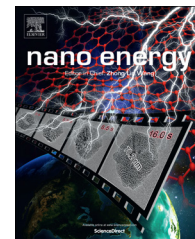Available online at www.sciencedirect.com

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RAPID COMMUNICATION

High-performance lithium/sulfur cells with a bi-functionally immobilized sulfur cathode

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Abstract
Lithium/sulfur (Li/S) cells have a theoretical specific energy five times higher than that of lithium-ion (Li-ion) cells (2600 vs. $\sim$500 Wh kg^{-1}). The conventional Li/S cells that use an organic liquid electrolyte are short-lived with low coulombic efficiency due to the polysulfide shuttle. We herein design carbon-coated NanoLi$_2$S (NanoLi$_2$S@carbon) composites, which consist of Li$_2$S nanoparticles as the core and a carbon coating as the shell. The carbon shell prevents the NanoLi$_2$S core from directly contacting the liquid electrolyte, which improves the performance of Li/S cells to provide longer cycle life and high sulfur utilization. The cyclability of Li/S cells is further enhanced by mixing the core-shell NanoLi$_2$S@carbon composites with graphene oxide, which chemically immobilizes polysulfides in the cathode through their functional groups. The resulting Li/S cell shows an initial specific discharge capacity of 1263 mAh g^{-1} (normalized to sulfur) at the C/10 rate and a capacity retention of 65.4% after 200 cycles. The capacity decay mechanism during cycling is also characterized in detail using near edge X-ray absorption fine structure (NEXAFS) spectra.
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Introduction

The depletion of fossil fuels and the effects of green house gases have aroused great interest in developing high energy density storage systems throughout the world [1-4]. The lithium/sulfur (Li/S) cell, consisting of lithium metal as the anode and elemental sulfur as the cathode, has been considered as the next-generation energy storage system for electric vehicles and large-scale grids. Based on the conversion reaction of

$$16Li + S_8 \rightarrow 8Li_2S \qquad (1)$$
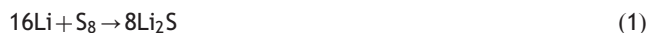
the Li/S cell can supply a theoretical specific energy of 2600 Wh kg^{-1}, which is five times greater than that of the lithium-ion (Li-ion) cell [5-7].

The conventional Li/S cell uses an organic liquid electrolyte. During discharge, elemental sulfur is reduced to form soluble polysulfides (e.g., Li_2S_x, $4 \leq x \leq 8$), which can dissolve into the organic liquid electrolyte. Since the elemental sulfur and its final discharge product Li_2S are neither electronically nor ionically conductive, the operation of Li/S cells depends on the dissolution of polysulfides in the liquid electrolyte [8-13]. However, the high solubility of polysulfides in the organic electrolyte represents a significant challenge in conventional Li/S cells, *i.e.*, the polysulfide shuttle. The polysulfide shuttle migrates sulfur species from the cathode to the anode, resulting in the loss of active material, short cycle life of the sulfur-based electrode, and low coulombic and energy efficiencies [14,15]. In order to prevent the polysulfide shuttle and improve the cycling performance, the construction of a solid, essentially insoluble sulfur cathode is a necessity in the conventional liquid-electrolyte Li/S systems. Moreover, cycling the metallic lithium anode in the organic liquid electrolyte also remains a problem. During recharge, the metallic lithium forms dendrites, which can penetrate the separator and short the cell [16-19].

Currently much Li/S research focuses on using an elemental sulfur cathode because of its high specific capacity (1675 mAh g^{-1}) and light weight. The prevention of the polysulfide shuttle by a conductive polymer coating is a common method for protecting the sulfur particles. Lithium sulfide (Li_2S) has been studied as the prelithiated sulfur electrode in Li/S cells because of its high melting point (1372 °C) and favorably high specific capacity (1166 mAh g^{-1}) [20-22]. The Li_2S cathode supplies lithium and may avoid the direct use of a metallic lithium anode [23,24]. The possible combination of the Li_2S cathode with a Si or Sn anode can dramatically enhance the energy density of traditional rechargeable lithium cells [8,25]. However, bulk Li_2S has low electronic and ionic conductivity as low as 10^{-14} and 10^{-13} S cm^{-1}, respectively; and it has been considered to be an electrochemically inactive material.

