

RAPID COMMUNICATION

Reactivation of dissolved polysulfides in Li-S batteries based on atomic layer deposition of Al_2O_3 in nanoporous carbon cloth



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Received 9 March 2013; received in revised form 23 April 2013; accepted 6 May 2013

Available online 14 May 2013

KEYWORDS

Al_2O_3 ;
Atomic layer deposition;
Li-S battery;
Porous carbons;
Sulfur chemistry

Abstract

This work demonstrates the effect of atomic layer deposited (ALD) Al_2O_3 on the reactivation of dissolved polysulfides in Li-S batteries. A 0.5 nm thick layer of Al_2O_3 is conformally coated onto highly porous carbon cloth by ALD, and then assembled in a Li-S battery between the sulfur cathode and the anode side (separator and Li anode) to function as a reactivation component. Compared to half cells with no ALD treatment, the ultrathin Al_2O_3 coating increases the specific discharge capacity by 25% from 907 to 1136 mA h/g at the 1st cycle, and by 114% from 358 to 766 mA h/g at the 40th cycle. Thus the ALD- Al_2O_3 improves the initial specific capacity and stabilizes the cycle life remarkably. Scanning electron microscopy and energy-dispersive X-ray spectroscopy results indicate that the ALD- Al_2O_3 coated carbon cloth sorbs (adsorbs/absorbs) more dissolved sulfur species from the electrolyte. Potential mechanisms for the improved sorption properties are proposed. The combination of an ultrathin ALD-oxide coating with highly porous carbons presents a new strategy to improve the performance of Li-S batteries.

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Introduction

Sulfur, an earth-abundant material, is one of the largest by-products of the petroleum industry [1,2]. As such, there is an

emerging research field interested in finding novel applications of these sulfur wastes [3]. In the area of energy storage, sulfur has been intensely studied as a promising cathode material for lithium ion batteries (LIBs). Sulfur is a low cost, non-toxic material with a high theoretical specific energy density, 3-5 times higher than current intercalation chemistry-based LIBs [4]. These properties indicate a large potential market for sulfur as a cathode material in the near future [5]. Sulfur

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and lithium polysulfides (intermediates in Li-S batteries), however, are electronic insulators and high-order lithium polysulfides (Li_2S_x , $3 \leq x \leq 8$) readily dissolve in liquid electrolytes. Particularly, the dissolution-associated behaviors of the intermediate polysulfides reduce the amount of active sulfur available at the cathode. Also, the dissolved polysulfides transport through the electrolyte and dissipate energy at the lithium anode *via* direct chemical reactions, which triggers the so-called shuttle effect in Li-S batteries [6]. As a result, Li-S batteries suffer from low practical capacity and poor cycling stability [7]. Eliminating the sulfur dissolution problem is the primary challenge for future applications of Li-S batteries.

A lot of strategies in the area have been done to address the problem. Except for the passivation of lithium anodes with LiNO_3 [8-10] and alteration of electrolytes, [11-13] the majority of efforts have been devoted to engineering cathode composites. The most common tactic is to confine sulfur within various porous carbons, including mesoporous carbons, [14] microporous carbons [15], bimodal porous carbons, [16,17] hierarchical porous carbons, [18] hollow carbons, [19,20] carbon nanotube (CNT)/porous carbons, [21] and graphene/porous carbons [22]. Confinement within various conductive polymer/carbon matrices, such as PEDOT:PSS [23] and polyaniline [24] has also been explored. To further enhance the restriction of polysulfide dissolution, oxide nanoparticles ($\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$, [7] Al_2O_3 , [25] $\text{Mg}_{0.8}\text{Cu}_{0.2}\text{O}$ [26]) and porous oxide nanoparticles (SiO_2 , [27] TiO_2 [28]) are added as sorption reagents of polysulfides. Another example is to restrict sulfur into polyacrylonitrile structures for cathode composites [29]. All of these technologies were developed to confine the sulfur within the cathodes. The volume fluctuations in the discharge/charge process, however, inevitably affect the mechanical strength and morphology, [30] and thereby the validity of *in-situ* confinement.

