Polysulfide shuttle control: Towards a lithium-sulfur battery with superior capacity performance up to 1000 cycles by matching the sulfur/electrolyte loading

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HIGHLIGHTS

- The polysulfide shuttle was tuned by the loading of sulfur and electrolyte.
- A high initial discharge capacity of 1053 mAh g^{-1} at a high rate of 1 C.
- An ultralow decay rate of 0.049%/per cycle during 1000 cycles.
- The polysulfide shuttle was suppressed to a shuttle factor of 0.02.

GRAPHICAL ABSTRACT
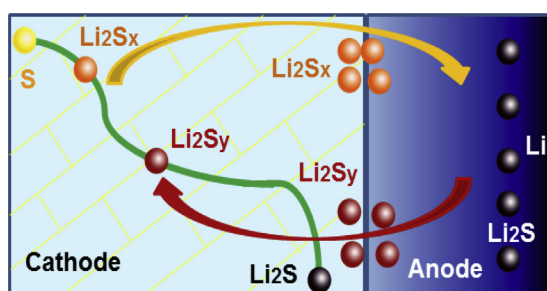
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ABSTRACT

Lithium-sulfur battery is one of the most promising alternative power sources, but the polysulfide shuttle between the anode and cathode induces low Coulombic efficiency, low utilization of the sulfur cathode, and severe degradation of cycle life. Herein, the polysulfide shuttle was tuned by the loading of sulfur and electrolyte in a Li-S cell. A lithium-sulfur cell with a high initial discharge capacity of 1053 mAh g^{-1} at a high rate of 1 C and an ultralow decay rate of 0.049%/per cycle during 1000 cycles was obtained by using carbon nanotube@sulfur cathode and suppressing polysulfide shuttle to a shuttle factor of 0.02 by matching the sulfur/electrolyte loading. The use of matching the sulfur/electrolyte loading is a facile way to tune the shuttle of polysulfide, which provides not only new insights to the energy chemistry of Li/S batteries, but also important principle to assemble a Li/S cell with recommend loading for their commercialization application in portable mobile devices and electric vehicles.

1. Introduction

The energy from the fossil fuels brings the flourish of mankind. However, the vast consumption of fossil-fuel causes the rapid decrease of its holding and increasing pollution of environment [1,2]. High-capacity energy storage systems are highly desirable to meet the requirement of electric vehicles and utilization of renewable energies like solar or wind energies. The broad applications of portable batteries in cell phones or laptops as well as large-packaged batteries in electric vehicles requires energy storage systems with high energy density, good safety, and low cost [3]. Li-ion batteries, which are approaching their theoretical specific

capacity at around 100–200 mAh g^{-1} based on the cathode's active material for traditional intercalation materials, cannot meet these requirements. With a theoretical capacity of 1675 mAh g^{-1}, elemental sulfur has been considered as one of the most promising alternative cathode materials [2,4,5]. The use of sulfur cathode has low cost, a low toxicity, and abundant resource [1,6,7]. Li–S batteries have a gravimetric energy density being the same or 2–3 times as high as Li-ion batteries.

However, the practical application of Li/S batteries is greatly hampered by some persistent problems including (1) sulfur and discharge products (Li$_2$S$_2$ and/or Li$_2$S) has a low electrical conductivity, affecting the reaction rate of the battery; (2) the Li$_2$S and other insoluble compounds are generated and cover the active compounds during cycling, which inhibits access of lithium ions and degrades the conductive network, and (3) the high-order soluble polysulfides can penetrate through the separator to the lithium negative electrode, where they are reduced to insoluble Li$_2$S or Li$_2$S$_2$, and the following polysulfides react with these fully reduced sulfides to form lower-order polysulfides, which become concentrated at the anode side and diffuse back to the positive electrode and are then re-oxidized into high-order polysulfides [7]. Such shuttle between the anode and cathode induces deposition of solid Li$_2$S$_2$ and Li$_2$S on the anode and loss of the active material, which leads to low Coulombic efficiency, low utilization of the sulfur cathode, and severe degradation of cycle life.

