Lithium Sulfide–Carbon Composites via Aerosol Spray Pyrolysis as Cathode Materials for Lithium–Sulfur Batteries

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We demonstrate a new technique to produce lithium sulfide–carbon composite (Li₂S-C) cathodes for lithium-sulfur batteries via aerosol spray pyrolysis (ASP) followed by sulfurization. Specifically, lithium carbonate-carbon (Li₂CO₃-C) composite nanoparticles are first synthesized via ASP from aqueous solutions of sucrose and lithium salts including nitrate (LiNO₃), acetate (CH₃COOLi), and Li₂CO₃, respectively. The obtained Li₂CO₃-C composites are subsequently converted to Li₂S-C through sulfurization by reaction to H₂S. Electrochemical characterizations show excellent overall capacity and cycle stability of the Li₂S-C composites with relatively high areal loading of Li₂S and low electrolyte/Li₂S ratio. The Li₂S-C nanocomposites also demonstrate clear structure-property relationships.

Keywords: aerosol spray pyrolysis, nanocomposites, lithium-sulfur batteries, lithium sulfide, sulfurization

INTRODUCTION

Lithium-sulfur (Li-S) batteries are regarded as one of the most promising electrochemical energy storage technologies due to their low cost, environmental benignity, and outstanding theoretical capacity (Wang et al., 2013; Son et al., 2015). However, despite tremendous research and development efforts, there are still a number of challenges hindering their commercialization. Among these key challenges are the polysulfides shuttle effect and high electrolyte/sulfur ratio, which are significantly magnified by the instability of the Li metal anode (Chen J. et al., 2017; Chen S. et al., 2017; Pan et al., 2018; Wu et al., 2018). Therefore, high capacity non-Li anodes, particularly those comprised of silicon-based materials, have been proposed as replacements for Li metal in Li-S batteries (Yang et al., 2010). The use of silicon anode materials would require a pre-lithiated sulfur cathode, i.e., lithium sulfide (Li₂S). In recent years, various methods to synthesize Li₂S-carbon composite materials have been reported, including high-energy mixing Li₂S with carbon (Cai et al., 2012; Jha et al., 2015), chemical lithiation of S-C composites (Hwa et al., 2015), Li₂S-C composites synthesis via dissolving and precipitating Li₂S in ethanol (Wu et al., 2014a,b,c, 2015, 2016), embedding Li₂S in carbon matrix via Li-nitrogen interaction (Guo et al., 2013), reaction between Li metal and carbon disulfide (Tan et al., 2017), converting LiOH to Li₂S via sulfurization with H₂S (Dressel et al., 2016), and thermal reduction of Li₂SO₄ by carbon (Yang et al., 2013; Kohl et al., 2015; Li et al., 2015; Yu et al., 2017; Zhang et al., 2017; Ye et al., 2018). In addition, the mechanism studies on Li₂S activation and capacity degradation were also reported (Vizintin et al., 2017; Piwko et al., 2018). In this work, we report a new scalable method for synthesizing Li₂S-C composites via aerosol spray pyrolysis (ASP) followed by sulfurization.
MATERIALS AND METHODS

Materials Synthesis

Three lithium salts including lithium nitrate (LiNO₃), lithium acetate (CH₃COOLi) and lithium carbonate (Li₂CO₃) were used as the precursors for Li₂S with sucrose as the precursor for carbon. Each Li salt was dissolved in deionized water with sucrose at different concentrations as listed in Table S1. The obtained solutions were used in the ASP process.

The ASP system in this study is illustrated in Figure S1. The commercial aerosol generator (TSI, Model 3076) consisting of a nebulizer and a solution reservoir is attached to a diffusion dryer followed by a tubular furnace and a filter collector. The diffusion dryer was composed by two concentric tubes: The outer tube is made of 3-inch inner diameter PVC tubing and the inner tube is made of 0.5-inch diameter steel mesh with the annular space filled with porous silica gel. The aerosol of the precursor solution was generated by the nebulizer and carried through the diffusion dryer by argon gas to desiccate the water content. The resultant dry particles were continuously carried into the tube furnace heated at 850°C to produce the Li₂CO₃-C nanoparticles, which are collected with a stainless-steel filter down stream outside the tube furnace.

