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Inverse Vulcanization of Elemental Sulfur to Prepare Polymeric Electrode Materials for Li−S Batteries

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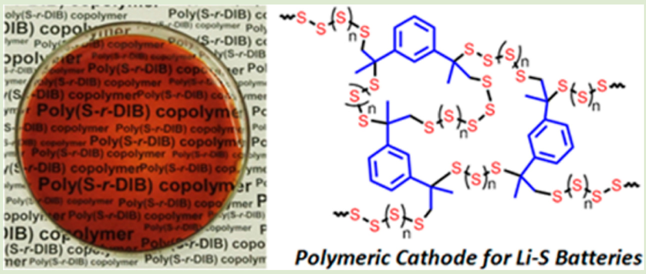
Supporting Information

ABSTRACT: Sulfur-rich copolymers based on poly(sulfur-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-DIB)) were synthesized via inverse vulcanization to create cathode materials for lithium−sulfur battery applications. These materials exhibit enhanced capacity retention (1005 mAh/g at 100 cycles) and battery lifetimes over 500 cycles at a C/10 rate. These poly(S-*r*-DIB) copolymers represent a new class of polymeric electrode materials that exhibit one of the highest charge capacities reported, particularly after extended charge−discharge cycling in Li−S batteries.



Polymeric Cathode for Li-S Batteries

Lithium−sulfur (Li−S) batteries are an intriguing candidate for electric vehicle (EV) applications because of the high theoretical specific capacity of sulfur at 1672 mAh/g, as well as the high specific energy of approximately 2600 Wh/kg.[1] While initial capacities of 1200 mAh/g are fairly common for standard Li−S batteries, rapid fading of charge capacity is observed.[2] This poor long-term performance has been associated with both "shuttling" of linear polysulfides dissolved into the electrolyte medium, in addition to irreversible deposition of solid lithium sulfide (Li_2S) and other mixtures of insoluble discharge products (Li_2S_2, Li_2S_3) on the cathode.[3] The addition of lithium nitrate ($LiNO_3$) to the battery electrolyte has successfully led to suppression of polysulfide shuttling, enabling high Coulombic efficiencies.[4,5] However, repeated cycling in Li−S batteries, ultimately leads to insoluble sulfide deposits that are encrusted on the carbon cathode framework resulting in both mechanical and electrical detachment from the electrode, leading to failure.

Since the recent advance of Nazar et al.,[6] a number of reports have demonstrated the preparation of sulfur-based nanocomposite materials as a route to improve the performance of Li−S batteries. Subsequent strategies to prepare enhanced cathode materials have aimed to encapsulate or sequester the elemental sulfur (S_8), which enabled in many systems excellent retention of charge capacity in Li−S batteries beyond 1000 charge−discharge cycles.[7−13] However, challenges still persist in the creation of chemistry for sulfur-based cathode materials that are inexpensive and amenable to large scale production, while retaining high charge capacity and electrochemical stability.[14]

Herein, we report the synthesis and characterization of poly(sulfur-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-DIB)) copolymers and explore composition effects on the electrochemical performance of these copolymers as the active cathode material in Li−S batteries. We previously reported on the synthesis of these copolymers via a process termed inverse vulcanization and demonstrated that Li−S batteries fabricated from these materials exhibited high specific capacity (823 mAh/g at 100 cycles).[15] In this report, we explore for the first time with these sulfur copolymers a direct structure−property correlation of copolymer composition with electrochemical properties to afford optimal polymeric materials for these battery systems. We further demonstrate improved Li−S battery lifetimes out to 500 charge−discharge cycles with excellent retention of charge capacity. The enhanced battery performance observed with these polymeric active materials arises from in situ generation of organosulfur additives (from DIB units) and linear polysulfide segments (Li_xS_y) via

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electrochemical fragmentation of the initial poly(S-*r*-DIB) copolymer. We propose that these organosulfur species suppress irreversible deposition of insoluble discharge products (Li_2S_3, Li_2S_2, Li_2S) and are mechanistically distinct from recent Li−S battery systems that nanoencapsulate sulfur to suppress dissolution of linear polysulfides. This sulfur based copolymer is also a new addition to an emerging class of electroactive polymers that have been used as polymeric electrodes for Li batteries, examples of which include conjugated polymers and nitrosyl radical functional polymers.[16−27] To our knowledge, these novel sulfur copolymers exhibit one of the highest capacities of any wholly polymeric material serving as the active material in batteries cycled to extended lifetimes.

