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Abstract: Poly[sulfur-random-(1,3-diisopropenylbenzene)] copolymers synthesized via inverse vulcanization represent an emerging class of electrochemically active polymers recently used in cathodes for Li−S batteries, capable of realizing enhanced capacity retention (1,005 mAh/g at 100 cycles) and lifetimes of over 500 cycles. The composite cathodes are organized in complex hierarchical three-dimensional (3D) architectures, which contain several components and are challenging to understand and characterize using any single technique. Here, multimode analytical scanning and transmission electron microscopies and energy-dispersive X-ray/electron energy-loss spectroscopies coupled with multivariate statistical analysis and tomography were applied to explore origins of the cathode-enhanced capacity retention. The surface topography, morphology, bonding, and compositions of the cathodes created by combining sulfur copolymers with varying 1,3-diisopropenylbenzene content and conductive carbons have been investigated at multiple scales in relation to the electrochemical performance and physico-mechanical stability. We demonstrate that replacing the elemental sulfur with organosulfur copolymers improves the compositional homogeneity and compatibility between carbons and sulfur-containing domains down to sub-5 nm length scales resulting in (a) intimate wetting of nanocarbons by the copolymers at interfaces; (b) the creation of 3D percolation networks of conductive pathways involving graphene-like outer shells of aggregated carbons; (c) concomitant improvements in the stability with preserved meso- and nanoscale porosities required for efficient charge transport.

Key words: S(T)EM, tomography, EELS, EDXS, Li−S batteries

INTRODUCTION

Rapidly growing demand for more effective electrochemical energy storage (EES) constantly requires high-energy density electrode materials to push electrochemical power sources beyond the barriers of current Li-ion batteries. Interest in prospective candidate Li−S and Li−O2 EES technologies is increasing because they offer the interconversion of chemical and electrical energy on a relatively short time scale, theoretically with higher efficiency than that of a heat engine and without releasing polluting gas emissions to the environment (Bruce et al., 2012; Li et al., 2015). However, high-energy density electrochemical rechargeable batteries should also be safe, inexpensive, nontoxic, and reliable through thousands of charge−discharge cycles to deliver long-term discharge capacities above 1,000 mAh/g and specific energy densities above 600 Wh/kg required for emerging practical applications, e.g., in high-endurance unmanned aerial vehicle systems (UAVs) and electric vehicles capable of traveling over 500 km on a single charge (Ji et al., 2009; Oleshko et al., 2009a, 2015a, 2015b). Specifically, light-weight rechargeable Li−S batteries based on the Li/S redox couple generating ~2.2 V with respect to Li+/Li° have the highest theoretical specific capacity of 1,672 mAh/g of active material among all solid elemental redox couples and a theoretical specific energy of 2,567 Wh/kg, assuming a complete two-electron reaction (Peled et al., 1989; Marmorstein et al., 2000):  

$$16Li^+ + S_8^-> 8Li_2S.$$  (1)

In practice, specific discharge capacities for reaction (1) often range from 800 to 1,400 mAh/g, which is four to five times that of current Li-ion technology (Ji et al., 2009; Xu et al., 2015). Moreover, the low cost and abundance of sulfur make Li−S batteries an attractive alternative to Li-ion batteries for commercialization during the next decade.
(Fang & Peng, 2015; Li et al., 2015). As a first practical proof of concept, the UAV Zephyr-7 (QinetiQ, Farnborough, UK) has established an official world endurance record for its flight from July 9 to July 23, 2010 (over 2 weeks) lasting 336 h and 22 min, being powered and charged with Si solar arrays (Unisolar, Quezon City, Philippines) during the day and then Li–S batteries (350 W h/kg; Sion Power, Tucson, Arizona, USA) by night (BBC News Science & Environment, 2010). Low temperature performance down to \( T = -60^°C \) with nonaqueous liquid electrolytes (Akridge et al., 2004) enables high-capacity Li batteries and 22 min, being powered and charged with Si solar arrays

Sony Corp. announced plans to introduce in 2020 new

lights (Airbus Defense & Space, 2014). In December 2015, Sony Corp. announced plans to introduce in 2020 new high-capacity Li–S batteries and Mg–S batteries, potentially with an energy density exceeding 1,000 W h/L that will enable smartphones and other devices to run 40% longer, which will also be 30% more compact while maintaining current run times (Nikkei Asian Review, 2015).

Although the demonstrated energy density of 350 W h/kg far exceeds that of current Li-ion systems, Li–S batteries have significantly suffered due to limited lifetime from either poor electrode rechargeability and limited rate capability or fast capacity fading and a poorly controlled Li/electrolyte interface (Bruce et al., 2012; Fang & Peng, 2015; Li et al., 2015). Initial capacities of 1,200 mAh/g are fairly common, but retaining this capacity out to several hundred cycles remains challenging. The poor long-term performance is mainly associated with the “shuttling” of linear polysulfides dissolved in the electrolyte from the cathode to the anode where they are reduced to lower polysulfides, which are then transported back to the cathode. Unlike insertion cathodes with layered structures, during cycling sulfur undergoes a series of bulk topochemical transformations which involve various soluble polysulfides, \( \text{Li}_2\text{S}_n \) (\( n = 8, 6, 4, 3 \)) and finally insoluble sulfides, \( \text{Li}_2\text{S}_2 \) and \( \text{Li}_2\text{S} \) (Ji & Nazar, 2010; Xu et al., 2015):

\[
\text{Anode: } \text{Li} = \text{Li}^+ + e^- \\
\text{Cathode: } \text{S}_8 \rightarrow \text{Li}_2\text{S}_8 \rightarrow \text{Li}_2\text{S}_6 \rightarrow \text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_3 \rightarrow \text{Li}_2\text{S}_2 \rightarrow \text{Li}_2\text{S} \quad \text{(discharging)},
\]

\[
\text{Cathode: } \text{Li}_2\text{S} \rightarrow \text{Li}_2\text{S}_2 \rightarrow \text{Li}_2\text{S}_3 \rightarrow \text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_6 \rightarrow \text{Li}_2\text{S}_8 \rightarrow \text{S}_8 \quad \text{(charging)}.
\]

As a result of reactions (2)–(4), utilization of the active cathode material in Li–S batteries is limited by the following factors (Oleshko et al., 2009a; Bruce et al., 2012; Helen et al., 2015; Xu et al., 2015): (a) the insulating nature of orthorhombic sulfur \( (5 \times 10^{-30} \text{S/cm at } 25^°C) \), (b) losses due to the formation of insoluble lithium sulfides, (c) an often rough dendritic Li anode morphology, and (d) the large volumetric expansion of sulfur (80%) during lithiation, which may cause capacity fading and limited cycle life. The gradual losses of active mass from the sulfur–carbon cathode into the electrolyte and onto the Li metal anode can lead to parasitic “shuttle” reactions followed by severe self-discharge, low Coulombic efficiency, and capacity decay (Ji et al., 2011b; Bruce et al., 2012; Xu et al., 2015).

The contamination of polysulfide species on the Li metal anode is equally, if not more severely, damaging to long-term cell performance. Initially, smooth Li metal anodes may continuously transform into porous or mossy Li metal structures, which cause its gradual erosion and an uncontrolled formation of dendrites (Aurbach et al., 2009, Huang et al., 2014; Cao et al., 2015). The latter may present safety issues, particularly at high charging rates. The electrochemical corrosion can repeatedly expose new Li surface areas that further react with the electrolyte to form unstable solid-electrolyte interface (SEI) layers, thus increasing internal cell resistance and accelerating capacity fade (Elazari et al., 2011; Jayaprakash et al., 2011; Vaughey et al., 2014). For Li–S batteries, where Li metal is coupled with sulfur cathode, the deposition and reduction of insoluble short-chain polysulfides on a Li anode partially mitigate the dendrite growth (Suo et al., 2013). The Li erosion, however, is compounded with the presence of dissolved polysulfides that are also involved in the continuous SEI formation. LiNO\(_3\) used as an electrolyte additive, helps to suppress deleterious reactions between polysulfides and Li, resulting in improved cell life (Aurbach et al., 2009; Cao et al., 2015). As the discharge proceeds, soluble high-order polysulfides are reduced to insoluble \( \text{Li}_2\text{S}_2 \) and \( \text{Li}_2\text{S} \) discharge products according to reactions (2)–(4). The final sulfides are insoluble in the nonaqueous ethereal solvents usually used in electrolytes and deposit as hard, intractable solids on the cathode surface (Oleshko et al., 2009a, 2009b). The volume expansion due to the formation of \( \text{Li}_2\text{S} \) can generate significant mechanical stress on the cathode framework (Islam et al., 2015).

