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Research Paper

Dendrite-Free Lithium Metal Anodes in High Performance Lithium-Sulfur Batteries with Bifunctional Carbon Nanofiber Interlayers

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ABSTRACT

Lithium sulfur (Li-S) batteries are highly prospective for future generations of transportation and grid storage due to their high energy density and low cost. However, the Li dendrite growth from the anode and the "polysulfide shuttle" from the cathode may cause poor cycling performance and safety concerns, hindering the practicality of Li-S batteries. Herein, we demonstrate a novel separator design by coating three-dimensional (3D) carbon nanofiber (CNF) interlayers on both sides of the separator to achieve a high performance Li-S battery. The CNF interlayer can not only render a uniform Li deposition on the anode by eliminating the "tip effect", but also restrain the polysulfide diffusion on the cathode with its porous and highly conductive 3D architecture, enhancing the utilization of S-related species significantly. So an average Coulombic efficiency of the Li metal anode protected by a CNF interlayer is up to 95% for 100 cycles at 0.5 mA cm^{-2}. Moreover, Li-S batteries with CNF interlayers can exhibit remarkable cycle performance, presenting an initial specific capacity of 1207.4 mAh g^{-1} at 0.5C and retaining at 828.1 mAh g^{-1} after 100 cycles. In addition, the low-cost raw materials and the simple preparation for CNF interlayers is suitable for industrial scale-up.

1. Introduction

High-performance rechargeable batteries have been demanded for portable electronics, electrical transportation and grid-scale energy storage systems, etc. And Li-S batteries may be considered as one of the most promising Li metal-based batteries due to their high theoretical energy density (2600 Wh kg^{-1}), low cost and natural abundance [1–3]. However, the low utilization of sulfur, the large volume expansion, the shuttle effect of highly soluble polysulfides in the ether-based electrolytes as well as the Li dendrite growth results in fast capacity fading and safety concerns, and has limited the commercialization of Li-S batteries so far [3–5]. To address the first few challenges from the cathode, significant efforts have been devoted to constructing advanced composite cathodes using various carbon materials [6–8], polymers [9–11] and metal-organic framework (MOF) materials [12,13]. Additionally, solid electrolytes [14–16], functional binders [17,18] and electrolytes additives [19] have also been studied to develop a viable Li-S battery. Recently, a cell configuration using a functional interlayer inserted between the sulfur cathode and separator has been suggested to be a remarkable method of improving Li-S batteries. For example, various polymer interlayers [20–22] or carbon interlayers [23–26] used in the batteries as a role of traps can effectively localize the polysulfides within the cathode side to enhance their reutilization. Furthermore, a highly conductive carbon nanofiber interlayer with a porous 3D architecture has been demonstrated to significantly enhance the reutilization of S-related species as both the electron pathways and the traps for dissolved polysulfides [27,28]. And this unique 3D architecture also contains sufficient inner space to accommodate the volume expansion of sulfur cathode during cycling.

Despite aforementioned considerable efforts in the sulfur cathode, the suppression of Li dendrite growth on the anode is another crucial factor for practical application of Li-S batteries. Due

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to its highly reactive nature, Li metal can react instantly with most organic electrolyte solvents and Li salts to form a solid electrolyte interphase (SEI) layer to prevent further consumption of Li and electrolyte [29–32]. However, the SEI layer cannot withstand the volume change from repeated Li plating/stripping process due to its low mechanical strength. Hence, Li ions would aggregate toward the fresh Li exposed to the electrolyte due to the "tip effect" [33] and the inhomogeneous Li-ion distribution would lead to uncontrolled Li dendrite growth. The growing dendrites can further magnify the inhomogeneous Li-ion distribution to cause continuous growth of tree-like dendrites [34] and their high surface area could further facilitate the consumption of electrolyte and Li, resulting in large interfacial resistance. Moreover, Li dendrites protruding from the anode surface may pierce through the separator and cause internal short circuits and safety concerns. Due to the low utilization of Li metal and rapid consumption of electrolyte resulting from the Li dendrite growth, the usage of Li metal and electrolyte is usually excessive for Li metal batteries, which is unfavorable to improve the specific energy density of batteries.

In order to deal with above challenges, employing electrolyte additives [35–38], artificial protecting layers [39–41], composite anodes [42–44], ionic liquid electrolytes [45–47], solid electrolytes [48–50] and novel separators [51–53] have been demonstrated to be effective approaches to stabilize the Li metal anode. To prevent Li dendrite growth from the origin, rendering a homogeneous distribution of Li-ion flux over the Li metal surface through functional interlayers [54–56] has been suggested. As low current density can slow the dendrite growth on the anode [57], conductive architectures have been proposed to accommodate Li deposition for Li metal anodes [57–59]. Along this line, a porous and conductive network on the anode may not only devote a uniform Li-ion flux near the anode surface but also render a low current density to suppress Li dendrite growth.

