a high cell-level energy density (excluding the current collectors) of 370.6 Wh kg−1 for the first cycle.

All-solid-state lithium batteries (ASSLBs) hold great potential to significantly improve the safety and energy density of today’s lithium ion batteries by using nonflammable, inorganic solid electrolytes.1–3 Solid electrolytes play a critical role in enabling ASSLBs. Among various lithium-ion-conducting materials, sulﬁde-based solid electrolytes are one of the most promising electrolytes because of their excellent ionic conductivity and mechanical property.4,5 The ionic conductivities of several sulﬁde electrolytes are comparable with or even higher than that of the organic liquid electrolyte,4–5 enabling all-solid-state lithium ion batteries with very high cycling and rate performances.5,10–13 However, a very thick solid electrolyte (~0.5–1.0 mm) was usually used in these ASSLBs.5,14–18 As a result, the cell-level energy densities of these ASSLBs are still limited to <200 Wh kg−1, which is lower than that of the commercialized lithium ion batteries.

There are many reports about preparing thin electrolyte layers.19–24 For example, Lee prepared a 64 μm thick electrolyte by creating a solid electrolyte-in-polymer matrix.19 Jung reported the fabrication of a 70 μm thick sulﬁde electrolyte using a poly(para-phenylene terephthalamide) nonwoven scaffold as a mechanical support.20 In addition, a submicrometer solid electrolyte membrane was also prepared using a self-assembly approach.21 However, integrating these thin electrolytes into a high-energy cell (e.g., Li/S) has never been achieved because the thin electrolyte layer is easy to break during cell fabrication or operation, especially for the S cathode and Li anode with a large volume change. Therefore, the cathode materials used in these cells are LiCoO2 and FeS2,19,20 while the anode materials are graphite, Li4Ti5O12, and Li1–In alloy,19,20 limiting the energy densities of ASSLBs.

In this present study, we report a method for fabricating cathode-supported ASSLBs with a thin electrolyte. Different from the conventional electrolyte-supported cell that starts from fabrication of the electrolyte layer and then the assembly of electrode layers on each side of the electrolyte, we start to build the cell from a stainless steel (SS)-supported Li2S cathode. Using a Kevlar nonwoven scaffold as mechanical support, a ~100 μm thick Li3PS4 (LPS) glass solid electrolyte was successfully integrated in the Li/S ASSLBs. The all-solid-state Li/S batteries with a Li2S loading of 2.54 mg cm−2 provided a high initial capacity of 949.9 mAh g−1 at 0.05 C at room temperature. Moreover, the cell also exhibited great...
Figure 1. Schematic illustration of the fabrication of the cathode-supported all-solid-state cell with a thin sulfide electrolyte.

Figure 2. Schematic of the cathode-supported all-solid-state Li–Li2S cell.

A photograph and SEM images of the key steps in the fabrication processes of all-solid-state cells are shown in Figure 3. A SS mesh with a pore size of around 200 μm (Figure 3a,b) was used as the current collector to enhance the mechanical strength and the integrity of the Li2S cathode. The unique mesh structure of the current collector allows a high loading of active material (Li2S: 2.54–7.64 mg cm−2). The Li2S–Li solid active material is uniformly spread on the SS mesh (Figure 3c,d). The web structure of the Kevlar nonwoven scaffold is shown in Figure 3e,f. LPS suspension was prepared in an argon-filled glovebox (Figure 3g), and the dried LPS particles are homogeneous and regular, with sizes of approximately 2–5 μm (Figure 3h). The LPS suspension was dropped into a Kevlar nonwoven scaffold with a designed amount to control the thickness of solid electrolytes. Figure 3i,j shows a photograph and SEM image of the cold-pressed LPS–Kevlar membrane, which clearly shows the reinforced structure.

