



# Nano-hydroxyapatite as an Efficient Polysulfide Absorbent for High-performance Li-S Batteries



Naiqiang Liu<sup>a</sup>, Fei Ai<sup>a</sup>, Weikun Wang<sup>b</sup>, Hongyuan Shao<sup>a</sup>, Hao Zhang<sup>b</sup>, Anbang Wang<sup>b</sup>, Zhichuan J. Xu<sup>c,\*</sup>, Yaqin Huang<sup>a,\*</sup>

<sup>a</sup> Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, 15 Beisanhuan East Road, Beijing 100029, China

<sup>b</sup> Military Power Sources Research and Development Center, Research Institute of Chemical Defense, 35 Huayuan North Road, Beijing 100191, China

<sup>c</sup> School of Materials Science & Engineering, Nanyang Technological University, 50 Nanyang Avenue Block, 639798, Singapore

## ARTICLE INFO

### Article history:

Received 17 July 2016

Received in revised form 13 August 2016

Accepted 18 August 2016

Available online 19 August 2016

### Keywords:

nano-hydroxyapatite  
polysulfides-absorbent  
Li-S batteries  
additives  
modified separator

## ABSTRACT

Lithium-sulfur (Li-S) battery is regarded as one of the most promising candidates for developing advanced energy storage system, but the polysulfide shuttle effect remains the biggest obstacle for its practical application. In this work, nano-hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) was used as an additive in the sulfur cathode and carbon-coated separator to prevent the polysulfide shuttle effect and thus to achieve the high performance. The sulfur cathode with nano-hydroxyapatite exhibited a higher reversible capacity and a more stable cycling performance than that of the pristine sulfur cathode. The improved capacity retention from 58% (100th) to 73% (200th) after introducing nano-hydroxyapatite into the sulfur cathode confirmed its strong polysulfide absorption ability. Furthermore, a nano-hydroxyapatite modified separator was developed to suppress the polysulfide shuttle effect and to facilitate the reutilization of sulfur species. The nano-hydroxyapatite particles served as polysulfide absorbents to bind polysulfides and suppress their diffusion to the anode. The batteries assembled with this separator exhibited a high reversible capacity of  $886 \text{ mAh g}^{-1}$  at 0.1C and  $718 \text{ mAh g}^{-1}$  at 0.5C after 200 cycles, with a low capacity fading of  $\sim 0.10\text{--}0.11\%$  per-cycle. At the highest sulfur loading of  $4.5 \text{ mg cm}^{-2}$  used for practical applications, the reversible areal capacity was much higher than the areal capacity ( $4 \text{ mAh cm}^{-2}$ ) of commercial lithium-ion batteries. Therefore, the strategy using nano-hydroxyapatite as polysulfide absorbent shows great potential for solving the polysulfide shuttle problem and developing high performance Li-S batteries.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Lithium-sulfur (Li-S) batteries are one of the most promising candidates for developing advanced energy storage systems, owing to their high theoretical specific capacity of  $1672 \text{ mAh g}^{-1}$  and the natural abundance and environment benignity of sulfur [1,2]. Despite these advantages, the commercialization of Li-S batteries has been hampered by their fast capacity fading and short lifespan [3–7]. Moreover, the insulating nature of sulfur and the final discharge product ( $\text{Li}_2\text{S}$ ) allows only limited utilization of the active material [8]. In particular, lithium polysulfide intermediate products are soluble in ether-based electrolytes, and during discharge/charge, the dissolved intermediates diffuse to the anode

side to be reduced and then shuttle back to the cathode, thus creating a polysulfide shuttle effect. This parasitic reaction continuously occurs in the cell, resulting in self-discharge, low coulombic efficiency, active material loss, and rapid capacity fading [9]. As a result, the polysulfide shuttle is one of the major hurdles that limits the practical realization of Li-S batteries; other hurdles include a low sulfur utilization ratio, high volume expansion, and lithium anode degradation [10]. To solve the polysulfide shuttle problem, many approaches have been used. Carbonaceous materials, including porous carbon [11], reduced graphene oxide [12–14], carbon nanotubes [15,16], and conductive polymer [17] have been developed to serve as the sulfur hosts and to suppress the diffusion of polysulfides. However, encapsulating sulfur within carbonaceous materials can decrease the dissolution/migration of polysulfides only in the short term, owing to the weak physical interactions between the carbon host material and lithium polysulfides. Therefore, strong interactions are required to effectively trap the polysulfides in Li-S batteries [18].

\* Corresponding author. Tel.: +86 10 6443 8266; fax: +86 10 6443 8266.  
E-mail addresses: [xuzc@ntu.edu.sg](mailto:xuzc@ntu.edu.sg) (Z.J. Xu), [huangyq@mail.buct.edu.cn](mailto:huangyq@mail.buct.edu.cn) (Y. Huang).

Recently, graphene modified with different functional groups and heteroatom-doped carbonaceous materials have demonstrated anchoring of lithium polysulfides via strong affinitive interactions [19–22]. Moreover, many additional agents, including hydrophilic polymer and polar host oxide materials such as PEG [23], PVP [24],  $\text{TiO}_2$  [25],  $\text{Ti}_4\text{O}_7$  [26], and  $\text{MnO}_2$  [27] in the sulfur cathodes, have been found to effectively confine the polysulfides and improve the electrochemical performance of Li-S batteries.