As the pioneering research on filling of dispersed mesoporous conductive carbons with molten sulfur initiated by several groups, e.g., (Wang et al., 2012; Liang et al., 2009; and Scordilis-Kelley et al., 2009), a number of reports have demonstrated the preparation of sulfur-based nanocomposite cathodes (Li et al., 2015). These strategies typically encapsulate the orthorhombic \( \alpha \)-S (and electrochemically generated lithium polysulfides) into the conductive matrix, which may comprise carbon nanoparticles, graphene, or core-shell colloids, to create enhanced composite cathodes for Li–S batteries (Yang et al., 2010; Cao et al., 2011; Demir-Cakan et al., 2011; Elazari et al., 2011; Jayaprakash et al., 2011; Ji et al., 2011b, 2011c; Li et al., 2011; Wu et al., 2011; Schuster et al., 2012; Zeng et al., 2015). Cui and co-workers (Seh et al., 2013) showed that yolk-shell \( \text{S}_n–\text{TiO}_2 \) colloids exhibit high capacity retention and extended lifetimes achieving roughly 700 mAh/g at 1,000 cycles at a C/2 rate (836 mAh/g). They also have developed a simplified one-pot dispersion polymerization method to prepare these types of core-shell colloids: an approach that has also demonstrated

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*Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.
the excellent capacity retention out to 1,000 cycles with a capacity decay as low as 0.046%/cycle (Li et al., 2013). Alternatively, the use of polyacrylonitrile (PAN) (Wang et al., 2003), sulfide polymers (e.g., 2,5-dimeracapo-1,3,4-thiadiazole) (Liu et al., 1991a, 1991b; Chao et al., 2011), and vulcanized polyaniline nanotubes (Xiao et al., 2012) has been investigated as a route for electroactive cathode materials. More recently, processing or carbonization with Li$_2$S salts has been explored to create bulk electroactive materials for advanced Li–S cathodes (Yang et al., 2010, 2012; Yao et al., 2014). A cycle life of over 1,000 charge–discharge cycles at a capacity of 1,470 mAh/g for cells comprised of prelithiated Si–carbon and all-carbon (non-Li) anodes coupled with sulfur-infused porous hollow sphere cathodes have been demonstrated (Brückner et al., 2013). Various designs of all solid-state Li–S batteries have been reported to obviate the issues associated with liquid electrolytes (Hayashi et al., 2003; Hassoun & Scrosati, 2010a, 2010b; Hassoun et al., 2011; Hassoun et al., 2012; Kinoshita et al., 2014; Chen & Adams, 2015). All of these systems represent advances in the creation of emerging electroactive materials to improve the electrochemical performance of cathodes for the next generation of high-energy density Li–S batteries. However, significant challenges still persist in the development of chemistries and electrode materials that are inexpensive and amenable to large-scale production, while retaining high charge capacity and electrochemical stability during a prolonged cycle life.

In order to enhance the performance of Li–S batteries, Pyun and co-workers (Chung et al., 2013; Simmonds et al., 2014; Griebel et al., 2014a, 2014b, 2015; Lim et al., 2015) have introduced a new synthetic route, termed inverse vulcanization, to prepare electroactive organosulfur polymers as alternative cathode materials for Li–S batteries (see also Kim et al., 2015). This approach represents an innovative alternative strategy to the aforementioned encapsulation schemes (Ji et al., 2009).

The sulfur copolymer-based cathodes exhibit an initial specific discharge capacity of 1,225 mAh/g, and retain high reversible specific discharge capacity and cycle stability (1,005 mAh/g at 100 cycles at rate = C/10) (Chung et al., 2013; Griebel et al., 2014a, 2014b; Simmonds et al., 2014). The poly [sulfur-random-(1,3-diisopropylbenzene)] [poly(S-r-DIB)] copolymers are part of an emerging class of electroactive polymers that can be utilized as electrode materials for Li–ion batteries such as conjugated conductive polymers, sulfide polymers, and nitrpsoyl radical polymers (Liu et al., 1991a, 1991b; Tatsuma et al., 1995; Kiya et al., 2007; Chao et al., 2011; Griebel et al., 2014a, 2014b). We previously examined the electrochemical properties of the cathodes utilizing poly[S-DIB] copolymers in Li–S cells and found that a poly[S-DIB] copolymer with 10% by mass of disopropynlbenezene (DIB) exhibits high specific capacity and cycle stability of 823 mAh/g at 100 cycles (Chung et al., 2013). However, the fundamental mechanisms responsible for electrochemical performance and underlying processing–structure–property correlations for new electroactive organosulfur polymeric materials have yet to be identified.

In the last several years, remarkable progress has been made in the development of advanced characterization techniques enabling deeper mechanistic understanding of the Li–S system and improving further the electrochemical performance of sulfur–carbon composite cathodes. Among the instrumental methods used for such purposes, high-resolution scanning and transmission electron microscopies (S/(T)EM) along with their associated techniques such as diffraction, electron energy-loss (EEL) and energy-dispersive X-ray (EDX) spectroscopies, tomography, and holography play an increasingly important role. Both analytical SEMs and TEMs are often employed for obtaining copious morphological, crystallographic, and chemical information down to the atomic level for the determination of structure–property relationships in electrode materials for Li–S batteries (Ji et al., 2009; Oleshko et al., 2009a; Scordilis-Kelley et al., 2009; Elazari et al., 2010; Cao et al., 2011; Demir-Cakan et al., 2011; Jayaprakash et al., 2011; Ji et al., 2011a, 2011b, 2011c; Li et al., 2011; Kim et al., 2013; Helen et al., 2015; Li et al., 2015; Wu et al., 2015; Yan et al., 2015). S/(T)EM methods permit real-time imaging and examination of Li–S batteries during galvanostatic testing of charge/discharge electrochemical reactions in situ (Xu et al., 2014; Tickey et al., 2015). In situ and ex situ S/(T)EM also enable probing of compression effects and the formation and spatial distribution of the SEI under varying processing conditions such as temperature and pressure (Oleshko et al., 2009a, 2009b; Xu et al., 2014). The research can be conducted using environmentally protected loading/transfer cell holders specifically designed for characterization and electrochemical processing of air-sensitive materials (Oleshko et al., 2009b; Elazari et al., 2010; Ruzmetov et al., 2012; Oleshko et al., 2014; Xu et al., 2014; Tickey et al., 2015). To be suited for real-time electrical testing in a S/(T)EM, a battery set-up, however, should have small dimensions (about 10 μm × 30 μm × 100 nm) and therefore the working current should be in the range of a few picoamperes. The latter is necessary to ensure that the actual current density will not exceed a few or tens of mA/cm$^2$; otherwise the batteries may catastrophically fail.

Complex interfacial phenomena and phase transformations that govern the operation of Li–S batteries vitally require reliable three-dimensional (3D) nanoscale characterization of their morphology and chemistry which is directly related to the capacity and electron-ion transport characteristics. However, Li-based batteries are usually sensitive to both environmental and radiation damage in the S/(T)EM, as Li as a light metal is vulnerable to knock-on displacement (Levin & Muller, 2013). The liquid electrolytes and labile SEI layers could be easily disrupted by ionization damage as well. Lowering accelerating voltage down to 20−60 kV could help reduce the knock-on damage. Sulfur is also generally problematic for electron microscopy because of its relatively high vapor pressure ~6 × 10$^{-7}$ Torr at room temperature, which is caused by relatively weak van der Waals intermolecular bonding between covalently bonded S$_8$ molecular units (Ferreira & Lobo, 2011). As a result, sulfur readily sublimates in a typical TEM vacuum (7 × 10$^{-9}$ Torr) with a rate of ~10$^{12}$ atom/cm$^2$/s or about one monolayer per second (Levin et al., 2014). The optimal imaging and
analysis conditions in such case could be achieved by several means, i.e., (a) by freezing a specimen to cryogenic temperatures with liquid nitrogen; (b) by encapsulation using suitable polymeric materials, e.g., PAN or in micropores of a host matrix; and (c) by employing an open air/low-vacuum S(T)EM (Wang et al., 2003; Ji et al., 2009; Oleshko et al., 2009a, 2009b; Scordilis-Kelley et al., 2009; Elazari et al., 2010, 2011; Cao et al., 2011; Jayaprakash et al., 2011; Levin & Muller, 2013; Levin et al., 2014).