Recently, the unique surface coating technique of atomic layer deposition (ALD) has gained attention for LIB fabrication [31]. Even on complicated 3-D nanostructures, ALD enables a conformal coating with precise thickness control at the atomic scale [32,33]. Most recently, the application of Al_2O_3 coatings on LiCoO_2 , [34,35] $\text{Li}[\text{Li}_{0.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, [36] and natural

graphite electrodes [37] by ALD greatly improved LIB cycling performance. It is suggested that the Al_2O_3 layer modifies electrolyte-electrode interface and prevents the active materials from dissolving.

In this work, we utilize an ALD- Al_2O_3 coating on porous carbon to solve the dissolution problem through a strategy of *ex-situ* collection (adsorption/absorption) and reactivation of the dissolved polysulfides in electrolyte. *Ex-situ* collection here refers to recovering the lost polysulfides from the electrolyte with a separate ALD layer, rather than confining sulfur species in an S-loading layer *in-situ*. Reactivation refers to the recovery of electrochemical activity of the collected sulfides given that the ultrathin ALD layer (<0.5 nm) is conductive. Fig. 1a illustrates a general configuration of Li-S batteries based on this strategy. Specifically, we employ a porous activated carbon cloth (ACC) as a basic reactivation layer. In the literature, nanosized Al_2O_3 particles have been shown to exhibit polysulfide adsorption in sulfur cathodes [25]. To enhance the sorption properties, a 0.5 nm thick ALD coating of Al_2O_3 is conformally deposited on the pore surfaces of the ACC fibers (Al_2O_3 -ACC). The porous structure and the electrical conductivity of the ACC are expected to be maintained in the Al_2O_3 -ACC samples, and the resulting Al_2O_3 -ACC is expected to collect and reactivate more polysulfides than bare ACC under the same conditions (Fig. 1b). Recently, Nazar and co-workers utilized surface-initiated growth of thin oxide coatings directly onto modified mesoporous carbon-sulfur structures, [38] and Manthiram and Su inserted a CNT film interlayer to dramatically improve Li-S battery behavior [39,40]. The focus of our work is to understand how the combination of ultrathin ALD- Al_2O_3 with porous carbon improves Li-S battery performance.

Experimental section

Materials

Sulfur powder, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), and tetraethylene glycol dimethyl ether (TEGDME)

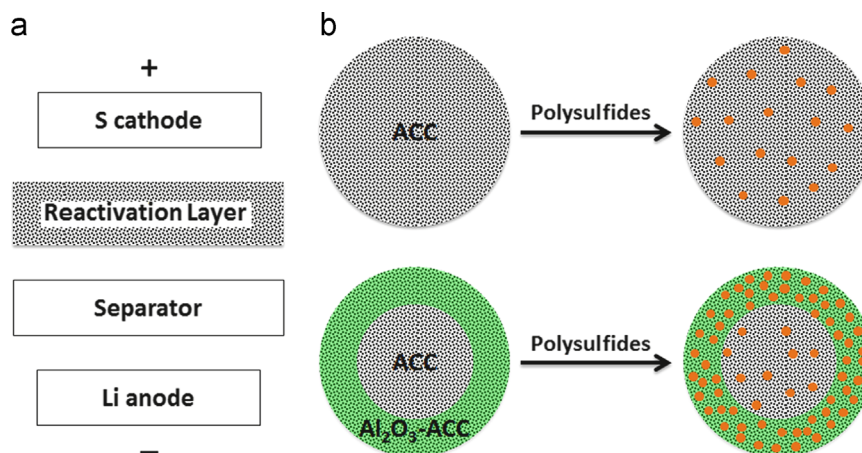


Figure 1 (a) Schematic of the Li-S battery with a conductive, porous carbon reactivation layer inserted between the sulfur cathode and separator. This reactivation layer functions to collect and reactivate the intermediate polysulfides (not shown) dissolved in electrolyte. (b) Illustrated cross-sections of ACC and ALD Al_2O_3 coated ACC (Al_2O_3 -ACC) before and after collection of polysulfides in electrolyte. The ALD- Al_2O_3 coated ACC fiber maintains the highly porous structure and electrical conductivity while improving collection (adsorption/absorption) and reactivation of polysulfides.

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