Insight into the Electrode Mechanism in Lithium-Sulfur Batteries with Ordered Microporous Carbon Confined Sulfur as Cathode

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Introduction

Sulfur is one of the most promising cathode candidates for next generation batteries due to high theoretical capacity (1675 mAh/g), natural abundance, low cost and environmental friendliness. However, the realization of rechargeable Li-S batteries suffers from low sulfur utilization and poor cycle life. Extensive efforts have been done to solve the shortages. Among them, the composites with sulfur embedded within conductive meso / micro-porous carbon framework have been proven promising. However, a precise principle how to choose proper electrolytes for various S cathodes with different supporting matrices and different morphologies is urgently needed, i.e., the criteria for electrolyte selection for Li-S batteries should be set up. Unfortunately, to our knowledge, hitherto no work has been reported on this issue.

In this work, we prepared a highly ordered microporous carbon and confined sulfur within it as cathode for investigating the electrochemical performances of S_{2-4} and S_8 in both ether-based and carbonate-based electrolytes. A preliminary electrolyte selection principle can be further proposed for Li-S batteries based on the experimental results.

Results and Discussion

Fig. 1 shows that the diffraction peaks of sulfur still exist in FDU/S-60, indicating that there is redundant sulfur outside the pores of the porous carbon, while FDU/S-40 shows only a broad amorphous peak, demonstrating that the sulfur on the carbon surface has almost been washed off, and the remanent sulfur is well confined within the micropores. From fig. 1 (inset), it can be seen that a certain amount of element sulfur adheres on the carbon particles in the FDU/S-60 sample, while for FDU/S-40, the composite particles almost have the same shape with the pure FDU carbon particles and no extra sulfur is observed.

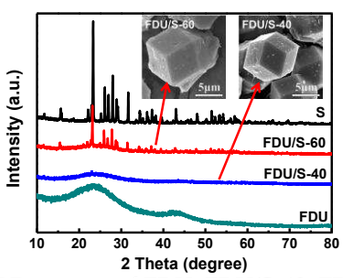

Fig. 1 XRD patterns of FDU, FDU/S-40, FDU/S-60, and S; inset: SEM images of FDU/S-60 and FDU/S-40.

Fig. 2 shows the electrochemical behaviors of FDU/S-60 and FDU/S-40 in two typical electrolytes, respectively. For the ether-based electrolyte (fig 2a–d), the discharge capacities of FDU/S-60 and FDU/S-40 are both higher than 900 mAh/g. The charge-discharge plateaus at different voltages correspond to different electrochemical reactions. For the carbonate-based electrolyte (fig 2e), the FDU/S-40 cathode shows almost the same discharge-charge capacity and plateaus as in the ether-based electrolyte, whereas the situation of FDU/S-60 is totally different. For FDU/S-60, the discharge capacity in the 2nd cycle decreases from 900 mAh/g in the ether-based electrolyte to less than 600 mAh/g in the carbonate-based electrolyte, and the plateaus at about 2.3 V and 2.0 V disappear. From the cycle performance comparison (fig. 2f), it is found that the combination of the small S_{2-4} molecules (FDU/S-40) and the carbonate-based electrolyte delivers better cyclability.

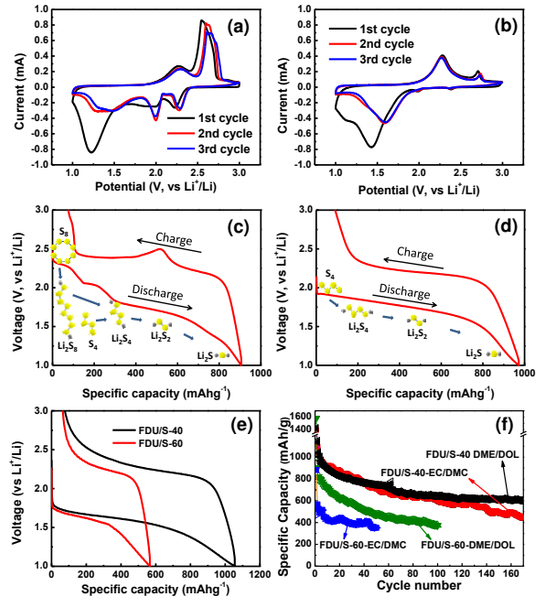

Fig. 2 CV curves and the 2nd charge-discharge profiles of (a, c) FDU/S-60 and (b, d) FDU/S-40 with ether-based DME/DOL electrolyte. (e)The 2nd charge-discharge profiles comparison of FDU/S-60 and FDU/S-40 with carbonate-based EC/DMC electrolyte. (f) The comparison of cycle performance with two kinds electrolytes at a current density of 500 mA/g.

Fig. 3 shows the typical cycle life of FDU/S-40 in the carbonate-based electrolyte. The specific capacity of FDU/S-40 is as high as 900 mAh/g after 280 cycles. This indicates that the carbonate-based electrolyte can match well with the sulfur-microporous carbon cathode materials, and promises an excellent electrochemical performance.

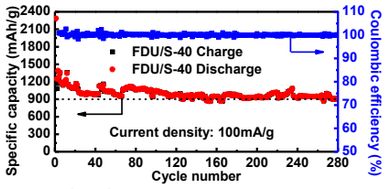

Fig. 3 cycle life of FDU/S-40 in the carbonate-based electrolyte of 1 M $LiPF_6$ in EC/DMC in the voltage range of 3.0-1.0 V vs Li^+/Li at current densities of 100 mA/g

In addition, our work proposes a simple strategy of electrolyte selection for sulfur cathode. The ether-based electrolyte is proper for open-type composite cathodes, and the carbonate-based electrolyte is only suitable for microporous structured sulfur composite cathodes.