Understanding the behavior of lithium (Li)-sulfur (S) cells under lithium polysulfide (LiPS)-saturated condition, especially determining whether LiPS solubility is an intrinsic limit for cell capacity, is of great interest for the development of high energy density Li-S batteries. In this work, sets of Li-S cells were tested under designed scenarios to demonstrate the effect of LiPS solubility on cell capacity. It revealed that when LiPS solubility limit is reached, though sulfur can be reduced to solid state LiPS, it cannot further convert to subsequent discharge products and contribute to cell capacity.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI:10.1149/2.1381706jes] All rights reserved.

Manuscript submitted February 16, 2017; revised manuscript received April 5, 2017. Published April 12, 2017.

Li-S batteries with a theoretical specific capacity of 1672 mAh g\(^{-1}\), are among the most promising candidates for next generation rechargeable batteries due to the high energy density, low raw material cost and environmental friendliness.\(^1\) Most of the current research on Li-S batteries has been performed using LiPS-soluble electrolytes. Although the dissolution of LiPS causes parasitic redox shuttle reactions, the electrolyte with high LiPS solubility and low viscosity is still favorable for high sulfur utilization and fast reaction kinetics.

Among the various technical issues with Li-S batteries, the challenge of LiPS solubility is less recognized due to the commonly high electrolyte/sulfur (E/S in mL g\(^{-1}\)) ratios used in the literature so that the established LiPS concentrations are well below the solubility limit. As a matter of fact, the energy density of practical Li-S batteries strongly depends on the E/S ratio.\(^2,3\) The E/S ratio sets an upper bound that the established LiPS concentrations are well below the solubility of LiPS species reported in the widely used ether solution (\([\text{S}] = \sim 6 \text{M}\)) corresponds to an E/S ratio of 5.2 mL g\(^{-1}\). If the minimum E/S ratio is determined by LiPS solubility, then in the above case electrolyte weight will dominate the battery weight and the theoretical specific energy of an ideal Li-S cell is less than 500 Wh kg\(^{-1}\) (see Supplementary Material). Therefore, achieving reversible electrochemistry under low E/S ratio condition is necessary for successful commercialization of high energy density Li-S system and LiPS solubility limit would become a crucial issue under the lean electrolyte condition.

In this work, three types of cathodes, i.e., sulfur-free 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 tested under designed scenarios to demonstrate the effect of LiPS solubility on cell capacity.

**Experimental**

A freestanding, three-dimensional macroporous carbon nanotube (CNT) foam was used as the sulfur host, whose synthesis method was reported elsewhere.\(^4,5\) It offers a constant carbon loading and eliminates the use of a current collector. The obtained foam has a controlled thickness of \(\sim 100 \mu\text{m}\) and porosity of \(\sim 94\%\). The selected LiPS species Li\(_2\)S\(_8\) was prepared by mixing stoichiometric amounts of Li\(_2\)S in solid phase. When a high Li salt electrolyte was used (\([\text{Li}^+]/[\text{S}^−] = 1\)) unless CC License in place (see abstract).

---

**Communication—Effect of Lithium Polysulfide Solubility on Capacity of Lithium-Sulfur Cells**

Chao Shen,\(^{a,b}\) Jianxin Xie,\(^{c,d}\) Mei Zhang,\(^{e,d}\) Jim P. Zheng,\(^{a,b,e,\ast}\) Mary Hendrickson,\(^f\) and Edward J. Plichta\(^f\)

\(^a\)Department of Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, Florida 32310, USA
\(^b\)Department of Industrial and Manufacturing Engineering, Florida A&M University and Florida State University, Tallahassee, Florida 32310, USA
\(^c\)Aero-Propulsion, Mechatronics and Energy Center, Florida State University, Tallahassee, Florida 32310, USA
\(^d\)High Performance Materials Institute, Florida State University, Tallahassee, Florida 32310, USA
\(^e\)Center for Advanced Power Systems, Florida State University, Tallahassee, Florida 32310, USA
\(^f\)Army Power Division, RDER-CCA, Aberdeen Proving Ground, Maryland 21005, USA

**Results and Discussion**

Fig. 1 plots the discharge profiles and CV curves of Li-S cells with regular and high Li salt electrolyte. The cathodes used were #2 C/LiPS cathodes. In the experiments, the first reduced product of sulfur, i.e., Li\(_2\)S\(_2\) was the selected LiPS species so that the over-saturation condition was expected to occur at early stage of discharge. The Li-S cell with regular electrolyte clearly presents two discharge plateaus, which correspond with the two cathodic peaks in its CV curve. The result is as expected since the solid state LiPS would dissolve in the regular electrolyte first and trigger the well characterized two-step reduction reactions, i.e., the conversion of high-order LiPS Li\(_2\)S\(_n\) (\(6 < n \leq 8\)) to low-order LiPS Li\(_2\)S\(_2\) (\(2 < n < 6\)) in liquid phase and the deposition of Li\(_2\)S in solid phase. When a high Li salt electrolyte was used instead, the solubility of LiPS would be reduced significantly due to the common ion effect.\(^6\) The voltage profile still exhibits a two-stage shape, but the operational voltage shifts to a lower value owing to the increased cell polarization, which was consistently observed by others who used C/S composites as cathodes in similar conditions.\(^6\) The much reduced peak current intensity also suggests that the reaction

\(^{\ast}\)Electrochemical Society Member.