To promote the electrochemical activity of Li_2S, herein we report a solid sulfur cathode prepared by an environmentally benign synthesis of nanostructured Li_2S (NanoLi$_2$S) via reacting elemental sulfur with lithium triethylborohydride (LiEt$_3$BH) in tetrahydrofuran (THF). The NanoLi$_2$S is coated with conductive carbon by heat-treatment of the Li_2S particles with a thin coating of polyacronitrile (PAN) polymer on the surface to form a core-shell structure (NanoLi$_2$S@carbon). This structure not only enhances the conductivity, but also inhibits the dissolution of sulfur species for improved cycling performance. The cyclability of carbon-coated NanoLi$_2$S is further improved by mixing it with graphene oxide (GO-NanoLi$_2$S@carbon), which chemically constrains polysulfides within the cathode by the functional groups (such as hydroxyl, epoxide, carbonyl and carboxyl groups). The resulting Li/S cell shows an initial specific discharge capacity of 1263 mAh g^{-1} (normalized to sulfur) at the rate of $C/10$ with a capacity retention of 65.4% after 200 cycles, which makes it a promising cathode material for Li/S cells.

Results and discussion

Figure 1a shows the synthesis schematic of core-shell carbon-coated NanoLi$_2$S as cathode materials for Li/S cells. First, NanoLi$_2$S was prepared by reacting elemental sulfur (S) with lithium triethylborohydride (LiEt$_3$BH) in tetrahydrofuran (THF), Eq. (2):

$$S + 2Li(CH_2CH_3)_3BH \rightarrow Li_2S\downarrow + 2\ (CH_2CH_3)_3B + H_2\uparrow \qquad (2)$$
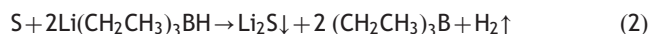
During the reaction, aggregates of Li_2S nanoparticles precipitated from the THF solution; and the particles are not very uniform in size since particle aggregates are found (Figure 1b). However, we can synthesize uniform NanoLi$_2$S spheres by modifying the preparation procedure [26]. The collected NanoLi$_2$S was washed, centrifuged, and dried at 140 °C under vacuum for 2 h prior to use. Before carbon coating, the NanoLi$_2$S was heat-treated at 500 °C under Ar for 0.5 h, and a thin carbon layer of 2-3 nm was formed on the surface of the NanoLi$_2$S. Carbon-coated NanoLi$_2$S composites were prepared by the pyrolysis of a PAN coating (from DMF solution) on the NanoLi$_2$S. After heat treatment at 600 °C in Ar for 1 h, a much thicker carbon layer is found on the surface of NanoLi$_2$S, e.g., the thickness of the coating layer is 20-30 nm when the carbon content is 10 wt% (Figure 1c).

Figure 2a shows the X-ray diffraction (XRD) patterns of as-prepared NanoLi$_2$S, NanoLi$_2$S after heat-treatment at 500 °C, and core-shell NanoLi$_2$S@carbon composites. The XRD patterns of the NanoLi$_2$S are identical to those of bulk Li_2S (JCPDS card no. 23-0369). These peaks are identified as a pure phase of Li_2S: 27.2° (111), 31.6° (200), 45.1° (220), 53.5° (311), and 56.0° (222), respectively. The XRD peaks of NanoLi$_2$S show significant peak broadening compared to those of the bulk Li_2S. The estimated crystallite size is 20-30 nm, which is much smaller than that of the bulk Li_2S particles (i.e., the particle size is ~1 μm). After heat-treatment at 500 °C, the peak widths become much narrower, which is due to the crystal growth of NanoLi$_2$S. The average size of the NanoLi$_2$S aggregates is 500 nm in diameter after heat-treatment. However, when the NanoLi$_2$S was further coated with carbon by the pyrolysis of the PAN polymer on its surface, the average size of the NanoLi$_2$S is preserved. The carbon coating procedure does not change the particle size of the NanoLi$_2$S with heat-treatment at 600 °C.

Raman spectra of NanoLi$_2$S, NanoLi$_2$S after heat-treatment at 500 °C and core-shell NanoLi$_2$S@carbon are shown in Figure 2b. Significant peaks are found in the wavenumber range from 250 to 2000 cm^{-1} in the Raman