



Inverse vulcanization of sulfur with divinylbenzene: Stable and easy processable cathode material for lithium-sulfur batteries



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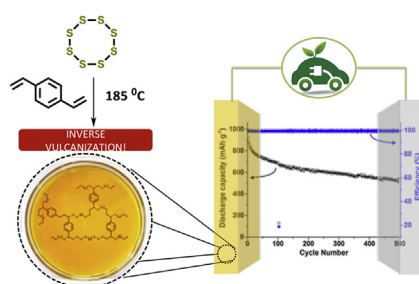
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HIGHLIGHTS

- Simple and low cost synthesis route for the active cathode material in Li-S battery.
- Use of copolymer as sulfur and divinylbenzene in Li-S cells.
- Good ultra long-term cycling performance of Li-S cells at high C/2 rates.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-Sulfur (Li-S) battery technology is one of the promising candidates for next generation energy storage systems. Many studies have focused on the cathode materials to improve the cell performance. In this work we present a series of poly (S-DVB) copolymers synthesised by inverse vulcanization of sulfur with divinylbenzene (DVB). The poly (S-DVB) cathode shows excellent cycling performances at C/2 and C/4 current rates, respectively. It was demonstrated poly (S-DVB) copolymer containing 20% DVB did not influence the electrochemical performance of the sulfur material, compared to elemental sulfur as high specific capacities over $\sim 700 \text{ mAh g}^{-1}$ at 500 cycles were achieved at C/4 current rate, comparable to conventional carbon-based S cathodes. However, the use of copolymer network is assumed to act firstly as sulfur reservoir and secondly as mechanical stabilizer, enhancing significantly the cycling lifetime. The Li-poly (S-DVB) cell demonstrated an extremely low degradation rate of 0.04% per cycle achieving over 1600 cycles at C/2 current rate.

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1. Introduction

Lithium-Sulfur (Li-S) battery technology is one of the promising candidates for next generation energy storage systems with low cost and high energy density. According to the complete reduction from elemental sulfur to lithium sulfide (Li_2S), sulfur is expected to

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deliver a specific capacity of 1675 A h Kg⁻¹. At the cell level, the best Li–S batteries offer specific energies on the order of 500–600 W·h/kg [1–5]. Furthermore, the elemental sulfur is naturally abundant, has low toxicity and it is a cheap raw material for chemical and petrochemical industry [6]. Beyond its interesting intrinsic properties, namely the high electrochemical capacity [7] and refractive indexes [6], sulfur possesses a very low conductivity and complex electrochemistry [8]. These two characteristics lead to a series of limitations on its performance as an active cathode material in batteries. Firstly, the cathodes need a large amount of conductive carbon additives to improve the low conductivity of sulfur which limits the real capacity of the batteries. Secondly, the chemical reactions involved in the Li–S cells generate several intermediates (lithium polysulfides (PS)), which subsequently form insoluble precipitate of Li₂S₂ and Li₂S [9,10]. Long chains PS, (Li₂S₈ and Li₂S₆) are dissolved in liquid electrolyte and cause parasitic reactions when they migrate towards the Li anode (loss of active materials, formation of insulating layer) [10]. This phenomenon, so called polysulfide shuttle, leads to very low battery efficiency, reduced cyclability and short cycle life [10,11].

To tackle the different problems related to the Li–S technology, different paths have been investigated and highlighted in recent reviews of Li–S batteries [5,10,12]. Most of the approaches were directed toward the protection of Li anode; the use of porous separators and development of new electrolytes; the use of structured microporous carbons, metal oxides and new binders in order to reduce the polysulfide shuttle problem [13–23].

In our opinion, a few efforts have been focused on modifying the chemistry of elemental sulfur itself as key parameter in Li–S batteries. Recently, Pyun and coworkers have proposed the inverse vulcanization of molten sulfur using low amount of dienes as route to prepare new sulfur polymers cathode [6]. The concept was demonstrated by crosslinking of elemental sulfur using 1,3-diisopropenylbenzene (DIPB) [6] which is an expensive crosslinker agent (DIPB) with slow copolymerization kinetics (alpha methyl group in the vinyl group). Other similar studies also have involved the use of expensive chemicals as cross-linkers. For instance, diethynylbenzene was used by Meng et al. to copolymerize sulfur at high temperature [29], 1,4-Diphenylbutadiene was used to prepare high sulfur content polymers as cathodic materials [31] or a thiophene monomer having allyl groups [32].

