Energy Density Limitation of Lithium-Sulfur Battery

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Abstract: Li-S batteries with a theoretical specific capacity of 1,672 mAh g⁻¹, are among the most promising candidates for the next generation rechargeable batteries due to their high energy density, low raw material cost and environmental friendliness. Despite this great potential, the complicated electrochemical process introduces many challenges for Li-S batteries, including low conductivity of both elemental sulfur and end discharge product Li₂S, large volume expansion of 80% upon discharge, and unfavorable redox shuttle effect due to soluble nature of intermediate LiPS.

Keywords: Li-S battery, energy density, lithium polysulfide, solubility

Introduction

The electrolyte plays a crucial role in the electrochemical performance of Li-S batteries. Sufficient ionic conductivity, high chemical and electrochemical stability, low volatility and toxicity are required for Li-S batteries electrolytes [1]. High LiPS solubility is also generally favored since dissolved LiPS has easy access to carbon support, resulting in better utilization of active materials and faster reaction kinetics. In fact, the most widely used ether based electrolytes for Li-S cells are polar-aprotic solvents which yield high solubility for LiPS molecules. However, the soluble LiPS can also cause a severe redox shuttle effect and therefore an effective passivation layer must be present on Li anode. Currently, LiNO₃ is the most common electrolyte additive to help passivate Li anode surface [2].

Despite recent improvement in rechargeable Li-S batteries, to the operation of Li-S batteries under lean electrolyte conditions remains a grand challenge because the practical energy density of Li-S batteries strongly depends on the electrolyte/sulfur ratio (E/S expressed in mL g⁻¹). In the literatures, high E/S ratios are commonly used and the large excess of the electrolyte dominates in cell weight. However, in practical applications, relatively low E/S ratio must be achieved in order to increase the energy density of these batteries [3-5]. Unfortunately, E/S ratio sets an upper bound on LiPS dissolution, and the solubility of LiPS species reported in the widely used 1,2-dimethoxyethane (DME): 1,3-dioxolane (DOL) binary electrolyte ([S]= ~6 M) [6] corresponds to an E/S ratio of 5.2 mL g⁻¹. Therefore, in order to enable full dissolution of LiPS, a minimum E/S ratio of 5.2 mL g⁻¹ is required. As a result, under low E/S conditions the low LiPS solubility causes severe performance degradation and electrolyte consumption from side reactions may even result in cell dry-out and failure [7]. On the anode side, solid electrolyte interface (SEI) formed under high LiPS concentration conditions was found out to lead to gradual etching of Li metal [8]. Thus, achieving reversible electrochemistry under low E/S conditions is necessary for commercializing sulfur battery chemistries and increasing the LiPS solubility would be of great significance for a lean electrolyte operation.

Experimental

In this work, a freestanding, three-dimensional macroporous multi-walled carbon nanotube (MWCNT) foam was used as carbon host for synthesizing three types of cathodes, which were then tested under designed scenarios to demonstrate the effects of LiPS solubility on cell capacity. The combined results underlined importance of LiPS solubility on fully exploiting high capacity of Li-S cells. Finally, the specific energy of an ideal Li-S cell was reevaluated taking into account of LiPS solubility limit.

Three types of cathodes, i.e., carbon-only cathodes (denoted as C-only cathodes), sulfur cathodes with solid state LiPS loading (denoted as C/LiPS cathodes), and sulfur cathodes with sulfur loading (denoted as C/S cathodes), were employed in test. The selected LiPS species Li₈S₈ were prepared by mixing stoichiometric amounts of sulfur powder (Sigma-Aldrich) and Li₂S powder in DME solution. The precursor solution was heated at 45 °C and stirred vigorously for 48 hours to produce the dissolved solution. In an argon-filled glovebox, C/LiPS cathodes were obtained by soaking CNT foams in LiPS solution with controlled concentration for a controlled time period and finally dried overnight to evaporate solvent. The #1, #2 and #3 C/LiPS cathodes have LiPS loading of ~4 mg, 2 mg and 1 mg, respectively.
C/S cathodes were made by infiltrating sulfur into CNT foams via the melting diffusion method. Sulfur powder was placed onto punched CNT foam electrode surface and heated at 158 °C on a hot plate until designed sulfur loading was met. The electrode was rotated regularly during sulfur infiltration. The #1, #2 and #3 C/S cathodes have sulfur loading of ~4 mg, 2 mg and 1 mg, respectively.

The regular electrolyte used was composed of 1 M bis(trifluoromethane)sulfonimide Li salt (LiTFSI) and 0.1 M LiNO₃ in DME: DOL (1:1 v:v). The high Li salt electrolyte was composed of 5 M LiTFSI in DME: DOL (1:1 v:v). The Li₂S₈ catholyte was prepared in the described method above except that the blank electrolyte used was 0.5 M LiTFSI and 0.1 M LiNO₃ in DME: DOL (1:1 v:v). The as-prepared cathode was assembled with a glass fiber separator (0.26 mm) and a Li foil anode (0.25 mm) subsequently into a CR2032-type coin cell. 60 μL of desired electrolyte was used in all cells. The assembled Li-S cells were discharged in galvanostatic mode under current density of 0.4 mA cm⁻². The linear sweep voltammetry (LSV) measurement was conducted by Gamry Instruments-Reference 3000 at a scan rate of 0.1 mV s⁻¹.

To synthesize CNT foams, PMMA microspheres were used as a template and PAN as a precursor to create cross-links among CNTs. SEM images in Fig.1 illustrate morphology of CNT foam at different magnifications. As seen in Fig.1, the cellular microstructure of CNT foams consisted of major spherical void, which were closely packed and interconnected with each other through junctions of MWCNT walls.

