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Improved Rate Performance of Lithium Sulfur Batteries by In-Situ Anchoring of Lithium Iodide in Carbon/Sulfur Cathode

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ABSTRACT

Lithium sulfur battery is one of the most cost-effective alternatives to meet the requirement of high energy density for power sources due to its high energy density and low cost. However, lithium sulfur battery still suffers from a rapid capacity fading and poor rate performance, which are mainly related to the shuttle effect of polysulfides during cycling and the insulating nature of sulfur as well as the reduced product of Li_2S or Li_2S_2. Here, we proposed an iodine-incorporated carbon/sulfur electrode to improve the rate performance of Li-S batteries. The resultant composite electrode exhibits good high-rate charge-discharge capability with a high discharge capacity of 479 mAh/g at 3C after 100 cycles. The excellent rate capability is mainly correlated to the iodine-doped carbon host with improved electronic conductivity, formation of lithium iodide (LiI) served as solid-state electrolyte in electrode during the first discharge process and the dissolution of iodine species into the electrolyte as additive for improving the ionic conductivity. This work offers an innovative, effective and facile method to ameliorate the electrochemical performance of lithium sulfur batteries.

1. Introduction

Nowadays, lithium ion batteries have been widely used as power sources for portable electronic devices and electric vehicles. However, lithium ion batteries suffer from a limited energy density mainly related to the current cathode materials with the practical specific capacity of no less than 200 mAh/g [1]. Lithium sulfur (Li-S) battery is a promising candidate for next generation electrochemical energy storage systems on account of its high theoretical specific energy of 2600 Wh/kg based on the sulfur with a high theoretical capacity of 1675 mAh/g as cathode material and lithium metal as anode [2,3]. Nevertheless, besides the safety issue related to lithium metal anode, the practical application of Li-S battery is still hindered by several aspects including the poor conductivity inside electrode caused by the insulating nature of sulfur and lithium sulfide, volume changes of sulfur and lithium metal electrode, the dissolution and "shuttle effect" of lithium polysulfides during cycling [4]. To date, several strategies have been employed to tackle these issues and improve the electrochemical performance of Li-S battery, such as modification of sulfur cathode materials [5–7], optimization of alternative electrolytes [8–10] and electrolyte additives [11–13]. Considering the electrically insulating nature of sulfur, novel conductive architectures encapsulating sulfur is proposed to enhance the cycle performance of Li-S batteries. Based on the fact that the carbon host possesses good electrical conductivity and mechanical properties, porous carbon/sulfur composite has been widely investigated as cathode materials for lithium sulfur batteries. In this case, the electrical conductivity inside the sulfur/carbon electrode can be improved when the active sulfur material is encapsulated into conductive carbon framework intimately. Nazar et al. [6] reported the CMK-3/sulfur as cathode material with a high utilization of the active sulfur material, where the porous carbon framework served as the mini-electrochemical reaction chamber and provided the intimate contact with the insulating sulfur and discharge product of lithium polysulfides. Inspired by this work, many carbon-based hosts including microporous carbon [14,15], macroporous carbon [16], graphene [7,17–20], carbon nanotubes [21,22], carbon spheres [23] or hollow carbon spheres [24], carbon Sponge [25], carbon derived from biomass [26] and so on, have been developed as the frameworks for the sulfur/carbon cathode materials. Furthermore, experimental and theoretical studies have also shown that the electronic electrical conductivity of carbon materials can be modified via heteroatom doping (e.g., N, P, B and I) by increasing

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the density of free charge carriers. The iodine-doped carbon nanotube has been proved to be of superior electrical conductivity [27,28], which motivates us to exploit porous carbon frameworks with high electrical conductivity.

Recently, some investigation involving the preparation of carbon materials doped with heteroatom, such as nitrogen [29,30], boron [31], sulfur [32,33], has been reported for Li-S batteries, and doping with heteroatoms for the carbon materials shows great promise in improving electronic conductivity and strengthening the interaction between polysulfides and the heteroatom-doped carbon hosts. Furthermore, as we all know, the solid state sulfur and its reductive products of Li_2S or Li_2S_2, which are both electronic and ionic insulators, reproduce as the segregated large particles inside the carbon host at the end of charge and discharge for traditional liquid Li-S batteries. In fact, both the ionic and electronic channels are important to ensure the high rate performance and good cyclic stability of Li-S batteries. Extensive research on enhancing electronic conductivity in electrode have been presented previously, but unfortunately, few work focused on the effect of ionic conductivity in the sulfur/carbon electrode on the electrochemical performance of Li-S battery beyond the advantages of the porosity of the carbon framework and the mobility of the organic electrolyte. Therefore, exploring sulfur-based cathode materials with high ionic and electronic conductivity may be an effective way to enhance electrochemical performance of lithium sulfur batteries. LiI with the inherent ionic conductivity of LiI is 10^{-7} S/cm at 25 °C has been identified as a promising electrolyte additive for Li-S battery. Wu et al. [34] reported that LiI electrolyte additive can induce the formation of Li-ion-permeable protective coatings on both positive and negative electrodes, preventing the dissolution of polysulfides on the cathode and the reduction of polysulfides on the lithium anode. In addition, LiI is the reductive product of I_2 in lithium-iodine battery, and the iodine–carbon composites also have been

