A modularly-assembled interlayer to entrap polysulfides and protect lithium metal anode for high areal capacity lithium–sulfur batteries

Yusheng Ye[a], Lili Wang[a], LiLi Guan[c], Feng Wu[a,b], Ji Qian[a], Teng Zhao[a,1], Xiaoxiao Zhang[a], Yi Xing[a], Jiaqing Shi[a], Li Li[a,b], Renjie Chen[a,b,*]

[a] Beijing Key Laboratory of Environmental Science and Engineering, School of Material Science & Engineering, Beijing Institute of Technology, Beijing 100081, China
[b] Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing 100081, China
[c] Sinopec Research Institute of Petroleum Processing, Beijing, 100083, China

A B S T R A C T

Polysulfide shuttle effect and the formation of lithium metal dendrite during the discharge-charge process are two primary challenges that limit the application of lithium sulfur (Li-S) batteries. To solve them effectively, a modularly assembled interlayer was prepared by agglomerating Vulcan XC72 carbon black nanoparticles into ellipsoidal superstructures through a double Fischer esterification reaction. The MAXC interlayer can efficiently trap soluble intermediate polysulfides and provide space to store electrolyte and reaction products. More importantly, it can keep lithium anode compact and stable, enabling prolonged cell cycling. A Li/MAXC-MAXC/ Li symmetrical cell sustained stable 180-cycles test and delivered only a 20 mV overpotential with a depositing/ stripping capacity of 1 mA h/cm^2 at 1 mA/cm^2. At a high sulfur loading of approximately 5.3 mg/cm^2, Li-S coin cells with the assembled MAXC interlayer maintained a high reversible capacity of 909.0 mAh/g and a high areal capacity of 4.75 mAh/cm^2 after 100 cycles at 0.1 C. This multi-functional interlayer affords a viable strategy for the fabrication of high-energy-density batteries with protected metal anodes.

1. Introduction

In contrast to conventional lithium ion batteries that are limited by relatively low theoretical capacities, lithium sulfur (Li-S) batteries are widely considered as one of the most promising candidates to meet the ever-increasing demand for high-performing, light-weight and economical energy storage devices for various applications [1–3]. However, elemental sulfur and final discharged lithium sulfide are electronically and ionically insulating, resulting in slow electrochemical reaction rate, especially at high currents. The shuttle effect associated with soluble polysulfides and the formation of lithium dendrite are two primary challenges associated with Li-S batteries [4,5]. During the discharge-charge process, the soluble intermediate polysulfides migrate towards the anode to establish a concentration equilibrium in the electrolyte. These species subsequently react with the Li metal anode, leading to issues such as poor cycling and low coulombic efficiency [6–8]. Because of the difference in chemical potential and the concentration nonequilibrium between the cathode and anode during cycling, it is typically difficult to fully suppress the diffusion of soluble poly-

sulfides towards the lithium anode [9]. Moreover, the stripping/plating of Li on the anode surface leads to infinite volume change and introduces the formation of cracks, pits, and crevices. These weaknesses eventually bringing poor cycle performance and serious safety hazards.

Numerous approaches have been proposed for the development of advanced Li-S batteries, including the use of novel cathodes [10–16], anode protection [17], new electrolytes [18,19] and additives [20–23]. One exciting way is to insert an interlayer between the cathode and the separator, trapping polysulfides and thereby enhancing reversibility and improving the current collection effect [24–27]. Metal organic frameworks [28], metal oxides [29,30], free-standing nanofibers [31], black phosphorus [32], graphene [33,34] and various polymers [35–37] have all been assessed as interlayers for Li-S batteries. Based on the results of these studies, suitable interlayers should have three characteristics. Firstly, the mass loading of the interlayers should not affect the energy density of the Li-S battery. Secondly, complex synthetic procedures and expensive materials should be avoided to facilitate large-scale production and ensure cost-competitive products. Lastly,

the interlayers should maintain their structural stability during cycling. Thus, carbon-based interlayers have been found to be more suitable for applications in Li-S batteries because they are readily available, lightweight, adsorptive and inexpensive.

Although various carbon-based interlayers can effectively improve the performance of Li-S cells during cycling, the poor chemical compatibility between non-polar carbon and the separator often leads to weak interfacial binding during the coating process. In the current work, we developed a modularly-assembled interlayer to enhance the cycling and rate performance of Li-S batteries. Vulcan XC72 carbon black nanoparticles (referred to as XC hereafter), were employed as building blocks and assembled into ellipsoidal microstructures through a double Fischer esterification process. This modular assembly process has previously been employed for the synthesis of novel materials from building blocks having enhanced, synergistic physicochemical properties [38]. The modularly-assembled XC72 carbon black (referred to as MAXC) nanoparticles efficiently trap soluble intermediate polysulfides, provide space to store the electrolyte and benefit to form a compact and stable lithium anode as to allow prolonged cell cycling. The Coulombic efficiency of Li/MAXC-Cu cell was 98.8% and maintained for 180 cycles. This MAXC interlayer acts as an upper current collector and thus increases the electrical conductivity and utilization of active materials. At a sulfur loading of 5.3 mg/cm^2, the resulting Li-S cell displayed good cyclability, with an areal capacity of 4.75 mAh/cm^2 after 100 cycles at 0.1 C. Li-S batteries based on this modularly-assembled strategy exhibit long cycle lifespans, high coulombic efficiencies, and superior areal capacities.

