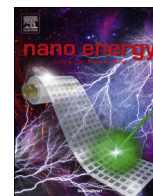




ELSEVIER

Contents lists available at ScienceDirect

Nano Energy

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

Li₂S nano spheres anchored to single-layered graphene as a high-performance cathode material for lithium/sulfur cells

Dan Sun^{a,b,c}, Yoon Hwa^{a,b}, Yue Shen^c, Yunhui Huang^c, Elton J. Cairns^{a,b,*}

^a Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States

^b Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

^c State Key Laboratory of Material Processing and Die & Mold Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan, Hubei 430074, China

ARTICLE INFO

Article history:

Received 27 March 2016

Received in revised form

13 May 2016

Accepted 20 May 2016

Available online 24 May 2016

Keywords:

Lithium batteries

Energy storage

Sulfur

Lithium sulfide

Graphene

Carbon coating

ABSTRACT

Fully lithiated lithium sulfide (Li₂S) has become a promising cathode material for Li/S cells due to its high theoretic capacity (1166 mA h g⁻¹) and specific energy (2600 W h kg⁻¹). However, low utilization of sulfur and poor rate capability still hinder the practical application of Li/S cells. In this paper, a carbon coated Li₂S/graphene composite (Li₂S/G@C) was developed by incorporating Li₂S nano spheres with single-layered graphene and further forming a durable protective carbon layer on the surface of the Li₂S particles using a facile CVD method. The high rate capability and remarkable cycle life of the Li₂S/G@C cathode were demonstrated, which was mainly attributed to the unique structure of the Li₂S/G@C that can significantly improve not only the electrical conductivity, but also the mechanical stability of the sulfur cathode.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

With increasing numbers of vehicles and growing demands on fossil energy in the past several decades, the coupled resource depletion and critical environmental pollution have raised an urgent need for alternatives to fossil fuels and combustion engines. The utilization of intermittent renewable energy such as wind and solar power, have attracted tremendous attention and provided an ecologically friendly and sustainable solution to meet the exponentially increasing demand for energy. Thus, high specific energy rechargeable battery systems of low-cost for energy storage are essential. Among the many candidates, the lithium-ion battery (LIB) is considered as “state-of-the-art” and has been used for portable devices and electric vehicles [1–7]. However, the traditional LIB seems to be insufficient for practical application in emerging markets due to the limited specific energy of the cell, which indicates that remarkable developments are necessary for applications such as electric vehicles [8–10].

Lithium/sulfur(Li/S) cells have been investigated since the 1960s and have drawn tremendous attention in recent years due to its rather high theoretical capacity of 1675 mA h g⁻¹ (S₈ + 16Li

→ 8Li₂S) and specific energy of 2600 W h kg⁻¹, indicating a superior energy storage capability. Furthermore, sulfur, which is ubiquitous in nature, is environmentally benign and low-cost. [4,8–15] Li/S cells have become one of the most promising rechargeable cell systems, showing great potential in meeting the rigorous needs for electrical vehicles and grid-scale stationary storage. Despite their advantages, Li/S cells still are affected by some intrinsic drawbacks. The dissolution of lithium polysulfides into organic liquid electrolytes and its “shuttle effect” together with mechanical degradation of the sulfur cathode (caused by severe volume change of sulfur particles (up to 80%) during cycling) limits the Li/S cell lifetime, meanwhile, the electrically insulating nature of sulfur and Li₂S causes sluggish reaction kinetics, resulting in low electrochemical utilization of the active material and poor rate capability [16,17]. As a result of efforts to address these issues significant improvements have been made in recent years by coupling sulfur to various carbon materials (e.g., graphene, graphene oxide (GO), and carbon fibers), polymers (e.g., polyethylene glycol (PEG), polypyrrole (PPY), polyacrylonitrile (PAN)) and transition metal oxides with novel hierarchical and core-shell configurations to overcome the drawbacks of the sulfur cathode [4,18–29]. In addition, another difficulty of the Li/S cells is the use of a metallic lithium anode, which is associated with dendrite formation on the surface of the Li metal anode caused by the inhomogeneous current distribution during cycling, leading to serious safety hazards and cell shorting [30–32].

* Corresponding author at: Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States.