The thicknesses of the electrolyte membrane and the cathode layer were demonstrated from cross-sectional SEM images (Figures 3k,l and 4a,b). The distribution of the elements from the EDS mappings in Figure 4d–i shows that the thicknesses of the cathode layer and the electrolyte layer are both about 100 μm as Fe, F, and I are present only in the
cathode and P and S are present in both the cathode and the electrolyte. Furthermore, the energy dispersive spectroscopy (EDS) results in Figure 4c confirm the high purity of the sample.
The electrochemical performances of all-solid-state full cells were evaluated at room temperature. Figure 5a shows the galvanostatic charge–discharge profiles of the Li–Li2S solid cell with a Li2S loading of 2.54 mg cm\(^{-2}\) in the potential range of 1.2–3.0 V at 0.05 C at room temperature. Different from the traditional liquid Li–Li2S cell, only one plateau is observed during charge and discharge processes. No polysulfide intermediates are formed during the conversion reaction that completely solves the issue of shuttle reaction in a liquid Li–Li2S cell.\(^{25,30,34}\) The cell in the first charge–discharge process

Figure 5. Charge–discharge profiles of the cathode-supported all-solid-state Li–Li2S cells at (a) 0.05 C, (b) 0.2 C, and (c) different rates from 0.05 to 0.5 C at 25 °C. Cycle performance of the cathode-supported all-solid-state Li–Li2S cells at (d) 0.05 and (e) 0.2 C at 25 °C. (f) Rate performance of the cathode-supported all-solid-state Li–Li2S cell at 25 °C. The specific capacities are calculated based on the mass of Li2S in the cathode composite. The Li2S loading is 2.54 mg cm\(^{-2}\).

Figure 6. Charge–discharge profiles of the cathode-supported all-solid-state Li–Li2S cells with Li2S loadings of (a) 3.82, (b) 5.10, and (c) 7.64 mg cm\(^{-2}\) at 0.05 C at 25 °C. (d) Cycle performance of the cathode-supported all-solid-state Li–Li2S cells with different Li2S loadings. (e) Cell-level energy densities of the cathode-supported all-solid-state Li–Li2S cells with different loadings.
displays a charge capacity of 1070.1 mAh g$^{-1}$ and a high discharge capacity of 949.9 mAh g$^{-1}$ with a Coulombic efficiency of 88.8%. The relatively large overpotential in the first cycle is attributed to the activation process.\textsuperscript{25} During the following cycles, the overpotential decreases, although it is still relatively large when compared with the cells using LiCoO$_2$ as the cathode.\textsuperscript{3} Possible reasons for the large overpotential include the addition of PTFE binder in the cathode composite and the low ionic conductivity of the electrolyte. The cell capacity is slightly reduced with charge-discharge cycles (Figure 5d). At 50 cycles, the all-solid-state cell with thin electrolyte still shows a high discharge capacity of 636.4 mAh g$^{-1}$. The excellent capacity retention of the solid cell benefits from the SS mesh current collector. The galvanostatic charge-discharge performance of the cell without the SS mesh current collector was also tested (Figure S9a). The cell showed a low initial discharge capacity of 840.5 mAh g$^{-1}$ with a poor cycle performance and large cell resistance (Figure S9b and S10) at 50 cycles. The results show that using a SS mesh current collector effectively improves the mechanical integrity of the Li$_2$S cathode that experiences a huge volume change during the charge-discharge process. The cycle performance of the cell at a high rate of 0.2 C is shown in Figure 5b,c. Although the increase of the current rate from 0.05 to 0.2 C reduces the discharge capacity and enhances the overpotential, the cell still shows high cycling stability at a capacity decay rate of only 1.16 mAh g$^{-1}$ per cycle from cycle 2 to cycle 100. In addition, the active cell exhibits a high rate capability at 25 °C (Figure 5c,f). Discharge capacities of 836.9, 692.2, 537.8, and 358.5 mAh g$^{-1}$ are achieved at 0.05, 0.1, 0.2, and 0.5 C, respectively. As one important advantage of all-solid-state batteries is the ability to operate at higher temperatures, we also tested the electrochemical performance of the cell at 60 °C (Figure S11). The cell was able to cycle stably at 0.1 and 0.2 C at 60 °C with enhanced kinetics.