To overcome these problems, many efforts have been explored to enhance the electrical conductivity of the cathode and suppress the loss of soluble polysulfide intermediates during cycling. The use of conductive nanocarbon (e.g. mesoporous carbon [8–11], carbon nanotubes (CNTs) [12–16], graphene [1,17–19], CNT/graphene hybrids [20], carbon hollow spheres [21], etc.) and polymers (Polyaniline [22,23], polyacrylonitrile [24], etc.) gives rise to advanced composite cathode with excellent conductivity, robust electron/ion pathway, as well as superior reversible charge–discharge capacity and cycling performance [5]. Up to now, how to retard the shuttle of polysulfides is still a key issue to obtain Li–S cells with superior Li storage performance. On one hand, the incorporation of polymer chains (such as polyethylene glycol [8,18,25], polyvinylpyrrolidone [16]) or porous polysulfide reservoirs [26] affords the surface of nanocarbon/sulfur cathode to become highly hydrophilic and a chemical gradient is constructed that the polysulfides would preferentially be trapped by oxygen-containing groups on the cathode surface instead of dissolving in the bulk electrolyte. Therefore, the concentration of polysulfide in the electrolyte inclines to be lower, and the redox shuttle is partially inhibited. On the other hand, an electrolyte with a highly concentrated lithium salt [27,28] or solvent-in-salt electrolyte [29] with ultrahigh salt concentration and high lithium-ion transference number were employed, in which salt holds a dominant position in the lithium-ion transport system; consequently, the polysulfide dissolution from the cathode can be easily controlled by the common ion effect, and a high discharge capacity with good cyclic capacity retention is available. The introduction of tetrabutylammonium triflate or N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide is expected to stabilize the polysulfide anions through a chemical interaction between the soft acid and soft base [30], and the LiNO$_3$ participates in the formation of a stable passivation film to effectively suppress the redox shuttle of the dissolved lithium polysulfides on Li anode [31]. However, the dissolution of polysulfide in a Li/S cell is highly dependent on the sulfur/electrolyte loading [32]. How to well fit the loading of sulfur and electrolyte to retard the shuttle of polysulfide is not well understood yet.

In this contribution, the fitting between CNT@S cathode and electrolyte was explored. The reason we select CNT@S cathode with excellent Li ion storage performance is that the CNTs with quite high electrical conductivity, tunable pore size distribution, and robust scaffolds had been mass-produced by fluidized bed chemical vapor deposition at a very low cost of less than 100 $ kg^{-1} [33,34], which is quite potential for the commercial industrial applications of Li/S cells. Herein, the mixed solution of the 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) ($v/v = 1/1$) with 1 mol L^{-1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was selected as the electrolyte. This is most popular electrolyte that is accepted for Li/S cells by many research groups due to its solvability of polar polysulfides and appropriate ion mobility, although its Coulombic efficiency is less than 90% in most case.

2. Experimental

The CNT@S cathode was prepared by a facile co-heating procedure similar to our previous reports [14,20]. The CNTs was mass-produced on a Fe based catalyst in a fluidized bed reactor, and routine purification was carried out to remove the residual catalyst [35]. The sulfur was mixed with the CNTs by ball milling for 3 h, and the as-obtained mixtures were set in a sealed bottle. The bottle was heated to 155 °C and maintained for 1.0 h, which allows sulfur to immerse into the CNT scaffold and form CNT@S cathode.

A JSM 7401F scanning electron microscopy (SEM, JEOL Ltd., Tokyo, Japan) at 1.0 kV and a transmission electron microscopy (TEM, JEOL Ltd., Tokyo, Japan) at 120.0 kV were employed to detect the morphology of cathodes. The Raman spectra of the CNT and CNT@S cathode were recorded using Horiba Jobin Yvon LabRAM HR800 Raman spectrometer (He–Ne laser excitation at 633 nm). The sulfur content of CNT@S electrode was determined by thermogravimetry analysis (TGA) using TGA/DSC1 STAR^e system with N$_2$ atmosphere and a temperature ramp rate of 10 °C min^{-1}. The N$_2$ adsorption–desorption isotherms were collected by using an N$_2$ adsorption analyzer (Autosorb-IQ$_2$-MP-C system) at 77 K. The sample was degassed at a low temperature of 50 °C until a manifold pressure of 2 mm Hg was reached before N$_2$ sorption isotherm measurements to avoid the sulfur sublimation. The surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution plot was available by the nonlocal density functional theory and Monte-Carlo method.

The composite CNT@S cathode was fabricated with PVDF binder in NMP with a mass ratio of CNT@S: PVDF = 85:15. A homogeneously mixed slurry was prepared by magnetic stirred for ca. 24.0 h. The as-obtained slurry was coated onto a 25 μm thick Al current collector by a doctor blade. The obtained electrode was dried in a vacuum drying oven at 60 °C for 12.0 h. After that, the foil was punched into 13 mm disks as the working cathodes. According to the SEM image, the thickness of the cathode electrode was 10–15 μm excluding the thickness of Al current collector. The electrodes were assembled in a two-electrode cells configuration using standard 2025 coin-type cells. 1 mm thick Li metal foil was selected as a counter electrode. The mixed solution of DOL and DME ($v/v = 1/1$) with 1 mol L^{-1} Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the electrolyte, and the Celgard 2400 polypropylene membranes as the separator. The assembling of cells was conducted in an Ar-filled glove box with oxygen and water content below 1 ppm. The coin cells were monitored in galvanostatic mode within a voltage range of 1.6–3.0 V using Neware multichannel battery cycler. To increase the discharge capacity of CNT/S cathode and Coulombic efficiency, an electrolyte with 0.1 M Li$_2$S$_5$ (with [S] = 0.5 M) and 0.5 M lithium nitrate (LiNO$_3$) dissolved in the above mentioned DOL/DME with 1 mol L^{-1} LiTFSI electrolyte was employed. Unless otherwise noted, the capacities hereafter are normalized to the sulfur content in the cathode. The amount of Li$_2$S$_5$ in the electrolyte was also calculated as the sulfur source.