2. Material and methods

2.1. Synthesis of the MAXC superstructure

The synthesis of the MAXC superstructure was based on an oil bath method. Briefly, 1 g Vulcan XC72 carbon (Cabolt, Shanghai) was dispersed in 60 mL concentrated HNO$_3$ and heated at 130 °C for 2 h under reflux conditions, to graft carboxyl groups onto the nanoparticles. The product was filtered, washed with ethanol and de-ionized water, and dried in a vacuum oven at 80 °C for 48 h. Following this, 1 g of the carboxylated VC was dispersed in 50 mL deionized water containing 0.5 g phytic acid (J & K). The resulting mixture was heated at 80 °C for 2 h to completely dissolve the phytic acid, then cooled to room temperature. Subsequently, 0.7587 mL ethylene glycol (equivalent to a phytic acid:ethylene glycol, molar ratio of 1:18) and 0.87 g ammonium persulfate were slowly added to the mixture with vigorous stirring. The mixture was heated at 130 °C for 6 h under stirring and then refluxed overnight. Washing the product with ethanol and de-ionized water followed by drying in a vacuum oven at 60 °C for 48 h gave the modularly-assembled XC72. Finally, the black powder was heated to 1000 °C for 10 h under a nitrogen gas flow, at a heating rate of 4 °C/min, to generate the MAXC superstructure.

2.2. Fabrication of the MAXC interlayer

MAXC superstructure and LA-132 binder (acrylonitrile copolymer) were dispersed in water at a mass ratio of 9:1 to obtain a slurry with a solid content of 8.5%. This slurry was then coated onto Celgard 2325 separator by the tape casting method, employing an automatic film applicator. After drying, a MAXC interlayer (0.3 mg/cm^2) with a thickness of 9 μm was attached to the Celgard 2325 separator.

2.3. Battery assembly

For cathode preparation, the acetylene black/sulfur/polyaniline composite (89 wt% sulfur) was mixed with acetylene black and LA-132 binder in a mass ratio of 80:12:8 to produce a slurry. After stirring for 24 h, the slurry was coated onto aluminum foil current collectors

and the resulting electrodes were dried in a vacuum oven at 60 °C for 48 h. The electrodes were subsequently cut into disks (11 mm diameter) to give cathodes with sulfur loadings of approximately 3.0 mg/cm^2. Two-electrode coin cells (CR2025) incorporating Li foil as the anode and MAXC as interlayer were assembled in an Ar-filled glovebox for the electrochemical experiments. A solution of 0.05 M Li$_2$S$_5$, 1 M lithium bis-(trifluoromethane)sulfonimide and 0.6 M LiNO$_3$ in a 2:1 (v/v) mixture of 1,2-dimethoxyethane and 1,3-dioxolane was used as the electrolyte. The electrolyte amount was about 20 ml mg^{-1} S. The coin cells were discharged and charged between 1.8 and 2.6 V at different current densities using an electrochemical station (LAND, Wuhan) to test their cycle lifespans.

For Li-Cu cells, the Cu foil was punched into 11.0 mm disks as the working electrodes, 1.0 mm thick Li metal foil was employed as the counter electrode, followed by assembly with a Celguard 2325 separator or MAXC-coated separator. 60 μL of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1M), lithium nitrate (0.6 M) in co-solvent of 1,2-dimethoxyethane and 1,3-dioxolane (DOL/DME, 2:1 by volume) was used as electrolyte. The Li-Cu cells were first discharged for 1 mAh/cm^2 and then charged to the cutoff voltage of 1.0 V. Coulombic efficiency was calculated as the ratio of capacity between plating and stripping.

2.4. Materials characterization

Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet iS10 spectrometer (Thermo, USA) from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. Nitrogen adsorption−desorption isotherms and BET surface area measurements were carried out with a Quantachrome Instruments Autosorb-IQ-MP. X-ray diffraction (XRD) data were acquired using a diffractometer (Rigaku) with a Cu Kα radiation source (λ = 0.154 nm). The morphology of each composite was examined by field emission scanning electron microscopy (FE-SEM, S4800, Japan) and high resolution transmission electron microscopy (HR-TEM, JEM-2100F, 200 kV, Japan and TECNAI G2 F30, 300 kV, USA).

3. Results and discussion

3.1. Structures and morphologies of the MAXC composites

Fig. 1a summarizes the molecular reaction that occurs during the modular assembly of Vulcan XC72 nanoparticles to form the MAXC via a double Fischer esterification. Phytic acid, with six phosphoric acid groups, acts as the core molecule to connect one end of polymerized ethylene glycol molecules and form polyphosphate esters. The Polymerized ethylene glycols then act as links by reacting with the polycarboxylated XC to form polycarbonate esters. The ester-based polymers function as linkages between the XC nanoparticles. In this manner, the original dispersed XC nanoparticles are reconfigured into superstructures that afford additional internal pores and improved structural stability, as shown in Fig. 1b. Scanning electron microscope (SEM) was used to investigate the morphological changes in the XC-72 before and after this assembly. Fig. 1c shows an SEM image of the scattered, independent XC particles. In contrast, the MAXC superstructure (Fig. 1d) exhibits agglomeration with larger particle sizes. Fig. 1e presents an HR-TEM image of the MAXC superstructure, from which it is evident that the carbon black nanoparticles were linked closely with one another to form an interconnected structure. The thin layer that evidently formed on the surface of the MAXC may correspond to the cross-linked connections (Fig. S1). This cross-linked structure potentially provides a three-dimensional electron channel and thus facilitates rapid ion transport.

Lithium anode is one of the most important factors that decides the cell cycle performance. Traditionally, the highly reactive lithium metal easily decomposes the electrolyte to form an unstable layer of solid