In this study, we explore the origins of the enhanced capacity retention by characterizing the multiscale 3D structural architectures of composite poly(S-r-DIB)-based cathodes with DIB content of 0, 10, and 50% by mass in relation to the electrochemical performance, conductivity, and physico-mechanical stability. We employ high spatial resolution analytical electron microscopy, including conventional amplification (SAED), multimode bright-electron microscope (HRTEM), selected-area electron diffraction (SAED), multimode bright-field- (BF)/annular dark-filed (ADF)-/high-angle ADF (HAADF)-STEM coupled with multivariate statistical analysis (MSA), tilt-angle STEM electron tomography (ET), and correlated energy-dispersive X-ray and electron energy-loss spectroscopic imaging (EDX/EEL-SI) tomography (ET), and correlative energy-dispersive X-ray and EDX spectroscopic analyses of the cathodes were performed at 300 kV in a Schottky field-emission FEI Titan 80–300 analytical S(T)EM (FEI, Hillsboro, Oregon, USA) with a point-to-point resolution of 0.19 nm and information limit below 0.1 nm. For high spatial resolution EDXs and EELS nanoprobe analyses, STEM mode was employed. The instrument was equipped with a Fischione 3000 model HAADF detector (E.A. Fischione Instruments, Inc., Export, Pennsylvania, USA), FEI BF- and ADF-STEM detectors, a Gatan Enfina electron spectrometer (Gatan Inc., Pleasanton, California, USA), and a 30 mm² EDAX Si/Li EDX detector (EDAX Inc., Mahwah, New Jersey, USA) with a 0.13 sr acceptance angle. To ensure optimal counting rates, the specimens were tilted 15° towards the EDX detector. The MSA of multimode STEM images was performed using a multivariate scatter diagram construction using a Gatan DM script (Gatan Inc.) based on earlier described analysis routines (Grogger et al., 1998) and an automatic AXSIMA software package as described elsewhere (Kotula et al., 2003).

STEM-ADF-based tomography was performed on air-dried powders of the poly(S-r-DIB10%) copolymer-based cathode using a C₃ probe-corrected FEI Titan 80–300 TEM/STEM. Due to the size of the poly(S-r-DIB10%) copolymer–carbon agglomerates, it was necessary to operate the instrument in such a way so as to produce a large depth of field. This was done by using a 10 μm probe forming aperture resulting in a probe semi-convergence angle of 0.6 mrad. As the use of such an aperture severely limits the final probe current, a low spot number was used along with a small inner collection angle for the annular detector (18 mrad) in order to increase the resulting image signal. STEM images were collected over a range of specimen tilts from −70° to +70° using a 1.5° tilt increment. Data were aligned using an intensity-based subpixel registration method (Thévenaz et al., 1998) and reconstruction was carried out using 30 iterations of the simultaneous iterative reconstruction technique (Agulleiro & Fernandez, 2011). Segmentation of the reconstructed volume was carried out using the Avizo software package.

To reduce beam-induced damage of the specimens, the electron beam dose rates were minimized down to 4.5 mm²/s and beam blanking was employed between acquisitions and during imaging and analyses. For cross-sectional examination of the cathodes, samples were

**Materials and Methods**

The poly(S-r-DIB) copolymer materials used in this study were synthesized by inverse vulcanization through direct dissolution and copolymerization of DIB in liquid sulfur as reported previously (Chung et al., 2013). This process is a bulk copolymerization of molten sulfur and DIB heated above the floor temperature ($T_f = 159°C$) for the free radical ring-opening polymerization of Sₘ. Although sulfur is classically known to form living polymers at temperatures above $T_f$, these macromolecules depolymerize upon cooling back to room temperature. The copolymerization of Sₘ with varying DIB ratios from 5 to 50% by mass has been shown to form high molecular mass sulfur-based copolymers that are not only stable at room temperature, but also retain the critical electroactive S–S bonds that are needed for battery function (Chung et al., 2013; Simmonds et al., 2014).

The cathode films were fabricated by coating a ball-milled slurry, consisting of either elemental sulfur or the poly(S-r-DIB) copolymers, mixed with Timcal Super C65 conductive carbons (TIMCAL Ltd., Bodio, Switzerland) and a polyethylene binder onto an aluminum current collector as described elsewhere (Oleshko et al., 2015a, 2015b). The mass ratio of the components (sulfur-containing material:carbon:binder) in the slurry was held constant at ~75:20:5, respectively. The composite cathodes for a standard 2032-coin cell were prepared with a Li metal foil anode and cycled at rate of C/10, according to procedures described previously (Simmonds et al., 2014).

The morphologies, microstructures, and elemental compositions of pristine and cycled composites of the poly (S-r-DIB) copolymer–carbon cathodes were analyzed using a cold field-emission gun Hitachi S4700 II FESEM (Hitachi Ltd., Tokyo Japan) at accelerating voltage $U = 5$ kV and $U = 20$ kV equipped with an Oxford high-speed 80 mm² X-Max silicon-drift EDX detector (Oxford Instruments NanoAnalysis Ltd., High Wycombe, UK). For FESEM, the cathode films were mounted on aluminum alloy stubs. Medium- and high-resolution imaging, SAED, EEL, and EDX spectroscopic analyses of the cathodes were performed at 300 kV in a Schottky field-emission FEI Titan 80–300 analytical S(T)EM (FEI, Hillsboro, Oregon, USA) with a point-to-point resolution of 0.19 nm and information limit below 0.1 nm. For high spatial resolution EDXS and EELS nanoprobe analyses, STEM mode was employed. The instrument was equipped with a Fischione 3000 model HAADF detector (E.A. Fischione Instruments, Inc., Export, Pennsylvania, USA), FEI BF- and ADF-STEM detectors, a Gatan Enfina electron spectrometer (Gatan Inc., Pleasanton, California, USA), and a 30 mm² EDAX Si/Li EDX detector (EDAX Inc., Mahwah, New Jersey, USA) with a 0.13 sr acceptance angle. To ensure optimal counting rates, the specimens were tilted 15° towards the EDX detector. The MSA of multimode STEM images was performed using a multivariate scatter diagram construction using a Gatan DM script (Gatan Inc.) based on earlier described analysis routines (Grogger et al., 1998) and an automatic AXSIMA software package as described elsewhere (Kotula et al., 2003).

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To reduce beam-induced damage of the specimens, the electron beam dose rates were minimized down to 4.5 mm²/s and beam blanking was employed between acquisitions and during imaging and analyses. For cross-sectional examination of the cathodes, samples were
embedded in a Spurr resin (purchased from SPI Supplies) and cured at 65 °C for 12 h. Ultrathin cross-sections with thicknesses of 80–120 nm were prepared by using a diamond knife in a Leica Ultracut UCT microtome at room temperature.

RESULTS AND DISCUSSION

Previously we described the effect of poly(S-r-DIB) copolymer composition on the electrochemical properties of these materials as the active material in cathodes for Li–S batteries (Simmonds et al., 2014). The poly(S-r-DIB) copolymers with 1% by mass DIB exhibited cycling performance comparable with 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. The copolymers with a composition of 10% by mass DIB were found to perform optimally (Figs. 1a and 1b). In the initial report for this copolymer as an active material in Li − S battery cathodes, a specific capacity 823 mAh/g at 100 cycles has been reported (Chung et al., 2013).

Further optimization of cathode-coating procedures has since yielded significant improvements in both the initial capacity and suppression of the capacity fade. An initial capacity of 1,225 mAh/g was observed in the Li − S batteries in the present study and with capacity of 1,005 mAh/g at 100 cycles (0.18% capacity decay rate/cycle) and 817 mAh/g at 300 cycles (0.11% capacity decay rate/cycle) with a Coulombic efficiency of 99% throughout. This system has been extended to 500 cycles while retaining a capacity of 635 mAh/g at a C/10 rate (0.1% capacity decay rate/cycle) (Simmonds et al., 2014). The analyses of normalized charge and discharge capacity curves with DIB content (Simmonds et al., 2014) suggest that the following reactions involving S–S and organosulfur moieties occur in both high- and low-voltage plateau regimes, regardless of the DIB content (for clarity, see also Supplementary Figs. 1Sa, 1Sb):

\[
Li_{4}(S_{x-3})_{4} - DIB + Li_{2}S_{8} \xrightarrow{\text{Discharge}} Li_{4}(S_{x-3})_{4} - DIB + Li_{2}S_{4},
\]

\[
Li_{4}(S_{x-3})_{4} - DIB \xrightarrow{\text{Charge}} (LiS)_{4} - DIB + Li_{2}S_{8}, x \sim 2-3,
\]

\[
Li_{2}S_{2} \xrightarrow{\text{Discharge}} Li_{2}S_{6}, x \sim 2-3,
\]

\[
4S^{2-} + S_{4} \xrightarrow{\text{Discharge}} (S_{4})_{4} - DIB.
\]

Supplementary Figures 1Sa and 1Sb

Supplementary Figures 1Sa and 1Sb can be found online. Please visit journals.cambridge.org/jid_MAM.

Organosulfur moieties from poly(S-r-DIB) copolymer strongly affect electrochemical lithiation reactions (5)–(8) in the cathodes in both regimes enhancing battery performance. In earlier research, these poly(S-r-DIB) copolymers were found to significantly improve the materials processing relative to elemental sulfur and were readily processed from either the melt or solution into thin films or free standing forms (Chung et al., 2013; Simmonds et al., 2014). In this study, we examine in detail the structural architectures of the composite poly(S-r-DIB)-based cathodes with different DIB content at the multiple scales and in 3D space in order to understand the ramifications of incorporating the DIB units. The morphological and compositional variations in the distributions of the poly(S-r-DIB) copolymers and conductive carbon nanoparticles in both the poly(S-r-DIB)_{10%}-based and poly(S-r-DIB)_{50%}-based composites will be compared, when possible, to the analogous elemental sulfur-based composite cathodes. Recently, we demonstrated that replacing the elemental α-sulfur (S8) with the poly(S-r-DIB) copolymers
may result in molecular level homogeneity and high-capacity/long-life cathode structures that more efficiently generate and transfer charge and are robust against the mechanical stresses that arise from the repeated expansions and contractions during charge/discharge cycling (Simmonds et al., 2014; Oleshko et al., 2015b).