The synthesized Li₂CO₃-C composite is placed in an alumina boat in a tubular furnace, followed by purging with argon for an hour. The furnace was then heated to 725°C and maintained at this temperature for 5 h under a flow of 5 vol.% H₂S and 95 vol.% argon. After 5 h the flow gas was switched to pure argon and the furnace was cooled naturally to room temperature. The product was collected in an argon-filled glovebox due to the sensitivity of Li₂S to moisture.

Materials Characterization

The nitrogen adsorption-desorption isotherms of the produced composite materials were obtained with a surface area and porosity analyzer (Micromeritics ASAP2020). For a particular analysis, approximately 200 mg sample was first degassed at 150°C for 3 h, then the nitrogen adsorption-desorption isotherms were measured from 0 to 1 relative pressure. The surface area was obtained with the Brunauer-Emmett-Teller (BET) method. The crystalline species in the composites were characterized by powder X-ray diffraction (XRD, PANalytical) with a CuKα source and a scan rate of 0.11° s⁻¹. Kapton tape was used to seal the Li₂S-C composites to protect Li₂S from reacting with the moisture in ambient environment during measurement. The morphology and microstructure of the composites were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM, Tecnai T12). Carbon content in the Li₂CO₃-C composites was measured with thermogravimetric analysis (TGA, TA Instruments). The TGA samples were held at 120°C for 30 min to remove the moisture absorbed from environment, followed by heating to 600°C at a rate of 10°C min⁻¹ with an isothermal step in dry air. The carbon contents in Li₂CO₃-C_NitS, Li₂CO₃-C_AceS and Li₂CO₃-C_CarS (Figure S2) are very consistent at 20.7, 22.8, and 21.2 wt.%, respectively. Assuming complete conversion from Li₂CO₃ to Li₂S without carbon loss, the Li₂S content in Li₂S-C_NitS, Li₂S-C_AceS and Li₂S-C_CarS can be estimated as 70.4, 67.8, and 69.8 wt.%, respectively. The accurate Li₂S content in the Li₂S-C composites is determined as follows: 100 mg Li₂S-C was thoroughly washed 4 times using 15 mL ethanol each time in the glovebox to remove Li₂S. The obtained carbon was weighed after dried at 120°C for 8 h in the glovebox. The Li₂S content is 71.3 wt.% in Li₂S-C_NitS, 69.1 wt.% in Li₂S-C_AceS, and 71.6 wt.% in Li₂S-C_CarS, which all agree very well with the estimated values.

Electrode Preparation and Cell Testing

The electrode is composed of 80 wt.% of Li₂S-C composite, 10 wt.% of carbon black additive, and 10 wt.% of polystyrene as the binder. Polystyrene was selected as the binder to avoid the use of polar solvents (both protic and aprotic), most of which dissolve Li₂S to some extent. Instead, mesitylene (Sigma-Aldrich) was used as the solvent for polystyrene in the electrode slurry. The electrodes were coated on carbon-coated aluminum current collector (MTI Corporation) in the argon-filled glovebox, with the average loading of Li₂S-C composite at 2 mg cm⁻². The electrodes were dried overnight in argon glovebox at room temperature, followed by drying at 120°C for 4 h. The dried electrodes are assembled into 2032-type coin cells with lithium foil anode (99.9%, Alfa Aesar) and Celgard® 2,500 separator. The electrolyte used in this study is 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) solution in a mixture of 1,3-dioxolane (DOL), dimethoxyethane (DME) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PyR14TFSI) (1:3:1 by vol.) with 1.5 wt.% of LiNO₃. The electrolyte to Li₂S ratio (µL/mg) was kept at 10 in all coin cells testing. To activate the Li₂S-C electrode, the first anodic scan in the cyclic voltammetry (CV) was to 3.9 V vs. Li⁺/Li, and the anodic limit in the following scans was 2.6 V vs. Li⁺/Li. Similarly, the first charge was run at a rate of 50 mA g⁻¹ (with respect to Li₂S) to a charge cutoff of 3.5 V. Subsequent cycles are run at 117 mA g⁻¹ between 2.6 V and 1.8 V vs. Li⁺/Li.

