Journal of Power Sources 351 (2017) 17–25

Contents lists available at ScienceDirect

Journal of Power Sources

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

A bifunctional ion-electron conducting interlayer for high energy density all-solid-state lithium-sulfur battery

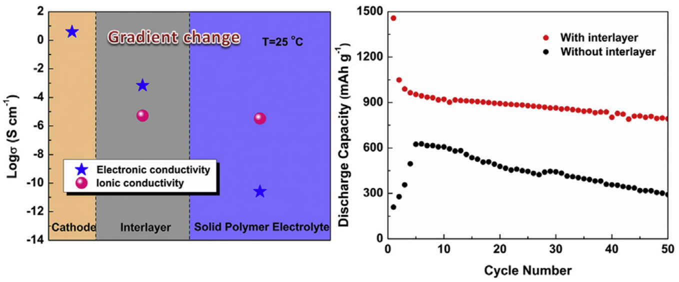
Yuewu Zhu, Jie Li, Jin Liu*

School of Metallurgy and Environment, Central South University, Changsha City, 410083, China

HIGHLIGHTS

- A bifunctional electron-ion conducting interlayer is designed for Li-S battery.
- This interlayer is intercalated between cathode and solid polymer electrolyte (SPE).
- A gradient change of electron-ion is formed in the Li-S battery system.
- Cathode/SPE interfacial compatibility is significantly enhanced.
- Li-S battery with the interlayer exhibits higher active material utilization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 August 2016
Received in revised form
23 January 2017
Accepted 17 March 2017

Keywords:
Ion-electron conductor
All-solid-state
Lithium-sulfur battery
Active material utilization
Battery configuration

ABSTRACT

A bifunctional ion-electron conducting layer is designed for all-solid-state lithium-sulfur battery. This layer consists of electronic conductor and solid polymer electrolyte that is intercalated between the cathode and electrolyte. By forming a gradient of electrons and lithium ions, the electrochemical performance and interfacial compatibility of the battery are obviously enhanced. When a pure sulfur powder is directly used as an active material of the cathode, the battery with the interlayer delivers the initial discharge capacity of 1457 mAh g^{-1} and the discharge capacity of 792.8 mAh g^{-1} after 50 cycles at 0.5 C and 80 °C, while the battery with the same cathode and without the interlayer only has the discharge capacity of 291.9 mAh g^{-1} after the same number of cycles.

1. Introduction

With rapid developments in advanced portable electronic devices, electric vehicles and energy storage systems, the demand for high energy density rechargeable batteries is continuously increasing [1–3]. The lithium-sulfur (Li-S) battery is one of the most promising systems due to its high theoretical capacity of 1672 mAh g^{-1} [4,5]. Moreover, elemental sulfur is a naturally abundant active cathode material that can reduce cost [6,7].

Despite the obvious advantages of Li-S battery, the practicality is limited by inherent poor electronic conductivity of both sulfur and Li_2S, dissolution of the intermediate lithium polysulfide species and the volume change during the discharge-charge process [8,9]. A variety of strategies such as elaborate designs of the cathode structure, optimization of the separator, specific additive of the electrolyte and anode protection have been employed to overcome the intrinsic problems [10–14]. In addition, new battery

---

* Corresponding author.
E-mail address: jinliu@csu.edu.cn (J. Liu).

http://dx.doi.org/10.1016/j.jpowsour.2017.03.072

configurations by introducing an interlayer between the cathode and the separator showed higher sulfur utilization and better cycle life for liquid electrolyte lithium-sulfur batteries [15–22].

However, reliability and safety are still insufficient in conventional liquid Li-S batteries due to the dissolution of polysulfides and the formation of lithium dendrites. Thus, all-solid-state Li-S batteries employing solid electrolytes to replace liquid electrolytes are attracting intense research interest [23–25]. Especially, all-solid-state Li-S batteries based on solid polymer electrolytes (SPEs) possess extraordinary flexibility, enabling design and manufacture of stylish energy storage devices and electric vehicles [25–30].

Previous studies have found that PEO-based SPEs show high electrochemical performance. A poly(ethylene oxide)-lithium triflate (PEO-$LiCF_3SO_3$) complex with nano-sized zirconia (ZrO_2) and lithium sulfide (Li_2S) was applied in all-solid-state Li-S batteries. The initial discharge capacity was 900 mAh g^{-1} at 0.05 C and 90 °C [25]. Lately, a metal-organic framework (MIL-53(Al)) modified SPE combined with a macro-structural sulfur cathode was used to inhibit polysulfide dissolution and shuttling in all-solid-state Li-S batteries [27]. After 1000 cycles at a current density of 4 C and 80 °C, a discharge capacity of 325 mAh g^{-1} was obtained. However, different from the liquid electrolyte, the solid electrolyte has difficultly infiltrating into the conductive matrix to maintain an integrated Li-ion conductive pathway. Since the electrochemical reaction takes place only when lithium ions and electrons contact the active materials [31,32], the electronic and ionic conductivities must be balanced and improved [33].