Secondary electron (SE) images and corresponding X-ray maps of the pristine conventional sulfur–carbon cathode film, the poly(S-r-DIB10%) copolymer-based cathode film, and the poly(S-r-DIB50%) copolymer-based cathode film are shown in Figure 2. Complementary, large-area plane view BF and dark-field light microscopy (LM) images together with low-magnification SE images of the same cathodes are shown in Supplementary Figure 2S to illustrate structural architectures of sulfur copolymer-based composite cathodes at the macroscale. The contrast in the FESEM images (Fig. 2, upper row) acquired with a through-the-lens Everhart–Thornley detector at a relatively low accelerating voltage of \( U = 5 \, \text{kV} \) is governed by the SE\(_1\) signal emitted from a shallow \( \sim 5\)-nm thick surface layer primarily reflecting the surface topography. Whereas the images acquired at higher accelerating voltage of \( U = 20 \, \text{kV} \) (Fig. 2, middle row) are comprised of a significant portion of SE\(_2\)s ejected from greater depth down to \( \sim 2 \, \mu\text{m} \) under particular conditions via excitations of high-energy backscattered electrons that possess a Z-dependence (Goldstein et al., 2003). Contrast variations due to the mixed signal nature are more complicated and reflect not only the surface topography of the specimen but to some extent its phase composition also shows sulfur-enriched microparticles as brighter areas with higher mean atomic number as compared with the surrounding carbon matrix. This is consistent with local chemical distributions revealed from the X-ray maps acquired over the same areas (Fig. 2, bottom row) at conditions which are favorable for the excitation of characteristic X-ray lines of the constituents, i.e., the S K\(\alpha\) series at
2.308 keV, the C Kα line at 0.282 keV, and the Al Kα series at 1.487 keV.

**Supplementary Figure 2S**

Supplementary Figure 2S can be found online. Please visit journals.cambridge.org/jid_MAM.

In the X-ray maps, the sulfur domains are colorized in orange, carbons in green, and aluminum (from the supporting current collector foil) in red. Both electron images and X-ray maps indicate marked structural and compositional transformations of the composite cathodes as the DIB loading increases. The conventional sulfur–carbon cathode film contains multiple cracks that are 10–20-μm wide (Figs. 2a1, 2a2). As the cathodes have yet to be cycled, these cracks must have developed during the blade coating of the cathode slurry and most likely stem from the significant volume reductions that occur as the coating dries. Constrained by the rigid substrate, this volume reduction induces mechanical stresses in the cathode film resulting in cracks when the mechanical strength of the composite is exceeded. It is striking that the inverse vulcanization process remarkably improves the mechanical integrity of the as-cast cathode composites; the propensity for cracking is strongly reduced in the cathodes made from the poly(S-r-DIB50%) copolymer, which appear to be practically crack-free (Figs. 2c1–2c3).

Second, large-scale compositional heterogeneity in the conventional sulfur–carbon cathode is present as phase separated domains, presenting either sulfur or carbon, on length scales that approach tens of micrometers (see Fig. 2; Supplementary Fig. 2S). Strong segregation between the α-sulfur microparticles, sometimes displaying faceted surfaces and aggregated spherical conductive carbon nanoparticles was confirmed by the X-ray mapping presented in Figure 2, bottom row. The encapsulation of α-sulfur particles inside “caves” and micropores formed by surrounding aggregated conductive carbons promotes its stabilization leading to reduced sublimation rates of sulfur in a vacuum of ~10^{-8} Torr in the FESEM specimen chamber. No evident changes in the examined cathode films caused by sublimation of sulfur were found during several hours of FESEM observations. Interestingly, the magnitude of the large-scale compositional heterogeneity significantly reduced as the DIB content increased. So, the FESEM images of the poly(S-r-DIB50%) composite in Figures 2c1 and 2c2 did not show any large-scale segregations either of the carbons or sulfur-rich particles. Simultaneously, the cross-linking agent also improves the stability of the copolymer particles against sublimation in the microscope vacuum. The enhanced compositional uniformity is confirmed with the EDS X-ray map shown in Figure 2c3. Higher magnification SE images in Figure 3 as well as BF-TEM images in Figure 4 displaying complex hierarchical cathode architectures and interfaces between conductive carbon nanoparticles and microparticles of elemental sulfur or poly(S-r-DIB) domains provide further insights into their multiscale structural arrangements by which the cathode performance is improved. The composite homogeneity in the poly(S-r-DIB) containing materials appears to result from an intimate mixing of the sulfur copolymer and C65 conductive carbon nanoparticles (see Fig. 3). This important aspect of how DIB affects the composite cathode morphology is evidenced at several different length scales. At working magnifications of ×50 k (middle row) and ×200 k (bottom row), the individual carbon nanoparticles can be seen with diameters ranging from 30 to 50 nm. In the conventional sulfur–carbon cathode these nanoparticles form large nodular aggregates of 10–80 μm in size with extended pores randomly distributed over the cathode. One can also see an individual sulfur particle in the center of the image (Fig. 3a1 and its enlarged fragment in Fig. 3a2) that is devoid of the carbon particles, demonstrating that elemental α-sulfur and carbons do not readily mix. By contrast, as the DIB concentration increases, one observes a muddled texture over the carbon nanoparticle aggregates. This suggests that the poly(S-r-DIB) copolymers wet the carbon nanoparticles and promote an intimate mixing of the two components although some local segregation can occasionally be found. In comparing the composite cathodes made of the elemental sulfur and the poly(S-r-DIB50%) copolymer, especially at the highest magnification of ×200 k (the bottom row, Fig. 3), it appears that the poly(S-r-DIB) copolymer microparticles are imbedded between the individual carbon nanoparticles. We believe that aromatic benzene rings in the DIB improve the compatibility of the organosulfur copolymer via van der Waals interactions with the carbon nanoparticles, which possess outer shells of similar benzene-like, hexagonal carbon rings.

BF-TEM imaging of air-dried powders of the pristine poly(S-r-DIB) copolymer-based composite cathodes with different DIB content (Fig. 4) revealed more details about the internal structural arrangements of the composite cathodes. These complex morphologies exhibit random chain- and/or branch-like 3D aggregates of the carbon nanoparticles, which form extended percolation conductive carbon networks embedding electrochemically active but electrically insulating micron- and submicron-sized particles of α-sulfur or organosulfur copolymers. Table 1 summarizes data on the mean sizes of segregated sulfur-containing particles and clusters of aggregated carbons for cathode compositions with different DIB content. The mean size of local segregations composed of α-sulfur and sulfur copolymer particles decreased with the DIB content from 75.6 ± 6.7 μm for the conventional cathode and 56.4 ± 9.2 μm for the poly(S-r-DIB10%) copolymer-based cathode down to 7.3 ± 1.7 μm for the poly(S-r-DIB50%) copolymer-based cathode. At the same time, the average size of the aggregated carbon clusters were estimated to be 610 ± 130 nm for the poly(S-r-DIB10%) copolymer-based cathode (Fig. 4, middle column) and 520 ± 110 nm for the poly(S-r-DIB50%) copolymer-based cathode (Fig. 4, right column), respectively. This is >200 times smaller than the large nodular
aggregates of carbon particles (132 ± 30.4 μm) found in the conventional cathode, reflecting the tendency to reduce the cathode heterogeneity as the DIB content increases. The mean diameter of individual C65 carbon particles determined by counting of 300 particles was \( d = 38.4 ± 1.0 \text{ nm} \). The particle size distributions fit satisfactorily to a normal distribution curve. SAED patterns (Fig. 4, upper insets) exhibit a series of broad diffuse rings indicating a short range ordering (SRO) defined as ordering of the first- or second-nearest neighbors of a carbon atom. The first ring indicates a spacing of 0.39 nm, which corresponds to the partially disordered onion-like fullerene shells. This is close to the natural spacing of the basal planes in graphite and suggests that the carbon nanoparticles have highly conductive shells. The other two rings at 0.21 and 0.12 nm are typical interatomic dimensions for amorphous carbon materials (Czigany & Hultman, 2010). Phase-contrast HRTEM (Fig. 5) shows that the carbons are partially coalesced onion-like particles with 3–6 nm ill-defined cores and 10–20 nm outer shells, exhibiting the typical 0.38–0.39 nm (002) graphite-like interlayer spacings. Partial crystallinity of Timcal Super C65 carbons containing internal layered graphitic features was also confirmed by X-ray diffraction (Suryanto & Zhao, 2016). In agreement with aforementioned SAED data and EELS analyses (see below Figs. 8a–8e), this suggests that aggregated carbon particles with electron conductive graphitic-like outer shells having hyperconjugated \( \pi \)-bonding form percolated and presumably conductive random networks, which propagate through the cathode matrix. These observations directly point to the origin of electron conductivity in the system, i.e., random percolation \( \pi \)-bonding networks formed by aggregated carbons. In the presence of the copolymer or sulfur, the conductive aggregated carbon particles could create electrochemically active interfaces where the reaction steps (5)–(8), including charge generation and transfer occur during cycling.