E-mail address: ejcairns@lbl.gov (E.J. Cairns).

Fully lithiated lithium sulfide (Li_2S) with a theoretical specific capacity of 1169 mA h g^{-1} Li_2S has become a more desirable cathode material for the Li/S cell due to its capability of pairing with a lithium-free anode such as silicon and some tin compounds which can obviate the safety concerns of the lithium metal anode when using sulfur [10,33–41]. Li_2S particles, as the end discharge product of the Li/S cell, shrink during charging and generate empty space to accommodate the volume expansion of sulfur particles during lithiation (discharge), thus the mechanical failure of the cathode can be alleviated, resulting in improved cycle life for the Li/S cell. Moreover, the higher melting point of Li_2S (1372°C) [42] enables modifications under high temperature treatment conditions such as chemical vapor deposition (CVD) that can provide a uniform and stable carbon coating on the particle surface [35,36,43]. Sharing the same reaction mechanisms, Li_2S cathodes inevitably encounter the same problems as for sulfur cathodes such as the dissolution of polysulfides into most liquid electrolytes, and its “shuttle effect” which can induce low utilization of active material, low coulombic efficiency and severe degradation of the cycle life. Meanwhile the low electronic and ionic conductivity of Li_2S also cause low sulfur utilization and poor rate capability of the sulfur cathode [10,44]. To address the above-mentioned problems, many approaches have emerged to improve the electrochemical performance of the Li_2S cathode, for example employing Li_2S nanoparticles, and encapsulating Li_2S with carbon, [1,10,35] conductive polymers or transition metal disulfides [37,45]. In addition, some functional carbon materials such as carbon nanofibers, graphene and GO are also used to enhance the electrical conductivity of the Li_2S cathode material [36,46–49].

Herein, an especially efficient structure of single-layered graphene bonded to carbon coated Li_2S nano spheres ($\text{Li}_2\text{S}/\text{G}@C$) is demonstrated and used as a cathode material for the Li/S cell, showing high specific capacity and excellent cyclability. Single-layered graphene was used as a conductive host for Li_2S nano sphere deposition and all the $\text{Li}_2\text{S}/\text{graphene}$ composites were further treated with the CVD method to form a very stable and electrically conductive carbon shell on the surface of the Li_2S nano spheres which can not only provide individual void spaces to accommodate the volume change caused by transition between Li_2S and elemental S, but also act as a protective shield against polysulfide dissolution during cycling. We found that the use of graphene flakes can greatly affect the morphology of the $\text{Li}_2\text{S}/\text{graphene}$ composite and CVD results. With the optimized procedure, a $\text{Li}_2\text{S}/\text{G}@C$ composite with uniformly distributed ultra-fine carbon coated Li_2S nano spheres ($\sim 100 \text{ nm}$) on both sides of single-layered graphene was synthesized. As the highly conductive substrate, graphene can facilitate the electron transport in the cathode material. In addition, the sluggish lithium ion diffusion through the insulating sulfur (or Li_2S) can be accommodated by the nano-sized Li_2S particles. The $\text{Li}_2\text{S}/\text{G}@C$ cathode exhibited excellent rate capability and long cycle life, high reversible initial capacities of 993 mA h g^{-1} of Li_2S (1420 mA h g^{-1} of S), 773 mA h g^{-1} of Li_2S (1105 mA h g^{-1} of S) and 743 mA h g^{-1} of Li_2S (1062 mA h g^{-1} of S) can be obtained at 0.5 C, 1 C, and 2 C rates respectively (1 C = 1166 mA h g^{-1} , Li_2S). After 1000 cycles at a rate of 2 C for both charge and discharge, a capacity of 314 mA h g^{-1} of Li_2S (451 mA h g^{-1} of S) still retained, which is significantly higher than that of a new Li ion cell.