Herein, we design and fabricate a bifunctional ion-electron conducting layer that is intercalated between the cathode and SPE. By forming a gradient change of electrons and lithium ions and constructing a structural similarity in electrode and electrolyte, the electrochemical performance and interfacial compatibility of the battery system are obviously improved. A pure sulfur powder can be directly used as the active material of the cathode without any modification. The all-solid-state Li-S battery delivers an initial discharge capacity of 1457 mAh g^{-1} at 0.5 C and 80 °C. After 50 discharge/charge cycles, the battery maintains the discharge capacity of 792.8 mAh g^{-1} that is three times higher than one without the interlayer.

2. Experimental section

2.1. Materials

Sublimed sulfur (S, 99.95%), super P, polyethylene oxide (PEO, $M_w = 4\,000\,000$, 99.9%), and acetonitrile (CH_3CN, chromatographic grade) were obtained from Aladdin. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, +99.5%) was purchased from Sigma Aldrich and stored in a glove box. N-Methyl-2-pyrrolidone (NMP, 99.5%) was purchased from Heowns. Metal-organic-framework (MOF) of MIL-53(Al) was prepared as the previous report [34].

2.2. Preparation of polymer membrane

The preparation of the interlayer membrane was carried out as follows: PEO was dried at 60 °C for 24 h and LiTFSI was dried at 100 °C for 24 h in a vacuum oven before use. Firstly, 0.0500 g MIL-53(Al) nano-particles, 0.0500 g super P, 0.5000 g PEO and 0.2170 g LiTFSI were mixed in acetonitrile, and stirred to form a homogenized solution. After that, the solution was cast and dried into a thin film at 80 °C for 24 h in an argon-filled glove box. Finally, a black thin film interlayer was formed. The SPE was prepared according to our previous report [34]. The effects of super P concentrations (5, 10 and 20 wt% of the amount of PEO) on battery performance were investigated. The battery with 10 wt% super P shows the best cycling and rate performance. Thus, 10 wt% super P was used in the work.

2.3. Electrochemical measurements of the membranes

The electronic conductivities of the interlayer, the cathode composition and interlayer without LiTFSI were measured by four-point probes (RTS-8). For the SPE, the electronic conductivity was measured by the Hebb-Wagner polarization method using a (−) Li/SPE/stainless steel electrode (+) asymmetric cell [35]. The ionic conductivities of the SPE and interlayer were determined by AC impedance spectroscopy and chronoamperometry measurements by using a PARSTAT 4000 system. In the AC impedance spectroscopy method, the cells were tested over the frequency range between 500 kHz and 10 Hz with perturbation amplitude of 10 mV. In the chronoamperometry measurements, polarization of the cells were carried out by a small voltage (ΔV) of 10 mV and Nyquist spectra were obtained in the frequency between 500 kHz and 0.1 Hz with an oscillation voltage of 10 mV before polarization.

2.4. Battery performance

Four kinds cathode composites were prepared by the blending method: $S_{60}C_{30}PAA_{10}$, $S_{60}C_{30}PAA_8SPE_2$, $S_{60}C_{30}PAA_5SPE_5$ and $S_{60}C_{30}PAA_2SPE_8$ (the subscript means the mass ratio of the compositions in the cathode). To prepare the cathode materials, a certain proportion of elemental sulfur powder, PAA binder, carbon black (super P) and SPE were mixed in N-methylpyrrolidone (NMP). The homogeneously mixed slurry was cast onto an aluminum foil and dried at 50 °C for 24 h to remove the solvent. Cathode disks with a diameter of 10 mm ($S = 0.7854$ cm^2), sulfur content of 60 wt % and average area sulfur loading of 0.7 mg cm^{-2} were punched. Electrochemical testing was performed with CR2025 coin type batteries. The battery was assembled by contacting in sequence the cathode of $S_{60}C_{30}PAA_{10}$, the interlayer, SPE, lithium metal foil anode ($d = 16.2$ mm), and nickel foam current collector. And the comparison battery was assembled by contacting in sequence the cathode of $S_{60}C_{30}PAA_{10}$, $S_{60}C_{30}PAA_8SPE_2$, $S_{60}C_{30}PAA_5SPE_5$ or $S_{60}C_{30}PAA_2SPE_8$, SPE, lithium metal foil anode ($d = 16.2$ mm), and nickel foam current collector. All batteries were assembled in a controlled argon-filled box with both humidity and oxygen content below 1 ppm.

The batteries were tested by galvanostatic cycling in a 1.5–2.8 V voltage range by using a LAND battery-testing instrument (Wuhan Land Electronic Co., Ltd. China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using a PARSTAT 4000 electrochemical measurement system. CV tests were performed at a scan rate of 0.2 mV s^{-1} in the voltage range of 1.5–2.8 V. EIS measurements were carried out at open-circuit potential (OCP) in the frequency range between 100 kHz and 0.1 Hz with perturbation amplitude of 10 mV. Before all measurements, the batteries were kept at the given temperature for at least 4 h to reach thermal equilibrium.

2.5. Physical and thermal characterization

Morphologies of the MIL-53(Al) nanoparticle, super P and interlayer were observed with a scanning electron microscopy (SEM, sirion 200). The thermal behavior of the cathode and sublimed sulfur samples were investigated by a thermogravimetric analysis (TGA, SDTQ600) under an Ar atmosphere at a heating rate of 10 °C min^{-1} from 30 to 800 °C.