RESULTS AND DISCUSSION

During ASP synthesis, three aqueous solutions containing sucrose (as carbon precursor) and either lithium nitrate (LiNO₃), lithium acetate (CH₃COOLi), or lithium carbonate (Li₂CO₃), denoted as NitS, AceS, and CarS, respectively, were atomized into aerosols with a pressure-enabled atomizer. The aerosols were subsequently carried by argon gas through a diffusion dryer and a tubular furnace for pyrolysis within an inert environment. The powder X-ray diffraction (XRD) patterns in Figure 1A clearly indicate that the obtained composites from all three lithium salts are Li₂CO₃-C composite with comparable carbon content (20.7 wt.% in Li₂CO₃-C_NitS, 22.8 wt.% in Li₂CO₃-C_AceS and 21.2 wt.% in Li₂CO₃-C_CarS via thermalgravimetric analysis, Figure S2). It is worth noting that sucrose solution without the lithium salts (i.e., precursors of Li₂CO₃) completely decomposes during the same ASP without any carbon formation. This observation reveals that Li₂CO₃ serves as the nucleation sites for carbonization of sucrose in ASP (Skrabalak and Suslick, 2006). However, the formation mechanisms of Li₂CO₃ from these three Li salts are clearly...
**FIGURE 1** | XRD patterns of (A) the Li$_2$CO$_3$-C composites obtained from ASP and (B) the Li$_2$S-C composites after sulfurization.

**FIGURE 2** | TEM images of (a) Li$_2$CO$_3$-C$_{NitS}$, (b) Li$_2$CO$_3$-C$_{AceS}$, (c) Li$_2$CO$_3$-C$_{CarS}$; TEM images of the carbon matrix of (d) Li$_2$CO$_3$-C$_{NitS}$, (e) Li$_2$CO$_3$-C$_{AceS}$, (f) Li$_2$CO$_3$-C$_{CarS}$ after Li$_2$CO$_3$ removed, and TEM images of (g) Li$_2$S-C$_{NitS}$, (h) Li$_2$S-C$_{AceS}$, (i) Li$_2$S-C$_{CarS}$. 
different. For LiNO$_3$, its thermal decomposition is known to proceed according to Reaction 1: (Stern and Weise, 1969)

$$2\text{LiNO}_3 \rightarrow \text{Li}_2\text{O} + 2\text{NO}_x + (2.5 - x)\text{O}_2 \quad (1)$$

Based on the XRD evidence of Li$_2$CO$_3$ with the absence of crystalline Li$_2$O, it can be speculated that carbon dioxide (CO$_2$) released from pyrolysis of sucrose further reacts with Li$_2$O to generate Li$_2$CO$_3$ according to Reaction 2:

$$\text{Li}_2\text{O} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 \quad (2)$$

CH$_3$COOLi undergoes thermal decomposition to generate Li$_2$CO$_3$ and acetone according to Reaction 3: (Roe and Finlay, 1952)

$$2\text{CH}_3\text{COOLi} \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_3\text{H}_6\text{O} \quad (3)$$

For the CarS precursor, Li$_2$CO$_3$ undergoes precipitation during ASP without decomposition, thus becoming directly embedded into the carbon matrix formed by the carbonization of sucrose.

