



A multi functional binder with lithium ion conductive polymer and polysulfide absorbents to improve cycleability of lithium–sulfur batteries



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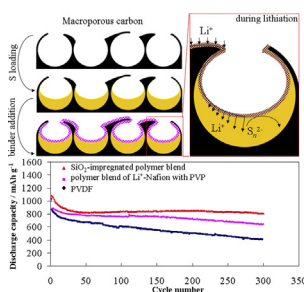
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HIGHLIGHTS

- Polysulfides with long chain show insignificant shuttle in Li–S battery.
- Existence of Li₂S₆ in macroporous carbon (MPC) promotes kinetic properties.
- SiO₂-impregnated polymer blend of Li⁺-Nafion with PVP as a binder is developed.
- The developed binder regulates tetrasulfide movement only in MPC pores.
- Resultant Li–S battery has low capacity degradation rate at 1C rate.

GRAPHICAL ABSTRACT



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ABSTRACT

A Li–S battery with enhanced cycleability is developed using a multi-functional binder with cation-conductive polymer and polysulfide absorbents. The binder is composed of Li⁺-Nafion, polyvinylpyrrolidone, and nano silica. Macroporous carbon (MPC) is employed for sulfur retention in cathode. The multi-functional binder regulates tetrasulfide movement only in MPC pores during lithiation and delithiation cycling. The resultant Li–S battery shows excellent performance in discharge capacity and rate cycleability. The sulfur lithiation capacity reaches 1373 mAh g⁻¹ at 0.2C (0.335 A g⁻¹ of S) and 470 mAh g⁻¹ at 5C (8.375 A g⁻¹ of S). A rate capacity as high as 809 mAh g⁻¹ has been achieved after 300 cycles at 1C charge–discharge rate. The Li–S battery showed very low capacity degradation rate of 0.08% per cycle at 1C rate.

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1. Introduction

Conventional Li-ion batteries are suffering from the low capacity

and high cost. Lithium–sulfur (Li–S) batteries attract considerable attentions because of high gravimetric and volumetric energy densities (2.6 kWh kg⁻¹ and 2.8 kWh L⁻¹ [1,2]) that are 3–5 folds higher than the conventional Li-ion batteries [3,4]. They have been considered as one of the most promising energy storage devices for next-generation power systems because abundant sulfur is a cheap and non-toxic cathode material.

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Li–S cell is composed of carbon–sulfur composite as the cathode (sulfur electrode) and metallic lithium as the anode with organic liquid electrolyte [5]. Sulfur has a strong tendency to catenation, which manifests itself not only in many forms of the element (S_n) but also in polysulfide ion (S_n^{2-}) [6]. Octasulfur (cyclo- S_8) molecule with a crown conformation is the most thermodynamically stable form. During cell discharge (sulfur lithiation), sulfur was electrochemically reduced to form Li_2S through a complex process with a series of polysulfide intermediates. The large volumetric expansion of sulfur during lithiation coupled with polysulfide shuttle resulted in the poor cycleability of Li–S batteries [7,8]. Many efforts have been made to enhance the cycleability *via* improving sulfur electrode integrity by encaging sulfur with semi-conductive metal oxides [8], carbon microspheres [9–11], porous carbon [12–16], and *via* suppressing polysulfide shuttle (PSS) by the employments of solid electrolyte [17,18] and functional separator [16,19,20].

Binder used for sulfur electrode requires not only strong adhesion for electrode powders against volumetric expansion of sulfur but also powerful capability to block polysulfide transport against PSS. Development of functional binders has become a new trend in the Li–S battery technology. Compared with the widely-used polyvinylidene fluoride (PVDF) [6], oxygen-rich polymers showed more significant effect on PSS suppression attributed to their higher polysulfide absorption ability than PVDF, such as polyethylene oxide [21], gelatin [22], polyvinylpyrrolidone (PVP) [23] and N-alginate [24]. Since sulfur electrodes contained only 10 wt.% binder, the effectiveness of these polymer binders on PSS suppression *via* polysulfide adsorption was limited. Li^+ -Nafion (lithiated sulfonated-tetrafluoroethylene based fluoropolymer-copolymer) was a cation permeable polymer, which suppressed PSS *via* blocking polysulfide (anion) transport (polysulfide repellency) [25–27]. A polymer blend of Li^+ -Nafion with PVP may suppress PSS more effectively, *via* a function combination of polysulfide repellency from Li^+ -Nafion and polysulfide adsorption from PVP.

Nano- SiO_2 has a strong affinity to polar molecules (including polysulfide). Nano- SiO_2 impregnation in Nafion membranes aided water retention of Nafion in proton exchange membrane fuel cells because of its good hygroscopic property [28]. Moreover, silica impregnation in gel polymer electrolyte enhanced Li^+ transport [29] because silica particles functioned as an intrinsically single ion conductor [30]. Therefore, the use of binder impregnated with nano- SiO_2 may improve the Li^+ conductivity to promote lithiation and delithiation kinetics.