It is quite challenging to analyze the internal structures of poly(S-r-DIB) copolymer–carbon composites due to their inherent heterogeneity and complex 3D structural

Figure 3. FESEM, higher magnification secondary electron images of the pristine cathodes displaying surface topography of the nanocomposites with different diisopropenylbenzene (DIB) contents, \( U = 5 \text{kV} \). (a1–a3) the conventional sulfur–carbon cathode; (b1–b3) the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB,con.)] copolymer-based cathode; (c1–c3) the poly(S-r-DIB,core) copolymer-based cathode. The sulfur-rich microparticles in (a1,a2) and (b1,b2) are marked by dash orange lines. The scale bars for the images in the first row correspond to a length of 1 μm, whereas the scale bars for the images in the second row and in the third row correspond to 200 and 100 nm, respectively.
arrangements. However, it is possible to simultaneously collect multiple STEM image signals and to inspect the relationships between them to produce pseudo-phase discrimination at high spatial resolution. A set of multimodal STEM images of a poly(S-r-DIB50%) copolymer–carbon composite (Fig. 6) recorded simultaneously in BF-, low-angle ADF-, medium-angle ADF- (MAADF), and HAADF-STEM modes shows characteristic features of its internal microstructure. Various contrast mechanisms and strong contrast variations resulting in complete contrast reversal (e.g., between BF- and MAADF-STEM images in Figs. 6a, 6c) reveal clearly nanoscale features such as the sulfur-rich poly(S-r-DIB) copolymer domains, carbon Timcal Super C65 nanoparticles, interfaces, and extended meso- and nanoscale porous networks even in several micrometer thick areas. The STEM offers evident benefits over the broad-beam

Figure 4. BF-TEM, air-dried powders of the pristine composite cathodes with different diisopropenylbenzene (DIB) contents displaying complex morphologies of mesoscale networks formed by randomly aggregated 30–60 nm conductive carbon particles (Timcal Super C65) interconnected with the organosulfur copolymers: (a1–a3) the conventional sulfur–carbon cathode; (b1–b3) the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB10%)] copolymer–based cathode; (c1–c3) the poly(S-r-DIB50%) copolymer–based cathode. The SAED patterns [upper insets in (a1), (b1), and (c1)] display a series of broad diffuse rings with 0.39, 0.21, and 0.14 nm spacings, respectively, indicating a short range ordering discussed in the text.
illumination TEM, which normally requires thin samples <100 nm in thickness (e.g., see Figs. 4, 6, 9a). The main advantage in this case is that the HAADF signal is generated by the incoherent Rutherford-like electrons scattered out to high angles, in which the registered images have different levels of contrast related to the atomic number (chemical composition) and the density and thickness (mass thickness) of the battery component (Pennycook, 2011). In STEM, partial temporal coherence may arise only because of the relatively low spread in energies of the illuminating beam if field-emission sources are used (Nellist, 2011). Contrary to conventional TEM, STEM imaging is not limited by the spherical aberrations of the objective lens, which may cause contrast delocalization (Bals et al., 2004). In addition, STEM enables higher contrast and less blurring in thick specimens up to several micrometer. With sufficiently small convergence angles of the incident beam (1–2 mrad), one can increase depth of field so that the entire thick sample will be in focus along its depth, i.e., z-direction. Utilizing an axial BF-detector instead of a HAADF detector reduces blurring of specimen features situated toward the bottom of thick samples. Even if diffraction effects are not completely avoidable, Z-contrast in the incoherent HAADF-STEM mode relates the image intensity monotonically to the atomic number, material density, and thickness making a much better approximation to a mass thickness image than a coherent BF image (Pennycook, 2011). The ability of HAADF-STEM to suppress diffraction and phase contrast, however, makes it insensitive to differentiating between crystalline and amorphous phases. Conversely, phase-contrast BF-STEM provides both crystallographic and orientation relationship information. Spatially correlated drift-corrected EDS X-ray and EELS maps (Figs. 7b–7f) and line profiles (Fig. 7c) acquired on the composite fragment marked by the red box in corresponding HAADF-STEM images (Figs. 7a, 7d) confirm elemental compositions of the major cathode components in selected areas. Ideally, by recording multiple STEM signals and analyzing correlations between the image intensity (structural fingerprints), morphology, crystallinity, and elemental compositions, one can identify and ultimately quantify all phase components.

<table>
<thead>
<tr>
<th>DIB Content (wt%)</th>
<th>Mean Size of Segregated Sulfur and Poly(S-r-DIB) Copolymer Particles (μm)</th>
<th>Mean Size of Clusters of Carbon Nanoparticles (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75.6 ± 6.7</td>
<td>132,000 ± 30,400</td>
</tr>
<tr>
<td>10</td>
<td>56.4 ± 9.2</td>
<td>610 ± 130</td>
</tr>
<tr>
<td>50</td>
<td>7.3 ± 1.7</td>
<td>520 ± 110</td>
</tr>
</tbody>
</table>

The errors are represented by 2σ SD corresponding to the 95% confidence limit. poly(S-r-DIB, poly[sulfur-random-(1,3-diisopropenylbenzene)].

Figure 5. HRTEM, the pristine composite cathodes with different diisopropenylbenzene (DIB) contents: (a) the conventional sulfur–carbon cathode; (b) the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB10%)] copolymer-based cathode; (c) the poly(S-r-DIB50%) copolymer-based cathode.
Figure 6. Multimode STEM of a thin section of the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB_{10\%})]-based composite: (a) bright field (BF); (b) low-angle-ADF (LAADF); (c) medium-angle ADF (MAADF); (d) high-angle ADF (HAADF). e: Trivariate scatter diagram of normalized BF, MAADF, and HAADF image intensities revealing distinct clusters corresponding to the major phase components. f: Phase image produced by selecting the outlined areas with clusters from the scatter diagram. Voids are in blue, an embedding epoxy resin is in green, a poly(S-r-DIB) domain is in yellow, and C65 carbon particles are in red, respectively. g: Similar phase image produced from all multimode STEM data using an automated AXSIA multivariate statistical analysis package (Kotula et al., 2003).
MSA used to analyze large data sets of multimode STEM images provides effective means for systematic multiparameter data evaluation and an unbiased classification of the phases (Jeanguillaume, 1985; Bonnet et al., 1997; Grogger et al., 1998; Olehko et al., 2014). In MSA, one can define an image by its components along the axis chosen in a hyper-dimensional space with as many dimensions as there are pixels in the image. It seeks correlations between the number of components and the “fingerprint” image or concentration of each component. Such components should be incorporated in a set of imaging and/or spectral data recorded from the samples in which the compositions of the constituent phases may vary with spatial positions (Muto et al., 2009; Sarahan et al., 2011). In the present study, we have adopted a multivariate scatter diagram construction using earlier described analysis routines (Grogger et al., 1998) in order to quantify spatial correlations between the intensities of three different input STEM signals and phase compositions of the poly(S-r-DIB) copolymer-based cathode.

When considering the correlations between two or more images, the points could be distributed over an ideal curve corresponding to the ultimate correlation; the distribution width reflects the contribution of the statistical noise. A trivariate scatter histogram of STEM intensity distribution in Figure 6e revealed distinct clusters of the major phases with the subtracted background in blue. The histogram is generated by comparison of the intensities contained within the source images and a sampling width \( w \) determined by the histogram resolution \( r = 128 \) pixels as

\[
w_{\text{signal}} = \frac{\max_{\text{survey}}(I) - \min_{\text{survey}}(I)}{r};
\]  

Figure 7. a,d: HAADF-STEM and (b–c,e–f) drift-corrected STEM/electron energy-loss spectroscopic imaging (EEL-SI) of ultrathin sections of the poly [sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB_{100})] copolymer-based cathode (a–c) and poly(S-r-DIB_{50}) copolymer-based cathode (d–f), respectively. Red rectangular boxes in (a) and (d) mark the areas where energy-dispersive X-ray (EDX) and electron energy-loss spectroscopy (EELS) analyses were performed; (b) overlaid carbon C K and sulfur S L_{2,3} EELS maps acquired over the same area; (c) S/C ratio line profile, at % across the carbon–poly(S-r-DIB_{100}) interface acquired along dash orange line in (b); (e) sulfur S L_{2,3} EELS map; (f) carbon C K EELS map acquired over the same area.
compatibility of the sulfur copolymer and carbon cathodes. HAADF-STEM imaging of thin sections of both poly(S-r-DIB) domains in yellow, and C65 carbon particles are in red. For comparison, Figure 6g presents a similar composite image obtained by an automatic MSA analysis of four STEM images (a)–(d) using the AXSIA package developed by Kotula et al. (2003). Here, voids and embedding media are in blue, the poly(S-r-DIB) domain is in green and C65 carbon particles are in yellow. In the last case, similar to the composite image in Figure 6f, local thickness variations can additionally introduce some red coloration of the embedding media. The composite images in Figures 6f and 6g show the major phases extracted in an agreement with each other and the copolymer fraction was 28.8% as estimated from the section area. For the analyzed cathode fragment, MSA indicates the structural correlation between STEM images and assigned (components) phases that enables complete phase classification, segmentation, and ultimate quantification.