\(^{\ast}\)E-mail: zheng@eng.fsu.edu
rate was lower in the high Li salt electrolyte. As a result, one would conclude that the reduction of Li$_2$S$_8$ can go through either a soluble or insoluble pathway as illustrated in Fig. 2. While the dissolution of LiPS is not a prerequisite for subsequent electrochemical reactions, it enables much faster reaction kinetics compared to the solid phase reaction.

Another set of tests was conducted using the C/S cathodes coupled with L$_2$S$_8$ catholyte ([S] = 5 M). The extreme high concentration of LiPS along with the co-salts made the solution almost saturated, thus prohibiting further dissolution of newly generated LiPS. As seen in Fig. 3, the upper plateaus in the voltage profiles show a monotonous increasing trend with increasing cathode sulfur loading. The increased capacities in the relatively flat region at early stage of discharge are attributed to the reduction of sulfur to Li$_2$S$_8$, while the capacities associated with the conversion from high-order LiPS to low-order LiPS (denoted as the dashed lines in the voltage profiles) remain almost unchanged. The above results imply that the reduction of sulfur to Li$_2$S$_8$ was not inhibited by the high concentration of Li$_2$S$_8$ in the electrolyte. Since the electrolyte was nearly saturated with LiPS, the newly generated LiPS was mostly in solid state. However, the generated Li$_2$S$_8$ did not further convert to low-order LiPS, indicating the full utilization of active material was prohibited owing to the LiPS solubility limit. It was also observed that the overall capacities of the cell with C/S cathodes decreased compared to that with a sulfur-free CNT foam cathode, which may result from the internal charge-transfer resistance increase caused by the unreacted sulfur in the cathodes.

C/LiPS cathodes were later tested under the same condition. A better illumination is expected since in this scenario all the cell capacities originate from the reduction of a single LiPS species. As seen from the voltage profiles in Fig. 4, the overall capacities especially the upper plateau capacities remain almost unchanged regardless of the solid state LiPS loading. Also there is no extra capacity increase even discharging the cells to 1.2 V (see Fig. S1 in Supplementary Material). Despite the possible pathways of either a LiPS-soluble liquid phase or a LiPS-insoluble solid phase reaction, only the liquid phase reaction for LiPS was observed in the experiments. The possible reason is that there existed a competition between the two reaction pathways and the LiPS-soluble pathway dominated in the liquid cell due to its much higher reaction rate. Therefore, the cell capacity was almost exclusively contributed by the LiPS in the electrolyte while LiPS solubility determined the maximum dissolved LiPS species available for subsequent electrochemical reactions. The addition of solid state PS did not further contribute to cell capacity once the over-saturation condition was reached.

**Figure 1.** (a) Voltage profiles of Li-S cells with regular electrolyte and high Li salt electrolyte; (b) CV curves of Li-S cells with regular electrolyte and high Li salt electrolyte.

**Figure 2.** A schematic showing the possible pathways of Li$_2$S$_8$ reduction in Li-S cells.

**Figure 3.** Voltage profiles of Li-S cells with C/S cathodes and Li$_2$S$_8$ catholyte ([S] = 5 M).
Figure 4. Voltage profiles of Li-S cells with C/LiPS cathodes and Li$_2$S$_8$ catholyte ([S] = 5 M).

While the overall redox reaction of a Li–S cell can be described by the simple reaction of sulfur with Li to form Li$_2$S, the reduction of sulfur proceeds through several distinct steps and therefore the full utilization of active material relies on the complete conversion of each intermediate LiPS species. The combined results above suggest that in a regular Li-S cell, when LiPS solubility limit is reached, although sulfur can be reduced to solid state LiPS, the following reduction reaction occurs in liquid phase exclusively and the maximum LiPS species number available for reaction is restricted by LiPS solubility. Thus LiPS solubility will become an intrinsic limit for the capacity of Li-S cells.

Summary

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 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.

Acknowledgments

This work was supported by US Army Power Division under contract No. GTS-S-15-014.

References

1. A. Manthiram, Y. Fu, S.-H. Chung, C. Zu, and Y.-S. Su, Chem. Rev., 114, 11751 (2014).
2. M. Hagen, P. Fanz, and J. Tübke, J. Power Sources, 264, 30 (2014).
3. B. D. McCloskey, J. Phys. Chem. Lett., 6, 4581 (2015).
4. D. Eroglu, K. R. Zavadil, and K. G. Gallagher, J. Electrochem. Soc., 162(6), A982 (2015).
5. J. W. Dibden, J. W. Smith, N. Zhou, N. Garcia-Araez, and J. R. Owen, Chem. Commun., 52, 12885 (2016).
6. Y. Cui and M. Zhang, ACS Appl. Mater. Interfaces, 5, 8173 (2013).
7. Y. Cui and M. Zhang, J. Mater. Chem. A, 1, 13984 (2013).
8. E. S. Shin, K. Kim, S. H. Oh, and W. II Cho, Chem. Commun., 49, 2004 (2013).
9. L. Suo, Y.-S. Hu, H. Li, M. Armand, and L. Chen, Nat. Commun., 4, 1481 (2013).