The Li−S battery using S_8 as the active material in the cathode functions as a liquid electrochemical cell, where discharge causes the reduction of S_8 into higher order linear polysulfides (Li_2S_8, Li_2S_6, Li_2S_4) that fully dissolve into the electrolyte medium.[3] Continued discharge results in the soluble higher order polysulfides being further reduced to insoluble lower order sulfides (e.g., Li_2S_2, Li_2S) that redeposit onto the carbon-binder cathode framework. Li−S batteries fabricated with poly(S-*r*-DIB) copolymers as the active cathode material are identical to traditional Li−S batteries using S_8, with the exception of soluble organosulfur species (i.e., thiolated DIB units) generated upon discharge of the copolymer. These organosulfur products co-deposit with other insoluble lower order polysulfides onto the carbon-binder cathode framework at the end of discharge, which we propose "plasticizes" these insoluble polysulfide discharge products, enabling more efficient battery cycling. This hypothesis was readily tested by the preparation and electrochemical evaluation of poly(S-*r*-DIB) copolymers with systematic variation of DIB content. It is important to note that poly(S-*r*-DIB) copolymers with a high content of sulfur initially exhibit poor solubility toward the electrolyte medium when cast onto the cathode, but form soluble products after discharge to lower polysulfides.

The poly(S-*r*-DIB) copolymers employed in this study were synthesized by inverse vulcanization through direct dissolution and copolymerization of DIB in liquid sulfur.[15,28,29] This process is essentially a bulk copolymerization of molten sulfur and DIB heated above the floor temperature (T_f) for the free radical ring-opening polymerization (ROP) of S_8 (Figure 1). The copolymerization of S_8 with varying DIB feed ratios from 1 to 50% by mass was conducted to prepare sulfur-based copolymer materials, where the incorporation of electroactive S−S bonds was directly controlled. Sulfur copolymers with 50% by mass DIB were found to be soluble in organic solvents (facilitating solution characterizations such as NMR and SEC),[15] while higher compositions of sulfur afforded sparingly soluble materials.

To investigate composition effects on battery performance, poly(S-*r*-DIB) copolymers were fabricated into 2032 type battery coin cells and cycled at a rate of C/10 (167.2 mA/g) with lithium foil employed as the anode (Figure 2). The sulfur copolymers with 1% by mass DIB exhibited cycling performance comparable to elemental sulfur, whereas copolymers with compositions of 20% or greater by mass DIB exhibited little to no improvement over elemental sulfur. However, poly(S-*r*-DIB) copolymers with compositions of 5, 10, and 15% by mass DIB all exhibited high initial capacities, low initial capacity loss, and consistently reduced capacity loss per cycle.