The compositional correlation between the analyzed STEM images and related phases was confirmed through spatially correlated elemental analyses of HAADF-STEM images coupled with EDX and EEL spectroscopies performed in the same areas, see Figures 7a to 7c and Supplementary Figures 3S and 4S. In HAADF-STEM, the image intensity varies monotonically with a mean atomic number, thus making it possible to visualize lateral distributions of poly(S-r-DIB) copolymer within the embedding media (Figs. 7a, 7d). The morphological evidence of the enhanced chemical compatibility at these molecular length scales again points to stronger cohesion between copolymers and conductive carbon nanoparticles in the poly(S-r-DIB)–carbon composite cathodes. Consistent with this notion, spatially correlated EEL/EDX elemental maps and line profiles shown in Figures 7, Supplementary Figures 3S and 4S reveal local distributions of sulfur in these interfacial regions near the carbon nanoparticles at the sub-5 nm length scales and within the copolymer matrix as well. Together with FESEM/ EDXS analyses (see Figs. 2, 3), multimode STEM imaging coupled with MSA and EDX/EEL spectroscopy data conclusively demonstrate that the film uniformity of poly(S-r-DIB) copolymer-based cathodes arise from the compatibility of the sulfur copolymer and carbon fillers at the sub-5 nm length scales, particularly when compared with the gross morphology of conventional sulfur–carbon cathodes. HAADF-STEM imaging of thin sections of both poly(S-r-DIB10%) and poly(S-r-DIB50%) cathodes, respectively, with some darker areas due to local thickness variations, reveals the convergence of the copolymers to form nearly conformal coatings with intimate contacts around the conductive carbon nanoparticles for both compositions. The poly(S-r-DIB) copolymers appear in wetting contact with the C65 carbon nanoparticles indicating intimate contact between the components at potential electrochemically active interfaces.

In addition to the elemental composition mapping, we employed EELS to probe the electronic states and bonding within different domains. Figures 8a and 8b present HAADF-STEM images of ultrathin cross-sections of the poly(S-r-DIB10%) and poly(S-r-DIB50%) cathodes, respectively, combined with low-loss EELS analyses in selected spots from different regions of the microstructures (Fig. 8c). Spectra taken from locations 1, 2, 3, and 4 in Figures 8a and 8b are shown in Figure 8c. The spectra reflect excitations of outer-shell (valence) electrons within the probed material that arise from the inelastic scattering of the electron beam. For insulating poly(S-r-DIB) composite cathodes, the valence electron energy-loss (VEEL) spectra from 0 to 30 eV are dominated by the collective excitations of plasmons and excitons. This leads to a net displacement at a given wavelength of the full momentum-dependent electronic structure of $2s^{1/2}, 2p^{3/2}$, and $2p^{1/2}$ occupied states (for carbon atoms) and $3s^{1/2}, 3p^{3/2}$, and $3p^{1/2}$ occupied states (for sulfur atoms), respectively. The low-loss region exhibits both $\pi$ and $\sigma+\pi$ plasmons as characteristic carbon–carbon bonding fingerprints in the 5.6–6.3 eV and at 21.5–25.1 eV ranges, respectively (Fig. 8c). The highest values for $\pi$ and $\sigma+\pi$ plasmon losses at 6.3 and 25.1 eV are observed in regions that correspond predominantly to the carbon nanoparticles [Fig. 8c, spectrum (2)]. The strong $\pi$ plasmon excitations observed along the percolated aggregates of carbon nanoparticles are consistent with local regions being electrically conductive pathways. However, strong $\pi$ plasmons were not evident from any of the poly(S-r-DIB) copolymer-rich regions, despite the existence of the benzene moiety in the DIB molecule. This is consistent with the electrical insulating nature of the poly(S-r-DIB) copolymers and reflects the strongly localized preferentially $\pi$ bonding as compared with carbon nanoparticle regions, where extended hyperconjugated $\pi$-bonding systems could be formed.

We are also able to discern subtle differences in energy of the bulk $\sigma+\pi$ plasmon peak between the two different copolymer compositions. For the poly(S-r-DIB50%) copolymer, the bulk plasmon peak occurs at 22.6 eV [spectrum (3) in Fig. 8c], whereas for poly(S-r-DIB10%) [spectrum (1) in Fig. 8c] the bulk plasmon peak shifts to 21.5 eV. The compositional variations in the bulk plasmon peak position indicate that the nature of the molecular bonding in the copolymer-rich regions changes with composition and
Figure 8. HAADF-STEM images (a,b), low-loss electron energy-loss (EEL) spectra (c) and core-loss EEL spectra (d,e) of an ultrathin cross-section of the poly[sulfur-random-(1,3-diisopropenylbenzene)] copolymer-based composite cathode acquired at points 1 (green), and 2 (blue), and of the poly(S-r-DIB50%) copolymer-based composite cathode in points 3 (red) and 4 (black). d: The net S L2,3-edge. e: The net C K-edge indicating mixed sp²/sp³ bonding in the poly(S-r-DIB) copolymers and C65 carbon particles. The spectral intensities in (d) and (e) are aligned by maximum for convenience.
suggest that in addition to HAADF-STEM one can employ VEELS to distinguish directly the poly(S-r-DIB50%) phase from the poly(S-r-DIB10%) phase and from onion-like conductive carbons [spectrum (2) in Fig. 8c] as well. In the core-loss region (Fig. 8d), the sulfur L$_{2,3}$-edge at 165 eV has a featureless and rounded profile that is likely dominated by atomic effects rather than solid-state band structure and coordination. This leads to a broad maximum delayed by 20 eV beyond the ionization threshold of 165 eV. At energies just above the ionization threshold, a centrifugal barrier prevents overlap between the initial 2p$_{3/2}$ and 3s$_0$ excitations from contributions of the angular momentum $l(l + 1) term in the radial Schrödinger equation describing corresponding final state radial wavefunction, which causes a maximum to appear in effective atomic potential (for details, see Egerton, 2011). The electron loss near-edge structure of the carbon C K-edge at 284 eV (Fig. 8e) reveals characteristic excitations from 1s to the π* band, corresponding to sp$^2$ bonding with a sharp peak just above the edge onset typical for graphitic-like outer shells as well as excitations from 1s to the σ band with a broad peak above 291 eV corresponding to sp$^3$ bonding. Contrary to the low loss, core π excitations are evident for both carbon nanoparticles and poly(S-r-DIB) copolymers, thus confirming the presence of the benzene moieties of the DIB fragments in the copolymer-rich regions.

STEM-based ET was employed to visualize 3D hierarchical structural architectures formed within the poly (S-r-DIB)-based composite cathodes. ET data were collected using small convergence angles of the incident beam down to 4 mrad in order to keep the entire sample in focus even in very thick specimen areas up to several μm (Figs. 9a–9c). For details, see also an isosurface rotation and a through plane view, Supplementary Movies 5Sa and 5Sb, respectively. The reconstructed and segmented ET views of the cathode structure show complex hierarchical morphology involving random percolation networks of conductive carbons and pores of varying shapes and sizes, which surround poly(S-r-DIB) domains (Figs. 9b, 9c). Due to high contrast and large focal depth, it was possible to visualize mesoscale cathode architectures involving random multifractal 3D percolation conductive networks formed around poly(S-r-DIB)$_{10\%}$ particles by 30–60 nm carbons as well as extended micro- and nano-sized porosity for large agglomerated cathode particles up to several micrometer in-depth followed by EDX-SI mapping (Fig. 9a, inset). The plot in Figure 9d presents mass distribution of the composite cathode as a function of vertical depth in an agglomerate calculated from the reconstructed tomogram. Mass distributions of two poly(S-r-DIB)$_{10\%}$ particles and carbons were derived from corresponding reconstructed volume distributions (Table 2). For the sulfur copolymer, the density was assumed to be $\rho \approx 2$ g/cm$^3$ (Steedul & Eckert, 2003). The mass was $m_1 = 2.63 \times 10^{-12}$ g for the first poly(S-r-DIB)$_{10\%}$ particle and $m_2 = 0.48 \times 10^{-12}$ g for the second, respectively. The total poly(S-r-DIB)$_{10\%}$ mass in the analyzed fragment was $m_r = 3.11 \times 10^{-12}$ g. The density of C65 carbons can be determined based on the strong dependence of the plasmon energy from the density for carbons derived earlier (Oleshko, 2012):

$$\rho = 0.0032E_{p_{\max}}^2$$

(10)

With $E_{p_{\max}} = 23$ eV for C65 carbon nano-onions, the C65 density was estimated as $\rho = 1.7$ g/cm$^3$ and the total C65 mass was about $29.4 \times 10^{-12}$ g. Finally, the maximum expected discharge capacity accumulated within the analyzed fragment can be derived from the estimated mass $m_r$ of the poly(S-r-DIB)$_{10\%}$ copolymer according to the following equation:

$$Q = 0.9 Fz_{min}/M = 1.7 \times 10^{-9} \text{ C or } 4.7 \text{ pAh}$$

(11)

Here, the Faraday constant $F = 964.853$ C/mol, the number of electrons participating in the charge transfer $z = 2$, and molar mass of sulfur $M = 32.065$ g/mol.

