Electrochimica Acta 200 (2016) 197–203

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

High performance lithium-sulfur batteries with a facile and effective dual functional separator

Zhangxiang Hao, Lixia Yuan*, Zhen Li, Jing Liu, Jingwei Xiang, Chao Wu, Rui Zeng, Yunhui Huang*

State Key Laboratory of Material Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form 21 March 2016
Accepted 26 March 2016
Available online 29 March 2016

Keywords:
Nafion/super P-modified separator
sulfur cathode
long-term cyclability
Li-S batteries

ABSTRACT

Lithium-sulfur (Li-S) batteries stand as an important candidate for next-generation high-energy secondary batteries due to its high specific capacity, low cost and environmental friendliness. However, practical application of Li-S batteries suffers from low rechargeability, poor rate capability and cycling instability of sulfur cathode, which can be mainly ascribed to the poor conductivity of sulfur and the dissolution of the intermediate polysulfides generated during discharge-charge cycles. In this work, a Nafion/super P-modified dual functional separator is designed to improve the long-term cycle stability and rate capability of the pure sulfur cathode. The electrostatic repulsion between the SO_3^- groups and the dissolved negative S_n^{2-} ions, and the trap and reutilizing effect of super P for polysulfides, provide double insurance to confine the polysulfides within the cathode side, leading to great improvement in both reversible capacity and cycling stability of the sulfur cathode as compared to the battery with pristine Celgard separator. With such dual functional separator, a simple elemental sulfur cathode with 70% S content delivers a high initial discharge capacity of 1087 mAh g^{-1} at 0.1C and a long-term cyclability with only 0.22% capacity fade per cycle over 250 cycles at 0.5C.

1. Introduction

Li-S batteries provide electricity by reducing elemental sulfur to Li_2S during discharge [1–4]. The two-electrons redox reaction brings a high theoretical capacity of 1672 Ah kg^{-1} and a high theoretical energy density of 2600 Wh kg^{-1}, almost 6 times larger than those of current lithium-ion battery [5–7]. As one of the most potential candidates for next-generation high-energy rechargeable batteries, the Li-S battery has gained increasing attention in recent years [8,9]. However, the commercial application of Li-S batteries is largely plagued by the low utilization of active material and the short cycling lifespan of sulfur cathode, which are mainly caused by the insulating nature of elemental sulfur and the diffusion of the dissolved intermediate long-chain polysulfides in organic electrolyte during charge-discharge process. In addition, the density difference between sulfur and the final discharge product (Li_2S) brings a volume expansion of 80% during lithiation process, which may cause structure collapse of the cathode and thus result in the deterioration of battery performances. Besides, the type and quantity of polysulfides vary with the state of charge-discharge, and the electrolyte composition changes accordingly, leading to an uncertainty of the solid electrolyte interface (SEI) on Li anode surface which is also responsible for the performance degradation in Li-S batteries.

Many efforts have been done to solve the problems. At current stage, the main strategy to solve the problems is to design various composite nanostructures. Various nanostructured carbon materials, like meso/microporous carbon spheres [10–12], activated carbon nanofibers [13–15], carbon nanotubes [16–20] and graphenes [21–26], have been widely utilized as conductive hosts to encapsulate elemental sulfur and cage polysulfides within the porous frameworks. More recently, a new strategy, trapping polysulfides within the cathode via chemical process, was reported. Some metal oxides (MnO_2, Ti_4O_7) [27–31], MXene nanosheets (Ti_2C) [32], metal organic frameworks (MOFs) [33–36], have been proved to be able to immobilize polysulfides via chemical interaction.

Although great progress has been achieved, it is still difficult to prevent the loss of dissolved S_n^{2-} completely. The conversion processes from elemental sulfur (solid) to dissolved intermediate Li_2S_n (liquid) and from Li_2S_n (liquid) to the final reduction products

---

* Corresponding authors. Tel.: +86 27 87558241.
E-mail addresses: yuanlixia@hust.edu.cn (L. Yuan), huangyh@hust.edu.cn (Y. Huang).

http://dx.doi.org/10.1016/j.electacta.2016.03.166
0013-4686/

Li_2S_2/Li_2S (solid) accompany with the liquid electrolyte's penetration in and out of the matrix. Despite the physical/chemical interaction between S_n^{2-} and the host, a certain amount of S_n^{2-} ions will escape from the "physical and/or chemical cage" inevitably along with the repeated "solid → liquid → solid" phase change. So, it is very difficult to totally immobilize sulfur species via the isolated structure design for cathode materials. In addition, the fabrication of the nanostructured porous carbon hosts and mesoporous oxides additives usually demands elaborate procedures, involving high-temperature process and complicated template-deleting process. These requirements can largely limit the mass product ability of the sulfur composite cathode materials.