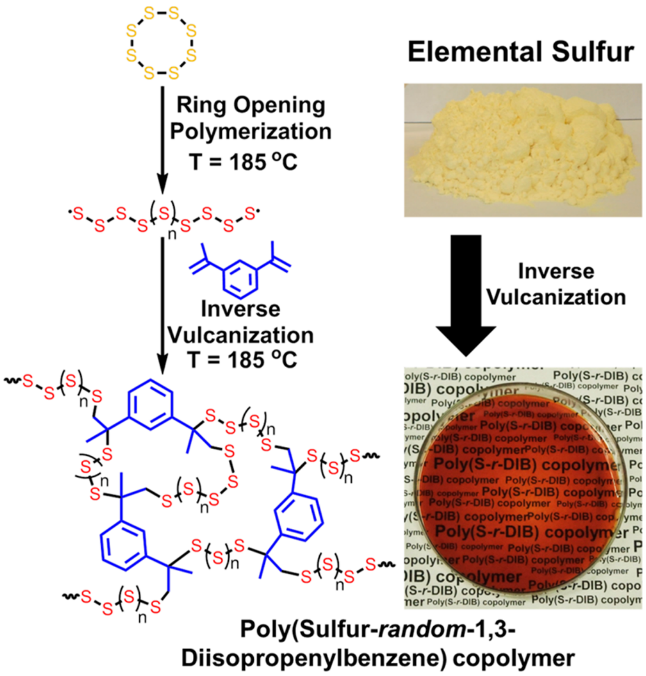

Figure 1. Synthetic scheme for the inverse vulcanization process yielding poly(sulfur-*random*-1,3-diisopropenylbenzene) copolymers.

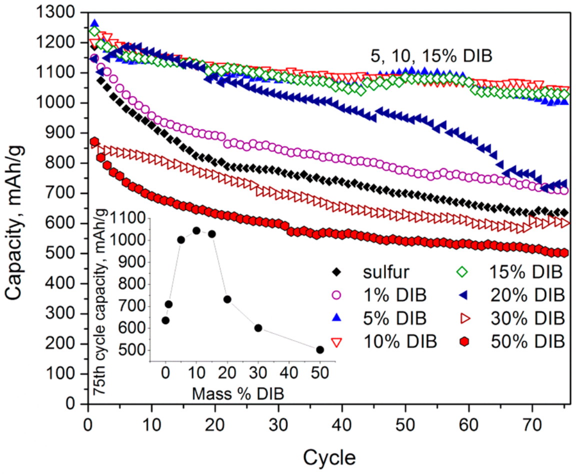

Figure 2. Cycling performance of Li−S batteries from sulfur copolymers of varying composition (0−50% by mass DIB) up to 75 cycles. Inset figure shows a plot of the specific capacity measured at the 75th cycle against sulfur copolymer composition.

From this survey of compositional effects on the electrochemical properties, copolymers with a composition of 10% by mass DIB were found to perform optimally (inset, Figure 2). Preliminary studies of this copolymer as an active material in Li−S battery cathodes exhibited a specific capacity of 823 mAh/g at 100 cycles.[18] Further optimization of cathode coating methods has yielded significant improvement in both initial capacity and suppression of capacity fading. An initial capacity of 1225 mAh/g was observed in the Li−S batteries fabricated in the present study and low capacity loss was exhibited as noted by the capacities of 1005 mAh/g at 100 cycles and 817 mAh/g at 300 cycles with a Coulombic efficiency of 99% throughout. Currently this system has been extended to 500 cycles while retaining a significant capacity of 635 mAh/g (Figure 3). Additionally, these sulfur copolymers were capable of sustaining high capacities at faster C-rates producing over 800 mAh/g at 1C (inset, Figure 3). Although, at 2C, the capacity is

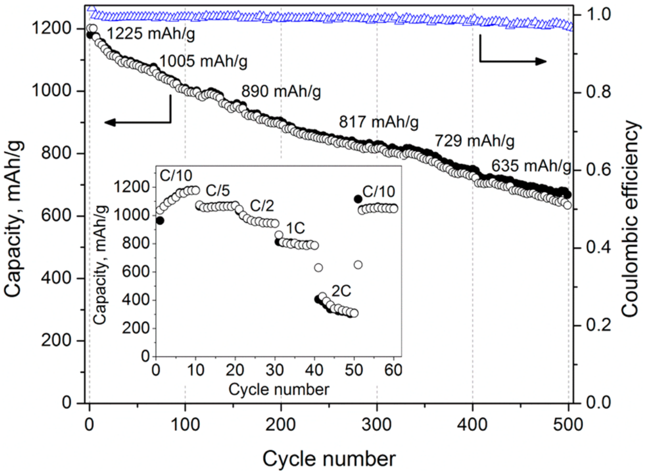

Figure 3. Cycling performance of Li–S battery from 10% by mass DIB copolymer batteries to 500 cycles with charge (filled circles) and discharge (open circles) capacities, as well as Coulombic efficiency (open triangles). The C-rate capability of the battery is shown in the figure inset.