**Results and Discussion**

Fig. 2 plots the discharge profiles and LSV curves of Li-S cells with regular electrolyte. Both discharge profiles clearly present two discharge plateaus, which correspond to the two cathodic peaks in their LSV curves. The specific capacity of the cell with C/S cathode was larger than that with C/LiPS cathode, the difference being due to the different starting points of reduction reaction.

When regular electrolyte is used, it becomes difficult to observe the over-saturation condition since either electrolyte amount is often in excess in cell assembly, or the reactions become too sluggish to fully utilize active material under low E/S conditions. One approach to create over-saturation condition is to decrease LiPS solubility in electrolyte deliberately by modifying electrolyte components. It was reported that when a high Li salt electrolyte was used, the solubility of LiPS would be reduced significantly due to common ion effect [9]. As a result, LiPS species would become mostly insoluble in electrolyte and the electrochemical reactions of Li ion intercalation would occur in solid phase. Fig. 3 (a) shows the cell performances with electrolyte containing 5 M LiTFSI. The voltage profiles still exhibit a two-stage shape, but discharge voltages shift to lower average values compared to those with regular electrolyte, which was also consistently observed by other groups in similar conditions [9,10]. The much reduced peak current intensity in Fig. 3 (b) suggests that the reaction rate was lower in high Li salt electrolyte compared to that in regular electrolyte.

In order to create an over-saturation condition with access to both liquid phase and solid phase reaction pathway needs to be created in the electrolyte. This can be realized by using a combination of a high concentration LiPS catholyte and a sulfur-containing cathode. Another set of tests was then conducted using C/S cathodes coupled with high concentration LiPS catholyte ([S] = 5 M). The extremely high concentrations of LiPS and co-salts make the solution almost saturated, thus prohibiting further
dissolution of LiPS and enforcing the appearance of LiPS insoluble pathway. As seen in Fig. 5 (a), the upper plateau capacities in voltage profiles show a monotonous increasing trend with increasing cathode sulfur loading. The upper plateau can be further divided into two parts as seen in the lower-left inset. First, the solid lines in the relatively flat region at the beginning of discharge are attributed to the reduction of sulfur to Li$_2$S$_8$. It is found that the increased capacities are due to this region and the higher cathode sulfur loadings yield to larger capacity with a relatively constant sulfur conversion rate of ~ 50%. Second, the dashed oblique lines are associated with the conversion from high-order LiPS to low-order LiPS. One could see that the slopes and associated capacities remain almost unchanged in this region. The above results imply that reduction of sulfur to Li$_2$S$_8$ is not inhibited by the high concentration of Li$_2$S$_8$ catholyte. However, the generated Li$_2$S$_8$ does not further convert to low-order LiPS, indicating the full utilization of active material is prohibited owing to LiPS solubility limit. One can also observe that the overall capacities of cell with C/S cathodes decreased compared to that with a carbon-only cathode, which results from the decrease of lower plateau capacity.

It is because the dissolved LiPS in electrolyte was well below saturation level and therefore solid LiPS in cathode would still dissolve first and undergo the liquid phase reaction. Consequently, cathode with higher LiPS loading would deliver higher upper plateau as well as lower plateau capacity. However, the increase of the capacity of the upper plateau was not observed when a higher concentration catholyte was used. The overall capacities especially the upper plateau capacities remained almost unchanged regardless of cathode LiPS loading when catholyte concentration was increased to [S]=5 M. The distinct behaviors under different LiPS concentrations clearly demonstrate the effects of LiPS solubility on LiPS dissolution.

Fig. 6. Voltage profiles of Li-S cells with C/LiPS cathodes and Li$_2$S$_8$ catholyte ([S]=1 M and[S]=5 M)

When LiPS is generated as a result of sulfur reduction, the battery is unlikely to deliver its entire theoretical capacity. The LiPS must be readily reduced electrochemically, otherwise it eventually becomes “dead” sulfur source. The combined results above suggest that the LiPS-soluble reaction pathway dominates in the Li-S cell with a liquid electrolyte environment. When the LiPS solubility limit is reached, although sulfur can be reduced to solid state LiPS, the subsequent reduction reactions can occur exclusively in liquid phase and the maximum number of LiPS species available for reaction is restricted by LiPS solubility, which becomes an intrinsic limitation for Li-S cell capacity.

With above findings the theoretical energy density of Li-S cells needs to be reevaluated under low E/S conditions. Fig. 7 presents a series of specific energy calculation of an ideal Li-S cell. Here only the weight of active electrode material, i.e., sulfur and Li, as well as electrolyte weight is included in calculation.
Fig. 7. Specific energy calculation of an ideal Li-S cell. (a) Weight percentage of cell components in an ideal Li-S cell under different E/S ratios. (b) Effective specific capacity of an ideal Li-S cell under different E/S ratios. (c) Specific energy of an ideal Li-S cell under different E/S ratios. (d) Specific energy of an ideal Li-S cell with different LiPS solubility.

Conclusion

The theoretical energy density of Li-S batteries strongly depends on the E/S ratio of the cell. When the minimal E/S ratio is determined by LiPS solubility in the current organic electrolyte, the theoretical energy density of Li-S batteries will become less attractive. Here some designed scenarios were evaluated for the effect of LiPS solubility on cell capacity. It revealed that the when LiPS solubility is reached, although sulfur can be reduced to solid state LiPS, it will not further contribute to cell capacity. Since lowering E/S ratio is essential to boost the energy density of Li-S batteries and LiPS solubility will be an intrinsic limit under low E/S condition, the importance of LiPS solubility cannot be overlooked. There is a pressing need for research on electrolyte and electrode chemistry to improve the reaction kinetics under LiPS-saturated or LiPS-insoluble condition.

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References