On the other hand, battery is a complicated system for the cathode, anode and electrolyte interact with each other. The interactions in the Li-S system are much stronger and more complicated than other lithium battery systems due to the soluble intermediate polysulfides. Compared with the isolated structure design of sulfur cathode materials, the modification of electrolyte [37] or developing functional membranes [38,39] may provide more effective approach for improving the electrochemical performance of Li-S batteries. For example, $LiNO_3$ can form a stable passivation film on the surface of the lithium anode and therefore effectively suppress the redox shuttle effect of polysulfides and maintain a high Coulombic efficiency of Li-S batteries [40–43]. Now $LiNO_3$ has been widely employed as electrolyte additive in the Li-S system. The solvent-in-salt electrolyte system shows great competence in suppressing lithium dendrite growth in the metallic lithium anode and inhibiting lithium polysulfide dissolution [37]. A lithiated Nafion ionomer membrane instead of common membrane (Celgard 2400) was first reported as functional separator for Li-S batteries in 2012, which can act as an electrostatic shield for polysulfide anions, and confine the polysulfides on the cathode side because the SO_3^- groups-coated channels allow Li^+ ion hopping but reject the negative S_n^{2-} ions due to Coulombic interactions [44]. In addition to modifying the membrane, a similar electrostatic shield could also be established via Nafion-coated sulfur cathode [45–47] or Nafion-coated separator to constrain the polysulfides within the cathode side [48]. Manthiram's group also reported a composite cathode structure containing AC-CNF current collector filled with lithium polysulfides and Nafion membrane to enhance the electrochemical performance of Li-S battery [49]. More recently, a kind of ternary-Layered separator was prepared via integrating polypropylene, graphene oxide and Nafion [50] to retard the shuttle of polysulfides for Li-S batteries.

In this work, a novel dual-functional separator was developed for the Li-S battery via a simple coating process. A mixture of Nafion and super P was coated on the cathode side. In this system, the SO_3^- groups in Nafion offers an electrostatic shield to block the polysulfides, while super P, which is adsorptive and electronic conductive, provides physical trap to obstruct the diffusion of polysulfides and meanwhile acts as an accessorial current collector to further reutilize the diffused polysulfides. Both of them form double insurance to confine the polysulfides within the cathode side. With this modified separator, a sulfur cathode prepared by commercial elemental sulfur with 70 wt.% sulfur content, reveals a high initial reversible capacity of 1087 mAh g^{-1} at 0.1 C and a long-term charge/discharge process of 250 cycles at 0.5 C, with a cycle decay value of 0.22% per cycle.

2. Experimental

2.1. Fabrication of Nafion/super P-modified separator and pure sulfur cathode

A Nafion/super P slurry was prepared by mixing 45 wt.% super P, 45 wt.% Nafion solution (5 wt.%, Sigma–Aldrich), 5 wt.% carboxyl methyl cellulose sodium salt (NaCMC), and 5 wt.% styrene butadiene rubber (SBR) in deionized water to form homogeneous slurry. This slurry was coated on one side of commercial Celgard separator by a glass rod, and then dried in a vacuum oven at 80 °C for 6 h. After drying, the Nafion/super P-modified separator was cut into wafers with diameter of 18 mm for cell assembly. The

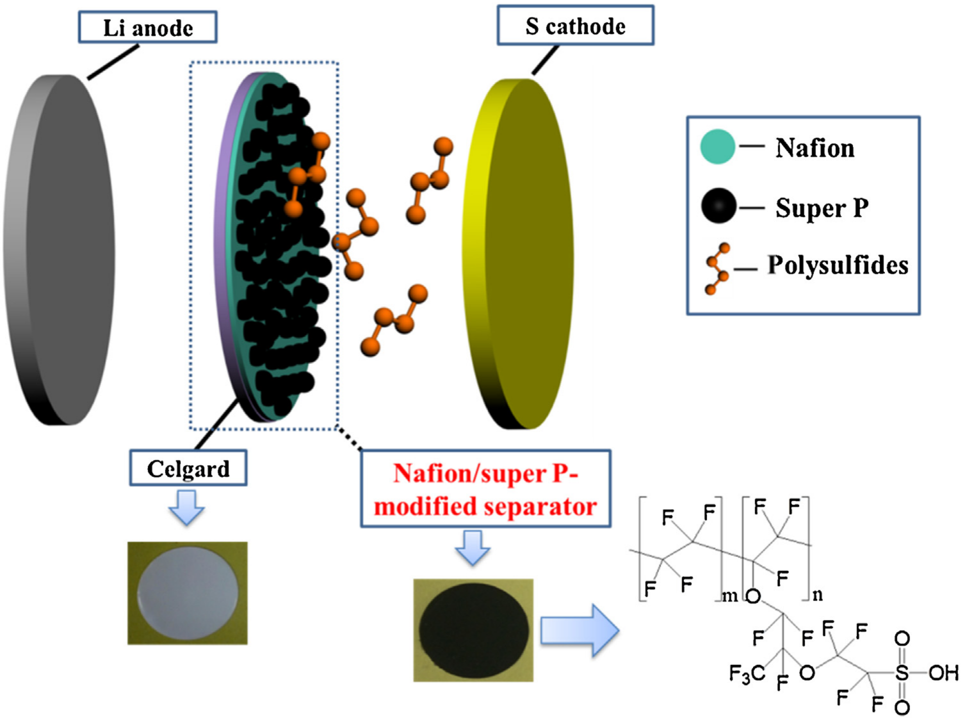

Fig. 1. Schematic illustration for the Li-S battery with a Nafion/super P-modified separator.