

Performance Booster: A Different Role of Polysulfide in Rechargeable Lithium-Sulfur Batteries

Shuru Chen, Fang Dai, Mikhail Gordin, Donghai Wang*

Department of Mechanical & Nuclear Engineering, the Pennsylvania State University, University Park, Pennsylvania 16802, USA
dwang@psu.edu

After decades of intensive development, lithium ion batteries are still incapable of meeting the energy density requirements of emerging application. It is thus necessary to explore new electrochemistry and new materials for high-energy battery systems.¹⁻²

The rechargeable lithium-sulfur (Li-S) battery is a promising candidate because sulfur has a high theoretical specific capacity of 1675 mAh/g and a high specific energy of 2600 Wh/kg. It operates by conversion of sulfur through a multistep redox reaction, forming different lithium sulfide products (Li_2S_x , $1 \leq x \leq 8$).³ Those lithium sulfide products, especially polysulfides, tend to dissolve in electrolyte and contribute to a shuttle phenomenon during charging process that results in poor coulombic efficiency. Worse still, active materials might keep losing due to the formation of insoluble, insulating Li_2S on the surface of both the cathode and the lithium anode, accompanying with the dissolution of polysulfide, leading to poor sulfur utilization and fast capacity fading.

Considerable effort has been devoted to engineering carbon/sulfur (C/S) composites that are capable of trapping soluble polysulfides by physical or chemical adsorption.⁴⁻⁶ Electrolyte additives, e.g. LiNO_3 , were reported to passivate lithium metal and suppress the redox shuttle of polysulfides, resulting in improved coulombic efficiency.⁷ Nevertheless, none of these approaches are sufficient to fully address the dissolution of polysulfides and the accumulation of Li_2S . Therefore, the cyclability of Li-S battery is still not satisfactory for practical applications.

In this work, we report a simple strategy for high performance Li-S batteries by using soluble lithium polysulfide-containing electrolyte. The idea of adding polysulfides as co-salts/additives in electrolyte is to provide extra capacity and compensate for the active mass loss. By optimizing the concentration of polysulfide species and the amount of electrolyte, we may also avoid the unfavorable formation of insoluble Li_2S and thereby dramatically improve the capacity, cyclability, and rate capability of the cell.

Polysulfide-containing electrolytes with the desired sulfur concentration ($[\text{S}]$) and average polysulfide chain length were prepared by chemically reacting stoichiometric amounts of sulfur and Li_2S in polysulfide-free electrolyte of 0.1 M LiTFSI + 0.2 M LiNO_3 in DOL/DME (1:1, v:v). To demonstrate the advantages of these electrolytes, cathodes containing 50 wt% sulfur prepared by ball milling were used rather than any novel porous carbon/sulfur composites.

The discharge/charge profiles of cells in 10 μL of polysulfide-free (Fig. 1a) and polysulfide-containing (Li_2S_9 , $[\text{S}]=2$ M) electrolyte (Fig. 1b) at a rate of C/3 (1C = 1680 mA g^{-1} of S in the cathode) show two similar voltage plateaus: a higher one at 2.4 V and a lower one at 2.0 V. The initial discharge capacities in the polysulfide-free and -containing electrolytes are 980 mAh g^{-1} and 1460 mAh g^{-1} , respectively (based on S in the cathode).

As shown in Fig. 2, capacity retention is dramatically improved by using 10 μL of polysulfide-containing electrolyte with $[\text{S}]=2$ M. The discharge

capacity is stabilized at *c.a.* 1460 mAh g^{-1} in this electrolyte, while with polysulfide-free electrolyte the capacity decreases to below 480 mAh g^{-1} after only 50 cycles. The cell capacity is almost doubled in comparison to cells with polysulfide-free electrolyte.

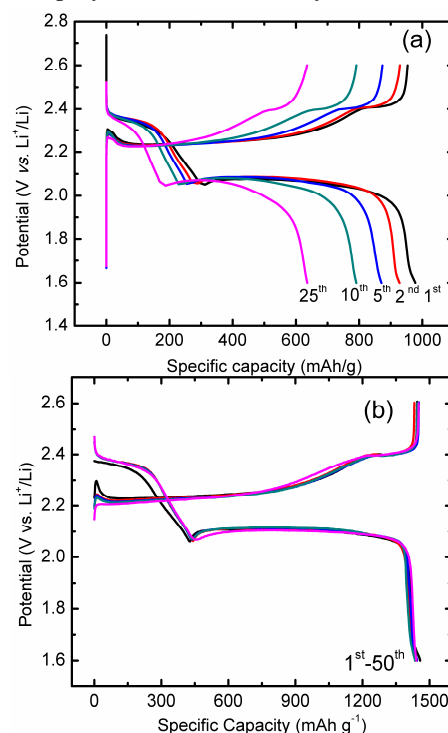


Figure 1. Voltage profiles at C/3 rate in (a) 10 μL of polysulfide-free and (b) 10 μL of polysulfide-containing (Li_2S_9 , $[\text{S}]=2$ M) electrolyte between 1.6 V and 2.6 V.

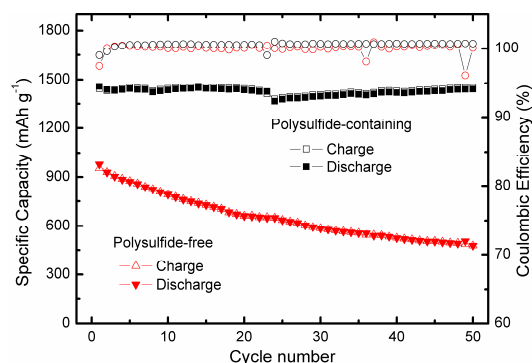


Figure 2. Cycling performance at C/3 rate in 10 μL of polysulfide-free and -containing (Li_2S_9 , $[\text{S}]=2$ M) electrolyte between 1.6 V and 2.6 V.

Our research also indicated that the concentration of sulfur species and the amount of electrolyte show significant effects on the performance of Li-S batteries, though performance is independent of polysulfide chain length.⁸ More results will be presented during the meeting.

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-EE0005475

1. J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.
2. P. G. Bruce, S. A. Freunberger, L. J. Hardwick and J. M. Tarascon, *Nature Mater.*, 2012, **11**, 19-29.
3. H. Yamin, A. Gorenshstein, J. Penciner, Y. Sternberg and E. Peled, *J. Electrochem. Soc.*, 1988, **135**, 1045-1048.
4. X. L. Ji, K. T. Lee and L. F. Nazar, *Nature Mater.*, 2009, **8**, 500-506.
5. S. R. Chen, Y. P. Zhai, G. L. Xu, Y. X. Jiang, D. Y. Zhao, J. T. Li, L. Huang and S. G. Sun, *Electrochim. Acta*, 2011, **56**, 9549-9555.
6. L. W. Ji, M. M. Rao, H. M. Zheng, L. Zhang, Y. C. Li, W. H. Duan, J. H. Guo, E. J. Cairns and Y. G. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 18522-18525.
7. Y. V. Mikhailik, 2008. U.S. Patent: 7,553,590.
8. S. R. Chen, F. Dai, M. L. Gordin, D. Wang, *RSC Adv.*, 2013, **3**, 3540-3543.