Although the obtained Li$_2$CO$_3$-C composites have consistent composition and carbon content, they have distinctively different microstructures as displayed by the transmission electron microscopy (TEM) images in Figure 2 (scanning electron microscopy images in Figure S3). The Li$_2$CO$_3$-C$_{\text{NitS}}$ nanoparticles in Figure 2A have a hollow-shell structure with irregular-shaped interior voids due to the release of NO$_x$ and O$_2$ gases during pyrolysis. The high solubility of LiNO$_3$ in water also contributes to the formation of this hollow structure. When water evaporates during ASP, LiNO$_3$ precipitates at the outer surface of the aerosol droplets following the surface precipitation mechanism (Messing et al., 1993). The microstructure of the Li$_2$CO$_3$-C$_{\text{NitS}}$ nanoparticles is further revealed by the TEM image in Figure 2D, after the removal of Li$_2$CO$_3$ using diluted hydrochloric acid (HCl). The carbon matrix of Li$_2$CO$_3$-C$_{\text{NitS}}$ has a highly porous structure after Li$_2$CO$_3$ removal, indicating that Li$_2$CO$_3$ occupies the majority of the volume in the Li$_2$CO$_3$-C$_{\text{NitS}}$ nanoparticles. The specific surface area of Li$_2$CO$_3$-C$_{\text{NitS}}$ before and after Li$_2$CO$_3$ removal obtained from the nitrogen adsorption-desorption isotherms (Figure 3 and Table S2) is consistent with this observation: the specific surface area of Li$_2$CO$_3$-C$_{\text{NitS}}$ is significantly increased from 26.8 to 608.2 m$^2$ g$^{-1}$ after Li$_2$CO$_3$ removal.

On the other hand, Li$_2$CO$_3$-C$_{\text{AceS}}$ nanoparticles show a denser spherical structure in Figure 2B. It is worth noting that the AceS precursor solution has a significantly lower sucrose/lithium salt molar ratio at 1:15 compared to 1:1.5 in NitS and 1:1.18 in CarS. Given the 22.8 wt.% carbon content in Li$_2$CO$_3$-C$_{\text{AceS}}$, it is believed the generated acetone during the pyrolysis of CH$_3$COOLi must function as the major source for carbon formation. The TEM image of the carbon matrix after Li$_2$CO$_3$ removal in Figure 2E reveals the distribution of Li$_2$CO$_3$ in the Li$_2$CO$_3$-C$_{\text{AceS}}$ nanoparticles is not as uniform as in Li$_2$CO$_3$-C$_{\text{NitS}}$. The carbon matrix has a golf ball-like structure with relatively large pores, previously occupied by Li$_2$CO$_3$, distributed within. The specific surface area of Li$_2$CO$_3$-C$_{\text{AceS}}$ is 76.3 m$^2$ g$^{-1}$, which increases to 184.9 m$^2$ g$^{-1}$ after Li$_2$CO$_3$ removal. This modest increase of surface area also indicates the relatively larger size of Li$_2$CO$_3$ compared to that of Li$_2$CO$_3$-C$_{\text{NitS}}$.

As shown in Figure 2C, the Li$_2$CO$_3$-C$_{\text{CarS}}$ nanoparticles clearly have a different structure resembling crumpled spheres, which is due to the much lower solubility of Li$_2$CO$_3$ in water than those of LiNO$_3$ and CH$_3$COOLi. The concentration of Li$_2$CO$_3$ in the CarS precursor solution is 0.1 M, which is close to saturation (Zou et al., 2013). Therefore, Li$_2$CO$_3$ undergoes fast and uniform precipitation from the aerosol droplets’ evaporation in ASP according to the volume precipitation mechanism (Messing et al., 1993). In addition, the ASP of CarS precursor also releases fewer gaseous species without decomposition of Li$_2$CO$_3$. Both factors contribute to better confinement and more uniform distribution of Li$_2$CO$_3$. After Li$_2$CO$_3$ removal, the carbon matrix retains its original structure with apparently higher porosity as shown in Figure 2F. The specific surface area of Li$_2$CO$_3$-C$_{\text{CarS}}$ nanoparticles is 43.7 m$^2$ g$^{-1}$, which increases to 443.6 m$^2$ g$^{-1}$ after Li$_2$CO$_3$ removal.