**Supplementary Movies 5Sa and 5Sb**

Supplementary Movies 5Sa and 5Sb can be found online. Please visit journals.cambridge.org/jid_MAM.

When combined with spatially resolved VEELS, the lateral distributions of mixed sp$^2$/sp$^3$ carbon–carbon bonding further corroborate the picture that the onion-like outer shells of partially coalesced carbon nanoparticles form electrically conductive percolated networks of conductive pathways. This approach can essentially complement traditional electrochemical techniques such as electrochemical impedance spectroscopy (EIS, see for details, e.g., Orazem & Tribollet, 2008; Cañas et al., 2013; Deng et al., 2013) by enabling real-space visualization and in-depth structural analyses of conductivity pathways and interfaces formed within the porous cathodes. Furthermore, such spatially resolved 3D visualization of cathode structural architectures could promote development of realistic physical models for equivalent circuits used in EIS for explaining fundamental mechanisms of charge generation and interfacial impedance phenomena during charge–discharge cycling of Li–S batteries and other related EES systems. The incorporation of the DIB drastically improves access of these conductive networks to the electrochemically active interfaces at the surfaces of electrically insulating poly(S-r-DIB) domains through enhanced compatibility. It could result in increased utilization of the electrochemically active poly(S-r-DIB) copolymer in the cathode and retention of this active material upon cycling. These findings are consistent with through-plane direct current (DC) conductivity measurements that show a slight increase in electrical conductivity of the cathode as the fraction of DIB content increases, despite the fact that DIB itself is electrically insulating (Oleshko et al., 2015a, 2015b). This indicates that the incorporation of DIB probably could simultaneously improve the electrical percolation of the carbon nanoparticles in the composite electrodes.
Furthermore, increasing the DIB content reduces the propensity for shrinkage-induced cracking, whereas the cathode composite films dried. This suggests that there is also an important benefit of adding the DIB for improving physico-mechanical stability of the cathodes. To examine the effects of organosulfur–DIB compatibility with conductive

Figure 9. Tilt-angle electron tomography (ET) of a poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB10%)]-based cathode powder using Cs probe-corrected STEM. a: A single HAADF frame with high depth of field extracted from a tilt series showing two copolymer particles marked as #1 and #2. The right bottom inset shows overlaid X-ray maps of the copolymer particle #1 with sulfur-rich areas in orange and carbon-rich areas in green. b: The reconstructed and segmented three-dimensional view of the agglomerated cathode fragment showing random percolation networks of conductive C65 carbons and extended pore structures. c: The same cathode fragment displaying two poly(S-r-DIB10%) copolymer microparticles colored in blue (#1) and green (#2), respectively, and surrounded by aggregated nanocarbons. d: Mass of the composite cathode as a function of vertical depth in an agglomerate calculated from the reconstructed tomogram.
carbon fillers on a cycle life, FESEM of the processed cathodes in their discharged state was used to evaluate the integrity of composite cathode films as a function of cycle number. In conventional Li–S batteries, capacity fading is often attributed to mechanical detachment of the cathode fragments from the current collector due to irreversible build-up of dense lower lithium sulfide discharge products (Li$_2$S$_x$, where $x \approx 2–3$) that block the active material during the prolonged cycling (Oleshko et al., 2009a, 2009b). The unevenly distributed Li$_2$S deposits, so called “slate,” can exacerbate the cracks incurred during fabrication due to mechanical stresses induced by repeated cycling. Cathode cracks foreshadow irreversible Li$_2$S deposition and therefore correlate with the lowered capacity retention. Figures 10 and 11 compare SE images and X-ray maps of discharged, solvent-rinsed cathodes made from either the sulfur copolymer with 50% by mass DIB at 30 cycles, 10% by mass DIB at 120 cycles, and elemental sulfur at 30 cycles, respectively. The conventional sulfur–carbon cathode (Figs. 10a1, 10a2, 11a1–11a3) revealed the deep cracks spreading throughout the cathode and extend down to the aluminum current collector. These reflect an integral effect of severe stresses incurred initially during drying of the cathode film followed by additional damage incurred through multiple charge/discharge cycles, which involve multiple Li$_2$S deposition/dissolution steps. These findings exemplify the limitations of the traditional fabrication scheme employing α-sulfur for providing sufficient capacity retention and long-term performance of Li–S batteries. On the contrary, SE images of a poly(S-r-DIB$_{50\%}$) copolymer-based cathode (Figs. 10, 11) exhibit at lower magnifications almost crack-free morphologies over large areas, whereas higher magnifications indicate that extended meso- and nanoscale porosity is preserved despite the prolonged cycling. We have also observed remarkably reduced cathode degradation at 120 cycles with 10% by mass DIB copolymers (see Figs. 10b1, 10b2, 11b1–11b3). BF-TEM images of the cycled poly(S-r-DIB) copolymer-based composite cathodes with different DIB

### Table 2. Volumes, Volume Percent, and Masses of the Major Components Within the Reconstructed Fragment of the Poly (S-r-DIB$_{10\%}$)-Based Composite Cathode Used for Evaluation of the Maximum Expected Discharge Capacity (see Fig. 9 and text for details).

<table>
<thead>
<tr>
<th>Part</th>
<th>Volume $\times 10^8$ (nm$^3$)</th>
<th>Volume Percent (%)</th>
<th>Mass $\times 10^{-12}$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer (particle #1)</td>
<td>0.159</td>
<td>0.24</td>
<td>2.63</td>
</tr>
<tr>
<td>Copolymer (particle #2)</td>
<td>0.027</td>
<td>0.04</td>
<td>0.48</td>
</tr>
<tr>
<td>Total copolymer</td>
<td>0.186</td>
<td>0.28</td>
<td>3.11</td>
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<tr>
<td>Aggregated C65 nanocarbons</td>
<td>2.115</td>
<td>3.19</td>
<td>29.4</td>
</tr>
<tr>
<td>Total</td>
<td>66.3</td>
<td>3.47</td>
<td>32.51</td>
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</tbody>
</table>

poly(S-r-DIB), poly[sulfur-random-(1,3-diisopropenylbenzene)].

![Figure 10. FESEM, $U = 20$ kV, large-area secondary electron images of the cycled composite cathodes (upper row) and corresponding overlaid S K, C K, and Al K X-ray maps from the same areas (bottom row) of the cycled cathodes. a1,a2: The conventional sulfur–carbon cathode after 30 cycles; (b1,b2) the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB$_{10\%}$)] copolymer–carbon cathode after the 120 cycles; (c1,c2) the poly(S-r-DIB$_{50\%}$) copolymer–carbon cathode after 30 cycles, all in the discharged state. Elemental distributions of sulfur, carbon, aluminum (from a current collector), are shown in the maps in orange, green, and red, respectively. The scale bars for images and X-ray maps correspond to 10 μm.](https://www.cambridge.org/core/core/terms.https://doi.org/10.1017/S1431927616011880)
content (Fig. 12) also show that characteristic chain-like and branch-like 3D aggregation morphologies and internal pore and core-shell particle structures of the composite cathodes, including the SRO, did not change drastically upon cycling (see Fig. 4 for comparison). HRTEM observations (Fig. 13) indicate that the core-shell structures of the conductive carbons were generally preserved during cycling although some gradual disruption and local expansion of (002) interlayer spacings for outer graphitic-like layered shells from 0.38–0.39 nm to 0.41 nm could occur. One can note multiple local defects and/or insertions into the outer shells of C65 carbon particles created during cycling (Fig. 13a). In addition, in agreement with local EDXS and EELS analyses, nano-sized precipitates lithium sulfides generated during cycling and deposited onto carbon particles were occasionally found. So, the red circle in Figure 13c marks a 4-nm diameter Li2S cluster exhibiting 0.32 nm (111) lattice fringes, which are consistent with a fcc BiF3 structure type, Fm-3 m (225) space group (Buehrer et al., 1991). In general, these observations correlate well with the electrochemical performance of the poly(S-r-DIB10%) copolymer-based composite cathode retaining high capacity of 1,005 mAh/g at 100 cycles (Fig. 1). Admittedly, the final result of the inverse vulcanization approach described here, increasing both the chemical homogeneity as well as the physico-mechanical stability and integrity of the cathode composite through the utilization of the high molecular mass poly(S-r-DIB) copolymers, is not unlike competing strategies which utilize various core-shell nanostructures to encapsulate the sulfur into nanoscale domains. Both approaches reduce large scale heterogeneity.