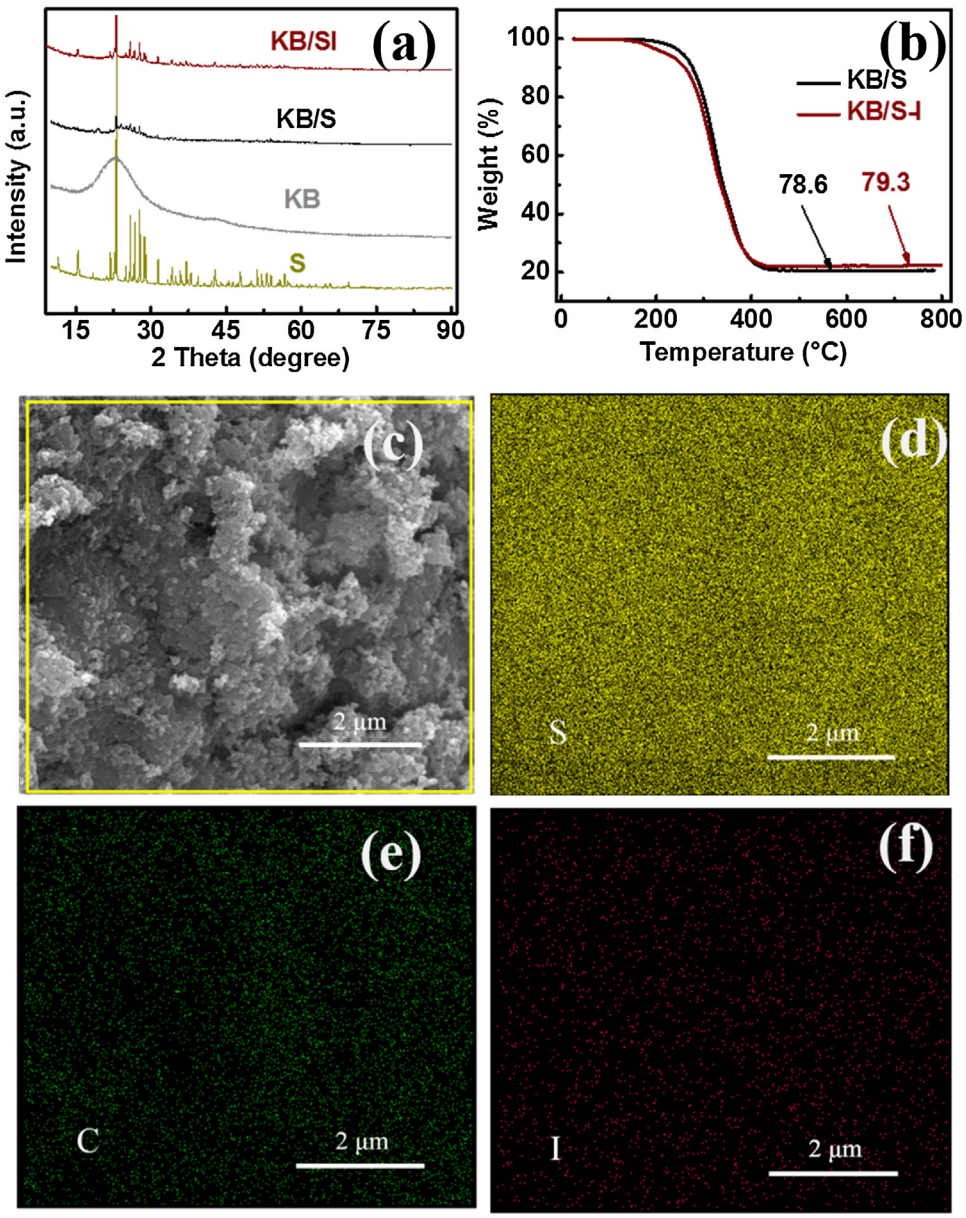

Fig. 1. a) X-ray diffraction patterns of I-modified KB/S-I, KB/S, KB and sulfur; b) Thermogravimetric analysis curves of the composites; c) SEM image and corresponding sulfur (d), carbon (e)and iodine (f) EDS elemental mapping of the I-modified KB/S-I.