2. Experimental section

2.1. Material synthesis

Due to the high sensitivity of Li_2S to moisture, all the synthesis procedures and furnace tube assembly/disassembly were

conducted in an argon-filled glove box with a moisture content below 0.1 ppm and oxygen level below 0.6 ppm. The $\text{Li}_2\text{S}/\text{G}@C$ Nano-composites were prepared as follows: Different amount of graphene (3 mg, 5 mg, 8 mg, 10 mg) were firstly dispersed in 4.2 mL 1.0 M lithium triethylborohydride in tetrahydrofuran (1 M LiEt₃BH in THF, Sigma-Aldrich) under ultra-sonication for 10 min. Then 3 mL toluene containing 2 mmol sulfur (Alfa Aesar, Sulfur powder ~ 325 mesh, 99.5%) was added into the prepared solution and stirred at room temperature. After 5 min, the mixture was heated to 90°C under continuous stirring to precipitate lithium sulfide nano-spheres. The $\text{Li}_2\text{S}/\text{G}$ composite was washed with THF and hexane via centrifugation twice. After being dried inside of a glove box overnight the collected sample was heat-treated at 500°C for 30 min. To estimate the weight percentage of pure Li_2S inside of the $\text{Li}_2\text{S}/\text{G}$ composite, a certain amount of $\text{Li}_2\text{S}/\text{G}$ powder after heat treatment was weighted and washed with deionized water via filtration for several times until the pH of the filtered solution reached 7, then the powder was dried under vacuum at 50°C overnight and weighted again. The Li_2S reacted with water during the process, so comparing the weight difference between $\text{Li}_2\text{S}/\text{G}$ and the washed powder would provide the weight ratio between pristine Li_2S and $\text{Li}_2\text{S}/\text{G}$ composite (90–97 wt%). To obtain carbon coated Li_2S spheres the $\text{Li}_2\text{S}/\text{G}$ composite was heated to 450°C and maintained at 450°C for 30 min using argon gas and acetylene (carbon precursor) with a flow rate of 100 sccm (standard cubic centimeters per minute) and 10 sccm, respectively. The amount of carbon deposited can be calculated by weighting the composite before and after the CVD process (8–19 wt%). To increase the stability as well as the electronic conductivity of the carbon shell, the as obtained $\text{Li}_2\text{S}/\text{G}@C$ composite was further heated at 750°C for about 30 min.

2.2. Electrochemical measurement

The cathodes were prepared by grinding a mixture containing active material, carbon black (super P) and polyvinylpyrrolidone (PVP; Mw $\sim 1300 \text{ K}$) (pure Li_2S : C: PVP = 60:30:10, by weight) for 10 min, then dispersing the mixture in N-methyl-2-pyrrolidinone (NMP) to make slurry with a concentration of 250 mg mL^{-1} and stirring for 4 h, coating the slurry onto an aluminum foil and evaporating the solvent under 50°C inside of a glove box and drying overnight. The electrode area is 1.13 cm^2 , the mass loading of Li_2S and S in the electrodes are $1.1\text{--}1.4 \text{ mg/cm}^2$ and $0.76\text{--}0.97 \text{ mg/cm}^2$ respectively. 0.7 M LiTFSI (Lithium Bis(Trifluoromethanesulfonyl)Imide) in PYR₁₄TFSI (N-methyl-N-butylpyrrolidinium bis(trifluoromethane sulfonyl)imide)/DOL(dioxolane)/DME(Dimethoxyethane) (2:1:1, by volume) containing 0.5 M LiNO_3 (lithium nitrate) was used as electrolyte. CR2325 coin cells were assembled in an argon filled glove box. The cell consisted of the electrodes fabricated, lithium metal foil anode (99.98%, Cyprus Foote Mineral) and porous polypropylene separator (Celgard 2400). Electrochemical performance of the cells was evaluated with a battery cycler (Arbin BT2000) between 1.7 V and 2.8 V after being charged to 4 V for the first charge.

2.3. Characterization

The structure of the samples was investigated with an X-ray diffractometer (XRD, Bruker AXS D8 Discover GADDS micro-diffractometer) with a Co K α radiation source. An air-free holder was used to provide an inert atmosphere for the Li_2S samples during the test. The morphology and particle size of the samples were examined using a field emission scanning electron microscope (FESEM, JEOL JSM-7500F) with elemental mapping using energy-dispersive X-ray spectroscopy (EDS, Oxford). High resolution transmission electron microscopy images were collected using a 200 kV FEI monochromated F20 UT Tecnai instrument.

Download English Version:

<https://daneshyari.com/en/article/7953489>

Download Persian Version:

<https://daneshyari.com/article/7953489>

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