**Figure 11.** FESEM, higher magnification secondary electron images of the cycled discharged composite cathodes, \( U = 20 \text{kV} \): (a1,a2,a3) the conventional sulfur–carbon composite cathode after 30 cycles, \( U = 20 \text{kV} \); (b1,b2,b3) the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB10%)]-based cathode after 120 cycles; and (c1,c2,c3) the poly(S-r-DIB50%) based cathode after 30 cycles. The poly(S-r-DIB) copolymer-based cathodes reveal reduced cracking and more uniform utilization and distribution of formed polysulfides (b1) even after 120 cycles. The conventional sulfur–carbon cathode exhibits multiple cracks and highly nonuniform utilization already after 30 cycles (a1); needle-like crystallites of an encapsulated LiTFSI imide salt (trifluoromethanesulfonimide lithium salt, NLi(SO2CF3)2) (a2) were found occasionally. The morphological differences between the cycled poly(S-r-DIB10%) copolymer-based cathode and the conventional cathode strongly correlate with their electrochemical performance. The scale bars for the images in the first row correspond to a length of 1 \( \mu \text{m} \), whereas the scale bars for the images in the second row and in the third row correspond to 200 and to 100 nm, respectively.
in the cathodes. However, the mechanisms by which this is accomplished are quite different. The simple one-pot mixing approach of blending the cathode components with a high molecular mass poly(S-r-DIB) copolymer offers several processing advantages. The fact that electrochemical reactions in both the low- and high-voltage plateaus are so similar between the elemental sulfur systems and the poly (S-r-DIB) organosulfur systems described here then raises intriguing questions about peculiarities of electrochemical activity of the sulfur copolymers. The latter suggests that upon discharge these organosulfur compounds are being broken down into the same low molecular mass lithium sulfides. This is validated by the similarity in cyclic voltammetry curves for the organosulfur reactions in comparison with elemental sulfur (Chung et al., 2013). The extreme cyclability of the poly(S-r-DIB)-based composite cathodes, however, may imply that the high molecular mass organosulfur polymers could then reform upon charging.

Figure 12. BF-TEM, the cycled discharged composite cathodes: (a1,a2,a3) the conventional sulfur–carbon composite cathode after 30 cycles (b1,b2,b3) the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly(S-r-DIB10%)] copolymer-based cathode after 120 cycles; and (c1,c2,c3) the poly(S-r-DIB50%) copolymer-based cathode after 30 cycles. The SAED patterns [upper insets in (a1), (b1), and (c1)] display a series of broad diffuse rings with 0.39, 0.21, and 0.14 nm spacings, respectively, indicating a short range ordering discussed in the text.
Comparative multimode S/(T)EM imaging of the pristine organosulfur cathodes (Figs. 2–5) and the cycled ones (Figs. 10–13) strongly support the notion that the cathode surface topography and morphology do not undergo dramatic changes upon cycling both at the microscale and at the mesoscale levels. However, the detailed electrochemical transformation steps of how the poly(S-r-DIB) copolymers evolve through charge and discharge cycling process still require further in-depth investigation. Additional studies are currently under way to address this important question.

**Conclusions**

Probing underlying structure–processing–property relations of the poly(S-r-DIB)-based composite cathodes by high spatial resolution analytical multimode scanning and transmission electron imaging and tomography at multiple scales provides critical insights into the origins of the enhanced capacity retention in prospective polymeric cathode materials for emerging high-energy density Li–S batteries. Using FESEM, conventional TEM/HRTEM, BF-/ADF-/HAADF-STEM imaging coupled with MSA, tilt-angle STEM ET, EDX/EEL-SI, and complementary LM, we have identified the topographic, morphological, and compositional effects of replacing elemental sulfur with electrochemically active high molecular mass poly(S-r-DIB) copolymers in the composite cathodes for DIB contents of 10 and 50% by mass. Furthermore, direct HRTEM observations supported by spatially resolved SAED and EELS analyses reveal the origin of electron conductivity in the system, i.e., percolated conductive 3D networks formed by aggregated onion-like carbon particles with graphitic outer shells having hyper-conjugated π-bonding, which randomly propagate through the cathode matrix. The core-shell structures of the conductive carbons were usually preserved during cycling although some gradual disruption and local expansion of (002) interlayer spacings for outer graphitic-like layered shells from 0.38–0.39 nm to 0.41 nm could occur. Local defects and/or insertions into the outer shells of C65 carbon particles as well as nano-sized precipitates of lithium sulfides generated during cycling and deposited onto carbon particles could be also occasionally found.

Multimode S/(T)EM imaging coupled with MSA and spatially correlated EDX/EEL-SI demonstrate that the enhanced uniformity of poly(S-r-DIB) copolymer-based cathode structures during cycling is a result of percolated conductive 3D networks formed by aggregated onion-like carbon particles with graphitic outer shells having hyper-conjugated π-bonding, which randomly propagate through the cathode matrix. The core-shell structures of the conductive carbons were usually preserved during cycling although some gradual disruption and local expansion of (002) interlayer spacings for outer graphitic-like layered shells from 0.38–0.39 nm to 0.41 nm could occur. Local defects and/or insertions into the outer shells of C65 carbon particles as well as nano-sized precipitates of lithium sulfides generated during cycling and deposited onto carbon particles could be also occasionally found.

**Figure 13.** HRTEM, the cycled discharged composite cathodes with different diisopropenylbenzene contents: (a) the conventional sulfur–carbon cathode; (b) the poly[sulfur-random-(1,3-diisopropenylbenzene)] [poly (S-r-DIB_{100})] copolymer-based cathode; (c) the poly(S-r-DIB_{50}) copolymer-based cathode. White circles mark ill-defined cores of partially coalesced carbon particles. White arrows in image (a) indicate multiple local disruptions and/or insertions in outer graphitic-like shells of C65 carbon particles formed during cycling. The red circle in image (c) marks a 4 nm Li2S cluster (a fcc BiF3 structure type) exhibiting 0.32 nm (111) lattice fringes.
composite cathodes arise from compatibilization of the copolymer and carbon fillers at the sub-5 nm length scales, particularly when compared with the gross morphology of conventional sulfur–carbon cathodes. STEM ET using a C$_{\text{r}}$-corrected electron probe and combined with spatially resolved VEELS was successfully employed to visualize complex 3D hierarchical aggregation architectures created in up to several micrometer thick areas of the poly(S–r-DIB)-based composite cathodes. This approach can essentially complement traditional electrochemical techniques such as EIS enabling real-space visualization and in-depth analyses of conductivity pathways and active interfaces formed within highly porous composite cathodes. It can promote developing realistic physical models for equivalent circuits used in EIS for explaining fundamental mechanisms of charge generation and interfacial impedance phenomena during charge–discharge cycling of Li–S batteries and related EES systems. Summarizing the results, we can conclude that the employed techniques demonstrate the following benefits of utilizing the novel organosulfur poly(S–r-DIB) copolymers in composite–carbon cathodes for the next generation of high-energy density Li–S batteries:

1. The DIB moieties significantly improve compatibility between the conductive onion-like carbon nanoparticles and the electrochemically active sulfur copolymer containing domains, leading to an intimate mixing of these components at a much finer length scale. This increases the effective interfaces between the electrically conductive pathways and domains of the electrochemically active poly (S–r-DIB) copolymers responsible for charge generation and transfer. Furthermore, compositional variations in the $\sigma + \pi$ bulk plasmon peak position indicate that the nature of the molecular bonding in the poly(S–r-DIB) copolymer-rich regions changes with composition and suggest that one can use shifts of the plasmon peaks in VEELS to distinguish the poly(S–r-DIB$_{50\%}$) phase from the poly(S–r-DIB$_{10\%}$) phase and from conductive carbons as well.

2. The enhanced compatibility and homogeneity between the components down to the 5 nm scale enables promotion of the creation of a unique hierarchical cathode morphology that is electrochemically and mechanically more robust. As a result, the pristine, as-cast poly(S–r-DIB) copolymer-based composite cathodes exhibit reduced levels of drying-induced cracking but preserve extended multiscale porosity that appears to persist as a function of cycling. Taken together, these factors contribute toward the increased capacity retention and enhanced cycle life over conventional Li–S batteries formulated with elemental orthorhombic $\alpha$-sulfur.

The realized improvements in both the electrochemical performance and physico-mechanical stability due to the introduction of the poly(S–r-DIB) copolymers show high potential for a technology breakthrough that will help to develop the next generation of long-cycle life light-weight high-energy density Li–S batteries for emerging applications.

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