We further tested the electrochemical performance of the cells with increased Li$_2$S loadings. The galvanostatic charge-discharge profiles with Li$_2$S loadings of 3.82, 5.10, and 7.64 mg cm$^{-2}$ are shown in Figure 6a–c. The initial discharge capacities of the three cells with different Li$_2$S loading are similar; however, the cell with a higher Li$_2$S loading shows a faster capacity decay (Figure 6d). The cell energy densities with different Li$_2$S loadings are summarized in Figure 6e.

Figure 7 compares the cell energy densities of all of the reported sulfide-based all-solid-state cells, with the detailed weights of the cell components shown in Table S1. The cell energy density is calculated from the average discharge voltage, cell capacity, and total weights of the cathode, solid electrolyte, and anode, but the weights of the current collectors and exterior package are excluded for calculation due to lack of information from the literature. One reason is that most of the previous reports used a lab-scale Swagelok cell to test the performance of the solid-state battery, wherein two SS (or Ti) rods were used as the current collectors.\textsuperscript{SS} As shown in the figure, the cell energy densities of most reported all-solid-state cells with sulfide electrolytes are <100 Wh kg$^{-1}$, which is much lower than that of commercialized liquid cells of ~200 Wh kg$^{-1}$ due to utilization of thick solid electrolytes. Our Li–Li$_2$S solid cell with a high Li$_2$S loading of 7.64 mg cm$^{-2}$ exceeds an energy density of 370 Wh kg$^{-1}$ at the cell level for the first cycle, which is the highest energy density reported to date. It should be noted that the cell-level energy density of the cell is not high if the weight of the SS mesh current collector is included in the calculation. Because the main purpose of using SS mesh as the current collector is to provide a matrix for the cathode composite, other electronically conducting materials with a 2D or 3D structure but with a lower density can also be used as current collectors. For example, the cell-level energy density (including current collectors) of the cell was largely increased (from S9 to 159 Wh kg$^{-1}$) by replacing the SS mesh (53.3 mg cm$^{-2}$) with Ni-coated Kevlar fiber (1.22 cm$^{-2}$) as the current collector (Figure S12).

In summary, we demonstrate thick cathode-supported ASSLBs with a thin electrolyte (~100 μm). LPS–Kevlar solid electrolyte membranes are formed by dropping the LPS suspension into the Kevlar nonwoven scaffold followed by drying/cold pressing onto a thick SS mesh-supported Li$_2$S–Li1 cathode. Using a Li metal anode, the Li–Li$_2$S cell with 2.54 mg cm$^{-2}$ Li$_2$S loading achieves a high reversible discharge capacity of 949.9 mAh g$^{-1}$ at 0.05 C and stable cycling for 100 cycles at 0.2 C. The all-solid-state Li–Li$_2$S cell with a high Li$_2$S loading of 7.64 mg cm$^{-2}$ exhibits an extremely high cell-level energy density of 370.6 Wh kg$^{-1}$.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b00430.

Impedance plot of the SS/80Li$_2$S-20LiI/SS cell, XRD pattern and SEM images of the cathode composite, XRD patterns and Raman spectra of the as-prepared LPS and LPS dried from the LPS suspension in toluene, SEM images of the surface of the LPS–Kevlar electrolyte, Nyquist plots of blocking cells, galvanostatic cycling of the Li/LPS–Kevlar/Li cell, charge–discharge profiles and cycle performance of Li–Li$_2$S solid cells without a SS mesh current collector, Nyquist plots of the Li–Li$_2$S cells, charge–discharge profiles of the cathode-supported all-solid-state Li–Li$_2$S solid cells at 60 °C, charge–discharge of the all-solid-state Li–Li$_2$S cell with Ni-coated Kevlar nonwoven as the current collector for the cathode, and summary of the cell-level energy densities of all-solid-state cells using sulfides as the electrolyte.
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Notes
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