significantly reduced as the charge/discharge rate becomes comparable with the inherent rate of diffusion required for the complete sulfur electrochemical conversion processes.

For further insight into the enhanced performance of poly(S-*r*-DIB) copolymers in Li–S batteries, the normalized charge and discharge profiles of batteries fabricated from copolymers with different DIB concentrations (5–50% by mass) were compared. While changes in the voltage versus normalized capacity curves with DIB content are observed, the curves have the same basic salient characteristics for all compositions. This fact suggests that similar reactions occur for both the S_8 and poly(S-*r*-DIB) copolymers proving that both S–S and organosulfur moieties in the copolymer were electroactive in both voltage regimes (Figure 4).

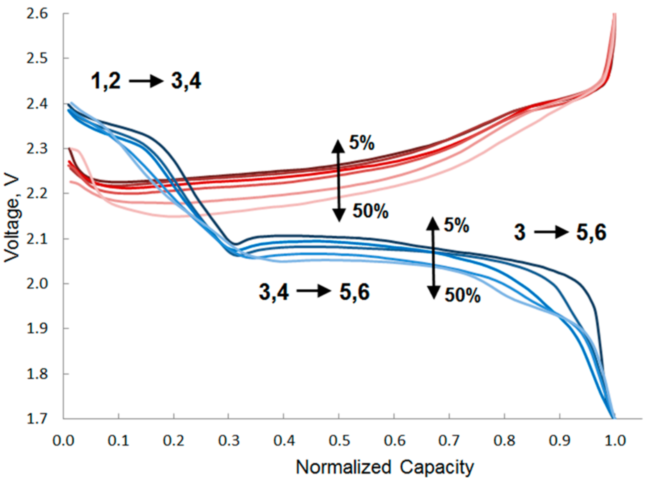

Figure 4. Normalized charge and discharge profiles of copolymer cathodes with different DIB composition. Charging profiles for 5% (dark red), 10%, 20%, 30%, and 50% (light red) and discharging profiles for 5% (dark blue), 10%, 20%, 30%, and 50% (light blue). Proposed assignments of chemical products formed during the discharge cycles are indicated in Figure 5a.

In the voltage versus normalized capacity plots, the effect of DIB concentration was most evident in the low voltage plateau of the charge and discharge profiles, where both profiles shifted toward lower voltage with an increase in DIB content (Figure 4). This trend provided support for the proposed mechanism of DIB-bound sulfur codeposition within a matrix of lower order sulfide discharge products (i.e., Li_2S_3, Li_2S_2, Li_2S). Initially during discharge of poly(S-*r*-DIB) copolymers in the high voltage plateau regime, we propose the formation of both higher order organosulfur DIB units and Li_2S_8 (**1** and **2** in Figure 5a); with further reaction generating organosulfur DIB units (with shortened oligosulfur units) and Li_2S_4 (**3** and **4** in Figure 5a). Continued discharge into the lower voltage plateau resulted in the conversion of **3** and **4** into fully discharged organosulfur DIB products and insoluble mixtures of Li_2S_3 and Li_2S_2 (**5** and **6** in Figure 5a), which codeposited on the cathode, as supported by XPS (see Supporting Information). Furthermore, the improved battery performance for these copolymers was not primarily from the electrochemical properties of organosulfur DIB discharge products, but rather that these organosulfur units function as "plasticizers" in the insoluble Li_2S_3/Li_2S_2 discharge product phase. Hence, we