In this work we propose the inverse vulcanization of sulfur using divinylbenzene (DVB) to create a sulfur/organic polymer network with good chemical stability and easy processability. DVB is a well-known relatively cheap chemical commonly used as crosslinker in polymer industry. Compared to most inverse vulcanization reports that show reaction times between 1 and 2 h [29–32], the high reactivity of DVB monomer makes possible to prepare copolymers in a very fast way 5 min at low DVB contents and 15 min at high DVB content. This is even faster than the inverse vulcanization of sulfur using DIPB, which was the fastest inverse vulcanization reaction reported so far, taking place between 10 and 20 min [6]. In this paper, we report the synthesis and characterisation of sulfur–DVB copolymers (poly (S–DVB)), together with its promising electrochemical performance and long term testing as cathodes in Li–S batteries.

2. Experimental

2.1. Chemical synthesis & characterization

Elemental sulfur (purum p. a.; 99.5%) and divinylbenzene (DVB) (technical grade 80%; Sigma–Aldrich) were used as received.

The general reaction of inverse vulcanization of sulfur with DVB was performed as follows. In a round bottom flask equipped with a

magnetic stir bar elemental sulfur (9 g, 0.281 mol) was added under argon atmosphere. Then the flask was placed in an oil bath preheated at 185 °C. When the liquid sulfur showed a cherry red colour DVB (1 g, 0.0077 mol) was added. Two phases were observed but they became a single one with the reaction time. The solution was stirred until the vitrification of the media. Then the flask was placed in a liquid nitrogen bath in order to quench the reaction as well as to break the solid block. Yellow transparent crystals were obtained. It is worth pointing out that for the copolymers with DVB content superior to 20 wt% an additional step was done. In this case, the reaction was allowed to stir until a rise in the viscosity was observed and then the reaction was quenched in a liquid nitrogen bath. In this case, opaque and soft material was obtained. In order to promote all the reaction of the DVB with free sulfur a curing step at 120 °C during 3 h in the oven was performed and the result was a hard and transparent copolymer.

The composition of the synthesised solids was determined via FTIR spectroscopy using a Vertex 70 (Bruker) FTIR System spectrometer with the ATR setup which allowed for sample examination in the form of powder. The thermal characterization of the poly (S–DVB) was carried out in the DSC (Q2000, TA instruments) from –40 °C to 140 °C with a heating rate of 10 °C/min. Two cycles of heating were carried out. The thermogravimetric analyses (TGA) of the elemental sulfur and the poly (S–DVB) were determined on a Netsch STA with a heating rate of 10 °C/min under N₂. The molecular composition was elucidated by ¹H NMR. The NMR measurements of the DVB monomer and poly (S–DVB) 50 wt% of DVB were carried out on a Bruker AVANCE 400 spectrometer with CDCl₃-d₆ as solvent. The elemental composition and the chemical state of the constituent elements of the poly (S–DVB) surface were assessed by means of X-ray photoelectron spectroscopy (XPS) in an UHV system equipped with a hemispherical electron energy analyser PHOIBOS 150 (SPECS GmbH) and a twin Al/Mg anode - X-ray source XR50 (SPECS GmbH) operated at 12 keV and power 100 W. The XPS spectra were acquired in the fixed analyzer transmission mode with pass energy 20 eV. The XPS spectra were peak-fitted using CasaXPS data processing software. Quantification has been done using sensitivity factors provided by the elemental library of CasaXPS.

2.2. Li–S cell electrochemical characterization

The cathode was prepared using 60% of poly (S–DVB) 30% of Super C65 carbon black (C65) and 10% of PEO as binder, with a loading of 2 mg_S cm⁻². The mixture was dried and added to a solution in NMP to form the cathodic slurry. The final solid content 48–50% slurries were prepared by mechanical mixer (RW 20 digital, IKA) at 600 rpm agitation rate. These slurries were blade cast onto a carbon coated aluminium foil and dried at 60 °C under dynamic vacuum during 12 h before cell assembling. The poly (S–DVB) (dark brown solid (Fig. 1)b) was dry ball milled prior to the cathode preparation (3000 rpm for 3 h), turning into a fine pale brownish powder (Fig. 1). c) One layer of Celgard 2400 separator, soaked with 40 µL of 1 M solution of Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) in 1/1 (v/v) mixture of dimethoxyethane (DME) (Sigma–Aldrich) and dioxolane (DOL) (Sigma–Aldrich), containing 2% (wt.) of lithium nitrate (LiNO₃) (Sigma–Aldrich) as additive, was placed between electrodes. Vacuum drying of electrodes and cell crimping has been performed in a dry room with dew point below –50 °C. The electrochemical behavior of the obtained poly (S–DVB) electrodes was evaluated at different C-rates in coin cells (2032, Hohsen) with Li metal (0.5 mm, Chemetall) as anode electrode. The cyclability of coin cells was investigated within 1.7–2.6 V interval at various C-rate from C/10 to 1C (1C = 1672 mA g⁻¹). The cells were rested for 20 h and then cycled by BaSyTec Cell Test System (Germany) at 25 ± 1 °C controlled by air conditioning.

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