Herein, we propose a novel strategy for dendrite-free and high performance Li-S batteries by coating CNF interlayers on both sides of the separator. With a conductive CNF interlayer on the top of the cathode, the utilization of S-related species can be enhanced significantly. With a porous CNF interlayer on the top of the anode, Li ions can be guided to deposit along the fiber scaffold uniformly and avoid Li dendrite growth effectively. This novel design simplifies the battery processing without complicated synthesis of composite cathodes or anodes, which is suitable to be applied to address the challenges of Li-S batteries.

2. Experimental

2.1. Materials

Ethanol absolute (≥99.5%, Aladdin), Sulfur (≥99.5%, Aladdin), super P carbon black (C-65, TIMCAL Graphite & Carbon Ltd.), N-methyl-2-pyrrolidinone (NMP, 99.9%, Aladdin), polyvinylidene fluoride (PVDF, Solef-5130), 1,3-dioxolane (DOL, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, Sigma-Aldrich). Bacterial Cellulose (BC) hydrogel used in this work was kindly provided by Hainan Yeguo Foods Co., Ltd., China.

2.2. Preparation of the CNF-modified separator

The BC hydrogel was purified with deionized water completely and then was freeze-dried to obtain the BC aerogel. Subsequently, the BC aerogel was carbonized at 900 °C for 2 h under flowing argon to get the CNF. The CNF was mixed with the PVDF binder (9:1 by weight) and the slurry was stirred intensely for 12 h. Then the slurry was coated on a PE separator (Celgard 2400) on both sides (or one side) using a doctor blade method. After dried at 50 °C for 24 h in a vacuum oven, the CNF-modified separator was roll-pressed and punched into circular disks with a diameter of 18 mm. A fabricated CNF interlayer has an average mass of 0.36 mg cm^{-2}, and the thickness of it is ~20 μm. Furthermore, the simple preparation for CNF interlayers can avoid the damage from peeling process of producing independent carbon-based interlayers.

2.3. Synthesis of the sulfur cathode

The sulfur cathode was prepared by coating an NMP-based slurry containing 70 wt % sulfur powder, 20 wt % super P and 10 wt % PVDF as a binder onto an aluminum foil. Then the coated foil was dried at 50 °C for 24 h under vacuum. Finally, the sulfur cathode was roll-pressed and punched into circular disks with a diameter of 12 mm. The areal mass loading of sulfur is approximately 1.4 mg cm^{-2}, counting the quality of sulfur with the whole cathode. To compare the CNF-modified separator with the pristine separator fairly, the mass of two CNF interlayers is also included in the cathode. When the mass of two interlayers is accounted into the 70 wt% sulfur cathode, the sulfur ratio in the cathode is equivalent to 53 wt%. Thus, the cycling performance of a 70 wt% sulfur cathode with a CNF-modified separator is compared with that of a 53 wt% sulfur cathode with a pristine separator.

2.4. Fabrication of batteries

For a Cu/Li battery, CR2025-type coin cells were assembled in an argon-filled glove box (MBRAUN, H_2O < 0.5 ppm, O_2 < 0.5 ppm) with Li foils as the anode and Cu foils as the cathode. The CNF interlayer was coated on the one side of the separator, connected with the Cu foil closely to investigate the Li plating and stripping process. The electrolyte was 1.0 M LiTFSI (lithium bis (trifluoromethanesulfonyl) imide) in DOL and DME (1:1 by volume) with a 0.1 M $LiNO_3$ additive. The cell tests were carried out by depositing 1 mAh cm^{-2} of Li onto the Cu foil, followed by Li stripping up to 2 V. Symmetrical coin cells were prepared using two Li metal foils as electrodes and the separator was coated with CNF interlayers on both sides. They were cycled over two-hour charge and discharge process at a current density of 0.5 mA cm^{-2}. For a Li-S battery, the interlayers were coated on both sides of the separator to protect both anodes and cathodes. The voltage range of Li-S batteries is from 1.5 V to 2.8 V for galvanostatic charge–discharge test. In addition, to standardize the measurement, the amount of the electrolyte added to each cell was controlled to 40 μl, and the cells were packed with the sealing machine (MSK-110) at the same pressure of 50 kg cm^{-2}.

2.5. Characterization and electrochemical measurements

The microstructure of the CNF and surface morphology of Li anodes were characterized using a scanning electron microscope (SEM, FEI Quanta FEG 250). The X-ray diffraction (XRD, Rigaku Ultima IV, Cu Kα radiation, 40 kV, 40 mA) patterns were recorded at a scanning rate of 10° min^{-1} in a 2θ range of 5°–50°. The Raman measurement was conducted on a Renishaw RM2000 using a 633 nm laser. The surface area and pore structure were characterized using a Micrometrics ASAP 2020 physisorption analyzer. The X-ray photoelectron spectroscopy (XPS) test was using a Physical Electronics 5400 ESCA. The contact angle was measured using a Data-Physics OCA-15E contact angle analyzer (DataPhysics Instruments GmbH, Filderstadt, Germany).

The galvanostatic charge–discharge measurement was conducted using a Land Battery Testing System (LAND CT-2001A). Electrochemical impedance spectroscopy (EIS) was performed on a CHI660D (Shanghai Chenhua Instrument) at a frequency range from 100 kHz to 10 mHz with an AC voltage amplitude of 10 mV.