Lithium-Sulfur Batteries with Porous Carbon Interlayer Configurations

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Introduction

Entering a new era of green energy, several criteria such as cost, cycle life, safety, efficiency, energy, and power need to be considered in developing electrical energy storage systems for transportation and grid storage.[1] Lithium–sulfur batteries are one of the prospective candidates in this regard as sulfur offers a high theoretical capacity of 1675 mAh g^{-1} at a safer operating voltage of ~ 2.1 V and lower cost compared to the currently used oxide and phosphate cathodes. With this perspective, there is increasing interest in recent years in Li–S battery research. Development of a high capacity (> 800 mAh g^{-1}) Li–S system with long, acceptable cycle life will give this system a greater opportunity to be commercialized in the near future.

Based on the fact that porous carbon plays a dual role in providing electron pathways and serving as traps for dissolved polysulfide species,[2,3] we present here an insertion of various porous carbon papers between the separator and cathode disk to improve the electrochemical performance of Li–S cells.[4,5] This design can effectively decrease the resistance of cells, resulting in an enhancement of active material utilization. Additionally, the carbon interlayers with different architectures used in this study facilitate the absorption of soluble polysulfides shuttling in the electrolyte and make them available to be re-utilized even during long cycles. This bi-functional carbon interlayer can be treated as a second current collector for accommodating the migrating active material from sulfur cathodes. This novel approach not only simplifies the battery processing without elaborate synthesis of composites and surface chemistry modification, but also improves the capacity and cycle life, thereby promoting the practicality of Li–S batteries.

Experimental

The interlayer was prepared as a free-standing multiwall carbon nanotube (MWCNT) film or a roll-pressed mixture of micro-/meso- porous carbon and polytetrafluoroethylene binder at a 3:2 mass ratio. Sulfur cathode was fabricated by tape-casting the mixture of 70 wt. % precipitated sulfur, 20 wt. % of carbon black (Super P), and 10 wt. % of polyvinylidene fluoride (PVDF) binder onto an aluminum foil and dried in an air-oven for 24 h at 50 °C. CR2032 coin cells were assembled with the sulfur cathodes, prepared electrolyte, various prepared carbon interlayers, polypropylene separator, and lithium foil anode.

Results and Discussion

The battery configuration of a Li–S cell with a bi-functional carbon interlayer is displayed in Figure 1. The conductive carbon interlayer has to be placed between the separator and cathode in order to capture the migrating polysulfides (Li_2S_x) from the cathode during electrochemical reactions, but without contacting the lithium anode.

The cycling performance of the Li–S cell inserted with a microporous carbon paper (MCP) is exhibited in Figure 2. The cyclability at 1C rate retains over 1000 mAh g^{-1} after 100 cycles, converting a retention rate of 85% with an average Coulombic efficiency of 97.6%. The charge efficiency of the first two cycles is higher than 100% due to the re-utilization of the sulfur core in the cathode as the cell is cycled. The re-utilization of the inactive core of the active material is generally found in the Li–S system, especially at high C rates during the initial cycles. At a higher rate of 2C for long cycles, the cell with the MCP outputs 846 mAh g^{-1} and an average Coulombic efficiency of over 97.5% after 150 cycles.

Figure 3 exhibits the pore size distributions of the MCP samples, where all specimens have no obvious pores with a diameter over 5 nm. The microporous/small-mesoporous peak of the MCP almost vanishes after cycling, implying that the migrating active polysulfides might be captured and fill these pores during the electrochemical cycling. Also, improved battery performance was also obtained when using a free-standing MWCNT film as the interlayer. The MWCNT network suppresses the migration of polysulfides during cycling and enables the re-utilization of the trapped active material.

In summary, various carbon interlayers have been developed to substantially improve the cycle performance of Li–S batteries. The flexible carbon paper provides fine contact with the cathode surface, offering electron pathways through the insulating sulfur/lithium sulfide and accommodating the migrating polysulfide intermediates. Moreover, the cells involve only a novel cell configuration by inserting an interlayer without requiring the formation of sulfur–carbon or sulfur–polymer composites, leading to facile and low-cost manufacturing.

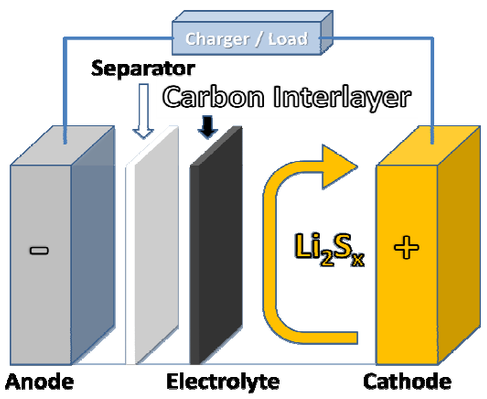

Fig. 1. Schematic configuration of a Li–S cell with a bi-functional carbon interlayer.

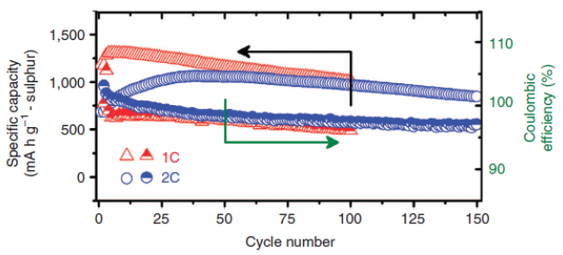

Fig. 2. Cycle life and Coulombic efficiency of the cell with a microporous carbon interlayer at 1C and 2C.

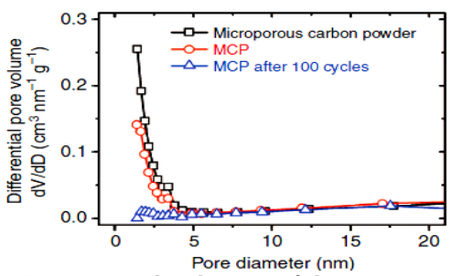

Fig. 3. Pore size distributions of the microporous carbon powder, MCP, and MCP as an interlayer in the Li–S cell at 1C rate after 100 cycles.

References

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