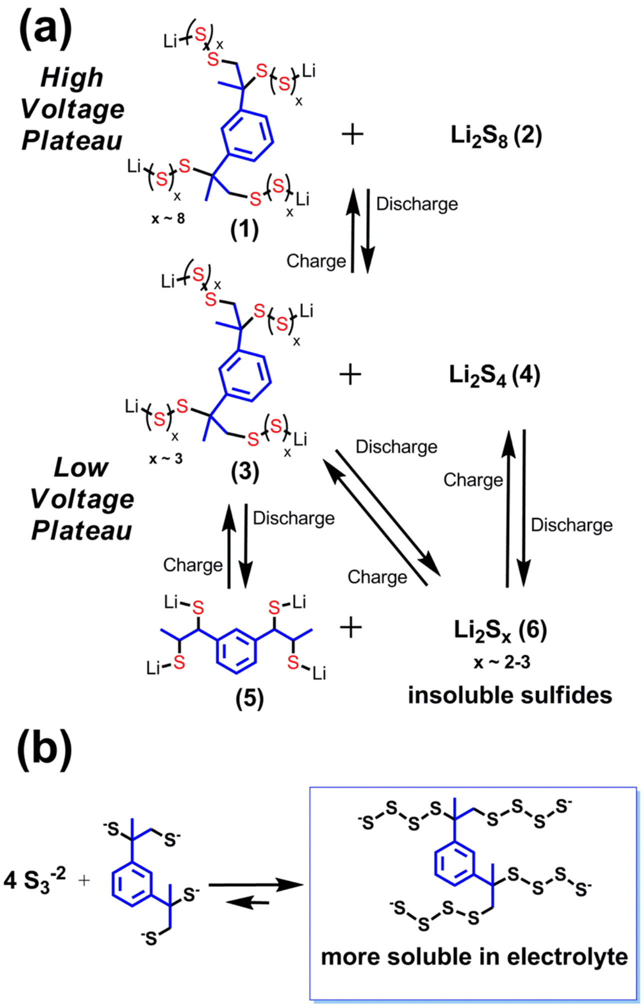

Figure 5. (a) Proposed electrochemisty of poly(S-*r*-DIB) copolymers in Li–S batteries; (b) proposed equilibrium between lower polysulfides and organosulfide discharge products, which at higher DIB compositions favors formation of soluble higher order polysulfides. Li^+ cations omitted for clarity due to the presence of excess cations in the electrolyte.

propose that the enhanced cycle stability of these Li−S batteries arises from the presence of these organosulfur units dispersed in the insoluble lower order sulfide phases to suppress irreversible deposition of these discharge products to abate capacity losses. However, at higher compositions of DIB in the copolymer (above 15% by mass), these organosulfur discharge products were presumably more concentrated in the electrolyte and in equilibrium with other free polysulfides, (e.g., Li_2S_3) to reform high order polysulfides (see Figure 5b). These high order polysulfides were more soluble in the electrolyte medium and hence, did not efficiently co-deposit with lower polysulfides on the cathode (see Supporting Information, Figure S5), resulting in rapid capacity fading, as shown in Figure 2.

The synthesis of sulfur copolymers via inverse vulcanization for enhanced cathode materials in Li−S batteries is reported. We demonstrate that this inexpensive, bulk copolymerization can sufficiently modify the properties of sulfur to improve the battery performance without the need for nanoscopic synthesis or processing. This system also demostrates for the first time that high capacity polymeric electrodes can be fabricated while also suppressing capacity fading after extended battery performance to 500 cycles.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental details for the preparation and characterization of sulfur copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

‡These authors contributed equally (A.G.S. and J.J.G.).

Notes

The authors declare the following competing financial interests: Professor Pyun is the cofounder of Innovative Energetics, which is a company focused on sulfur materials developed for Li−S batteries.

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