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Inverse vulcanization of bismaleimide and divinylbenzene by elemental sulfur for lithium sulfur batteries

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ABSTRACT

A novel approach to fabricate sulfur rich thermosets as materials for Li—S batteries is described. For this purpose, polybismaleimide copolymers were synthesized by reacting bismaleimide (BMI) monomer and elemental sulfur at 180 °C. Parameters such as monomers and feed ratios on the polymerization were studied. Divinylbenzenes were also used in the formulation to increase sulfur feed ratios up to 70 wt%. The thermal stability of the copolymers was also investigated by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). BMI based copolymers had shown excellent thermal stability and yielded up to 40% char yield at 800 °C. The obtained insoluble copolymers were used in Li—S battery applications. Thus, galvanostatic discharge–charge experiments were carried out to evaluate the electrochemical performance of these materials. Both 30% sulfur containing, poly(S-BMI)30%, and 70% sulfur containing, Poly(S-BMI-DVB)70%, composites exhibited a staircase voltage profile which is typical for Li—S batteries. These materials, as Li—S battery cathodes, demonstrated around 400 mA h/g specific capacities at 50 cycles.

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1. Introduction

Elemental sulfur has been recognized as a valuable chemical agent since antiquity and it was used as an antimicrobial drug, in gun powders and explosives and for medical applications, respectively [1]. Also, for decades, sulfur was in the center of the main pursuit in Alchemy with a fallacious ambitious to convert metals into gold. In 19th century, sulfur was recognized as vulcanization agent for natural rubber and found huge potential in industry. The vulcanization ability of sulfur stems from radical formation during heating thus can react easily with double bonds of polybutadienes [2,3]. The cost of such processes is relatively low because sulfur is the third most abundant element in fossil fuel after carbon and hydrogen. Natural-gas and petroleum refining operations produce vast amounts of elemental sulfur as by-product. And due to this vastness, the majority of sulfur produced cannot be consumed in industry and therefore, massive sulfur piles were raised in urban areas. Today, sulfur is mainly utilized in sulfuric acid production [4]. Some other applications include agricultural usage as pesticidal compound [5,6], synthesis of materials with high refractive indexes and materials with high transparency in the IR region for IR optical materials [7], and utilization of dynamic covalent character of S—S bonds for smart materials [8,9]. Apart from these conventional usages, a recent application of sulfur was reported for the reaction of molten sulfur and

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diisopropenylbenzene above 180 °C affording stable polymeric materials with high sulfur contents such as 80–90 wt% [10–12]. Interestingly, in contrast to pristine polysulfide which readily reverts back to cyclic S_8 structure, these polymers resist against auto-decomposition. It appears that vinylic monomers even in small amounts have a significant impact on the stability by decreasing the reversibility of S—S bonding in S_8 re-formation path. Thus, this reaction is called as ''inverse vulcanization". Generally, such copolymers could readily be processed into free-standing lenses that exhibit excellent IR transparency and high refractive indices. Besides, such lenses can be thermally healed due to dynamic covalent properties of S—S bonds [7,13,14]. By this way, damaged lenses and windows from these materials were reprocessed to recover their IR imaging performance. In a recent study from the authors' laboratory, completely diverse usage of elemental sulfur was reported. In this work, polybenzoxazines, known as high performance thermosets [15–22], were combined with elemental sulfur through simultaneous inverse vulcanization and ring-opening reactions. Notably, such strategy provided possibility to reduce curing temperature of benzoxazines usually occurs at high temperatures [23].

Sulfur has also applications in energy storage systems. At first, two oxysulfur cathode systems, Li-SO_2 and Li-$SOCl_2$, were studied yielding high energy density with excellent discharge characteristics [24,25]. However, the systems have persisted their severe safety problems over the years. Moving from oxysulfur to sulfur, elemental sulfur is used as cathode active material for rechargeable batteries, including well-known commercially available sodium–sulfur (Na–S) [26,27] as well as lithium–sulfur (Li—S) battery technologies [28]. Li—S batteries are considered to be one of the options as next generation energy storage system since it offers threefold increase in energy density compared with the present Li-ion batteries. Despite the considerable advantages of the Li—S batteries, there are several major issues that have prevented their practical realization and commercialization until recently. The problems originate from every cell compartment, namely sulfur cathode, lithium anode and liquid electrolyte, with the result of being a short cycle life, safety issues, low charging efficiency and a high self-discharge rate [29].

Although Li—S batteries have been studied since 1960s [30], they recently have regained great deals of attention [31]. During the past few years, researchers have mainly focused on solving the challenges associated with the sulfur cathode mostly using conductive porous carbon skeletons to confine sulfur [32–38]. Moreover, electroactive polymers containing S—S units and sulfur based solid-state electrolyte systems have also been developed. Despite recent advances in enhanced electrode and electrolyte materials for Li—S batteries, the development of facile chemistry and the use of inexpensive materials amenable to large scale production still remains a significant challenge. Apart from this issue, it was found that high sulfur content in a Li—S battery is particularly important to ensure superior performance compared to Li–ion batteries [39,40]. Thus, scalable synthetic methods for polymers with high sulfur content became important in materials science. Recently, encapsulation of S_8 with core-shell poly(N-vinyl pyrrolidone) colloids afforded high capacity Li—S batteries and this process shown to be scalable [41]. Nevertheless, quest for well-defined materials with high sulfur content is a severely ongoing challenge. In this respect, inverse vulcanization as a scalable reaction to prepare high sulfur content polymers for Li—S batteries became an appealing method. These sulfur copolymers are electrochemically active and could serve as the electroactive material in Li—S battery cathodes. Batteries fabricated from inverse vulcanization of S_8 and 1,3-diisopropenylbenzene (DIB) exhibited enhanced capacity up to 1000 mA h/g and device lifetimes [4,10–12]. It should be emphasized that the chemistry used for such materials allows design flexibility for alternative systems. Accordingly, this paper investigates the usage of bismaleimides (BMI) as an alternative monomer instead of DIB. By this way, tailored cathode materials for Li—S batteries were produced using BMI alone or BMI and divinylbenzenes (DVB). These materials were characterized in terms of their cycling performances in a Li—S cell and their thermal stability.

2. Experimental

2.1. Materials

Sulfur (S_8, colloidal powder, reagent grade, Aldrich), 1,1′-(Methylenedi-4,1-phenylene)bismaleimide (Acros, 95%), Divinylbenzene (technical grade, Aldrich, 80%) were used as received.

2.2. Characterization

FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One spectrometer. Differential Scanning Calorimetry (DSC) was performed on Perkin–Elmer Diamond DSC from 30 °C to 320 °C with a heating rate of 10 °C min under nitrogen flow. Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 20 °C min under nitrogen flow.

2.2.1. Electrochemical measurements

For the electrode preparation, 80 wt% different amount of sulfur containing polymer composites and 20 wt% Ketjen black first were ball milled for 15 min at 150 rpm. Then, they were used as electrode materials in a classical two-electrode Swagelok-type™ cell. Galvanostatic cycling measurements were performed using 1 M LiTFSI containing tetraethylene glycol dimethyl ether/dioxalane (TEGDME/DOL) mixture electrolyte with C/10 current density (which corresponds to the current

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