This work presented a SiO_2 -impregnated polymer blend of Li^+ -Nafion with PVP for rate cycleability enhancement of Li–S battery. The nano- SiO_2 was employed to enhance polysulfide adsorption and Li^+ conduction. Based on the studies on the capacity decay behavior of sulfur electrode in different potential ranges of lithiation and delithiation, the effects of the polymer blending and nano- SiO_2 impregnation on the rate capacity and cycleability were investigated and discussed with aids of material characterizations and electrochemical analyses.

2. Method and procedures

The synthesized samples were identified *via* X-ray diffraction (XRD) (Rigaku D/MAX-2550-PC) with Cu $K\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$). Their morphologies were observed *via* field emission scanning electron microscopy (FESEM, Zeiss Ultra55) at 5 kV and transmission electron microscope (TEM, Hitachi H-9500) at 300 kV.

The hierarchical macroporous carbon (MPC) was synthesized as previously reported [31,32]. Sulfur-loaded MPC (S/MPC) was

prepared *via* calcination of the ball-milled mixture of sulfur and MPC with a mass ratio of 7:3 at 155 °C for 4 h in N_2 atmosphere [16].

$LiOH \cdot H_2O$ (25.2 mg) was added in a Nafion suspension (10 ml, 5 wt%) and then stirred for 2 h at 60 °C for Nafion lithiation. After filtration, the obtained solution was then subjected to vacuum drying at 60 °C for 36 h to prepare Li^+ -Nafion. The polymer blend solution of Li^+ -Nafion with PVP was obtained after dissolving Li^+ -Nafion and PVP with a mass ratio of 1:1 in NMP. A homogeneous polymer blend was formed after drying the polymer blend solution in vacuum at 60 °C, revealing the feasibility of the blend as a binder. Commercial nano- SiO_2 was then dispersed to the obtained polymer blend solution (mass ratio of SiO_2 : Li^+ -Nafion: PVP = 1: 4.5: 4.5) to form a homogeneous suspension, ready for sulfur electrode fabrication.

Coin cells (CR2025) were assembled in an Ar-filled glove box by using a lithium foil as the counter electrode and Celgard 2400 membrane as the separator. The working electrode was prepared by casting the electrode slurry on an Al foil before drying at 60 °C for 12 h in vacuum. The slurry was composed of S/MPC (70 wt.%), super P (20 wt.%), and prepared binder (10 wt.%) in NMP. The sulfur content in cathode was 49 wt.%, measured by the thermogravimetric analyzer. A total of 80 μ l electrolyte and 2 mg electrode materials including S/MPC, super P, and binder were employed in the test cell. The electrolyte consisted of lithiumbis(trifluoromethane sulfonimide) ($LiTFSI$: 1 mol L^{-1}) and $LiNO_3$ (1 wt.%) in a DOL-DME solution (1:1 ratio in volume, DOL: 1,3-dioxolane, DME: 1,2-dimethoxyethane).

Cyclic voltammograms (CVs) were recorded at a scan rate of 0.1 $mV s^{-1}$. The galvanostatic charge and discharge tests were conducted within 1.8–2.6 V (vs. Li^+/Li). Electrochemical impedance spectroscopy (EIS, CHI604E) measurements were carried out from 0.1 Hz to 100 kHz with the amplitude of 5 mV. All electrochemical measurements were performed at 25 °C.

3. Results and discussion

3.1. Lithiation and delithiation to different potentials

Typical CV curves of a Li–S cell with PVDF binder are shown in Fig. 1. Both lithiation and delithiation capacities degraded rapidly with lithiation and delithiation cycling. Two separated cathodic

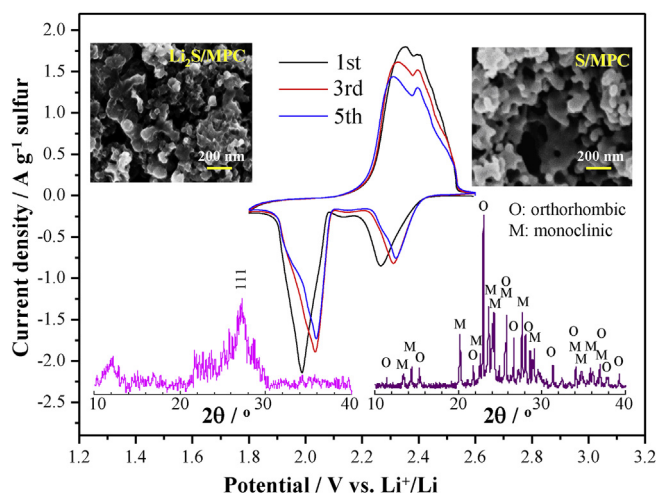


Fig. 1. CV curves of Li–S cell with PVDF as binder at 0.1 $mV s^{-1}$ scan rate and 25 °C. Inserts are morphologies (upper figures) and XRD patterns (lower figures) of S/MPC before (right) and after (left) lithiation.

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