In this study, we investigated the use of nano-hydroxyapatite (HA,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) as an additive to solve the “polysulfide shuttle” problem in Li-S batteries. HA is the main mineral constituent of bones and teeth and has outstanding biocompatibility [28]. More importantly, HA shows a high adsorption capacity and a strong binding affinity to some organic compounds, and it has been used as a sorbent for removal of heavy metal ions from wastewater [29]. The presence of the  $-\text{OH}$  group in the crystal lattice, the  $-\text{P}=\text{O}$  bond in phosphate, and the high surface energy of nano-HA afford stronger interactions for the enhanced absorption of polysulfides [30,31]. The Li-S batteries with nano-HA as an additive in their cathodes and carbon-coated separator exhibited better capacity retention and higher reversible capacity. The experimental results demonstrated strong affinitive interactions between nano-HA and polysulfides. Moreover, the high sulfur loading cathode ( $4.5 \text{ mg cm}^{-2}$ ) with the nano-HA-modified separator exhibited better electrochemical performance in practical applications. This study provides a new type of absorbent to trap the polysulfides within the cathodes in Li-S batteries.

## 2. Materials and Methods

### 2.1. Materials

Sublimed sulfur (99.5%, analytical grade, Beijing Yili. Corp., China) and acetylene black (AB, Jinpu. Corp., China) powders were

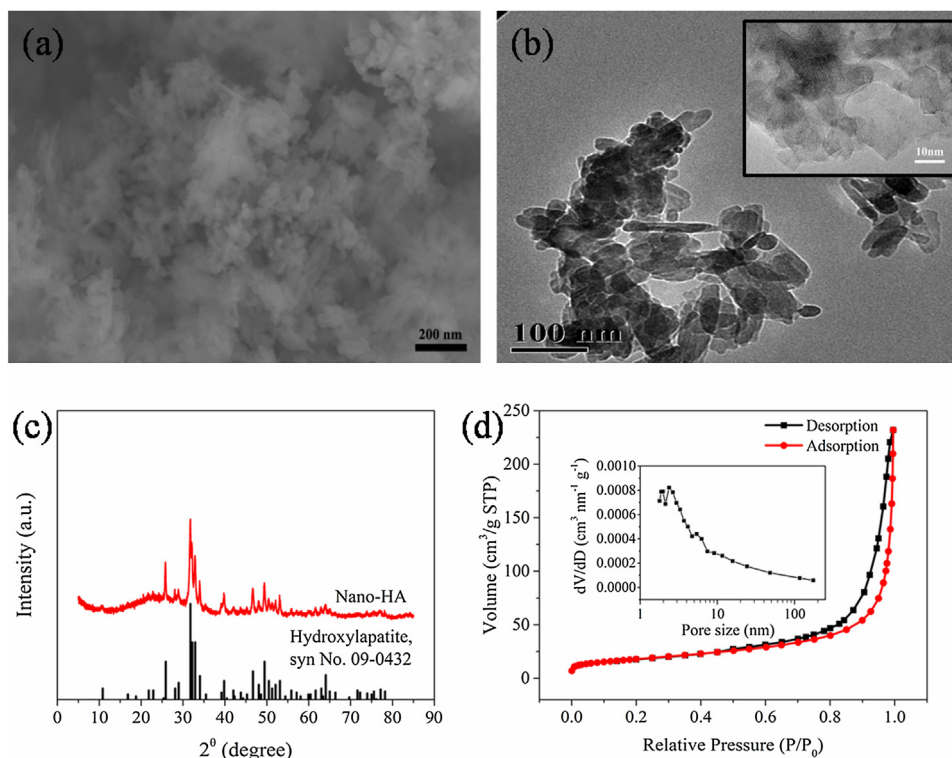
dried at  $60^\circ\text{C}$  for 10 h under vacuum before use. Nano-HA ( $\sim 20 \text{ nm}$ ) was purchased from Beijing DK Nano Technology Co., LTD. PVP was purchased from Sigma-Aldrich Inc. Gelatin (160 Bloom, type B) was derived from bovine bones. A polypropylene film (Celgard 2400) was used as a pristine PP separator. The electrolyte was a mixture of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Beijing Chemical Reagent Research Institute) and 0.4 M  $\text{LiNO}_3$  dissolved in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v:v, Beijing Chemical Reagent Research Institute).

### 2.2. Cathode preparation

The pristine sulfur cathode was prepared by mixing sulfur, AB, and PVP at a weight ratio of 60:30:10. The sulfur cathode with nano-HA (HA sulfur cathode) was prepared by adding nano-HA (10 wt% sulfur+AB+PVP in the cathode). Then, both the well-mixed slurries were coated onto the carbon-coated Al foils by using a doctor blade and subjected to vacuum drying at  $60^\circ\text{C}$  for 10 h. The sulfur loading in the cathodes varied from 2.0 to  $4.5 \text{ mg cm}^{-2}$ . The reference HA cathode was also prepared under the same conditions by using a well-mixed slurry of nano-HA, AB, and PVP at a weight ratio of 50:40:10.

### 2.3. Preparation of the nano-HA modified separator

The slurry for the nano-HA-modified separator (HA separator) was prepared by mixing AB with nano-HA (8:2 by weight), and then the mixture was stirring with the gelatin solution at a ratio of 80:20 by weight for 12 h. The obtained slurry was coated onto one side of a Celgard PP separator using a doctor blade and then vacuum-dried at  $60^\circ\text{C}$  for 10 h. The amount of the coating layer was  $0.5 \text{ mg cm}^{-2}$ .



**Fig. 1.** (a) SEM image and (b) TEM image of nano-HA. (c) XRD patterns of nano-HA particles. (d) BET isotherm curve and (inset) pore size distribution curves of nano-HA (BJH method).

Download English Version:

<https://daneshyari.com/en/article/6473111>

Download Persian Version:

<https://daneshyari.com/article/6473111>

[Daneshyari.com](https://daneshyari.com)