The Li$_2$CO$_3$-C nanoparticles obtained via ASP were subsequently reacted with mixed hydrogen sulfide and argon gas (H$_2$S/Ar at 5/95 vol.%) at 725°C to yield the Li$_2$S-C composites.

**Figure 3** | N$_2$ adsorption-desorption isotherms of (A) Li$_2$CO$_3$-C nanoparticles and (B) the carbon matrix after Li$_2$CO$_3$ removal.
according to Reaction 4, confirmed by the XRD patterns shown in Figure 1B.

\[
\text{Li}_2\text{CO}_3 + \text{H}_2\text{S} \rightarrow \text{Li}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \tag{4}
\]

The TEM images of the Li$_2$S-C composites in Figures 2G–I (scanning electron microscopy images in Figure S4) demonstrate that these nanoparticles sustain their original structures after the conversion to Li$_2$S from Li$_2$CO$_3$.

Figure 4 shows the first three CV cycles of the Li$_2$S-C vs. Li counter/reference electrode in two-electrode cells. The cathodic peak in the first delithiation scan of Li$_2$S-C$_{\text{NitS}}$ is centered at 3.5 V with a small shoulder at 3.4 V. The Li$_2$S-C$_{\text{AceS}}$ composite demonstrates a broader delithiation peak at the same potential.
In contrast, \( \text{Li}_2\text{S-C}_{\text{CarS}} \) shows two distinct cathodic peaks at 2.75 and 3.4 V vs. Li\(^+\)/Li. The lower cathodic peak of the \( \text{Li}_2\text{S-C}_{\text{CarS}} \) composite at 2.75 V indicates a lower energy barrier for the delithiation reaction (Zhou et al., 2017). The \( \text{Li}_2\text{S-C}_{\text{CarS}} \) composite also demonstrates the highest peak current in the consecutive lithiation-delithiation scans. The superior performance of \( \text{Li}_2\text{S-C}_{\text{CarS}} \) may be reflective of the intimate contact of \( \text{Li}_2\text{S} \) and the carbon matrix. \textbf{Figure 5} displays the representative charge-discharge curves and the cycle stability of the \( \text{Li}_2\text{S-C} \) composites. The electrolyte/\( \text{Li}_2\text{S} \) ratio is 10:1 (\( \mu \text{L}/\text{mg} \)), and all \( \text{Li}_2\text{S-C} \) composites are first charged to 3.5 V (activation) vs. Li\(^+\)/Li with a current density of 50 mA g\(^{-1}\). The charge-discharge curves demonstrate similar cycling behavior of these three \( \text{Li}_2\text{S-C} \) composites. However, \( \text{Li}_2\text{S-C}_{\text{AceS}} \) shows the highest charge-discharge hysteresis, which is consistent with the lowest surface area of its carbon matrix. On the other hand, although \( \text{Li}_2\text{S-C}_{\text{GNIS}} \) shows the highest voltage hysteresis due to the highest surface area of its carbon matrix, its capacity rapidly fades. As a composite with the balanced microstructure, \( \text{Li}_2\text{S-C}_{\text{CarS}} \) demonstrates the best overall performance: After 200 cycles, \( \text{Li}_2\text{S-C}_{\text{CarS}} \) can retain a capacity of 540 mAh g\(^{-1}\), superior to 385 mAh g\(^{-1}\) of \( \text{Li}_2\text{S-C}_{\text{GNIS}} \) and 460 mAh g\(^{-1}\) of \( \text{Li}_2\text{S-C}_{\text{AceS}} \), indicating the effectiveness of the \( \text{Li}_2\text{S-C}_{\text{CarS}} \) composite architecture in sequestrating polysulfides. The overall performance demonstrated by \( \text{Li}_2\text{S-C}_{\text{CarS}} \) in terms of areal loading, E/\( \text{Li}_2\text{S} \) ratio, overall capacity, and cycle stability, is on par with the best performance reported to date (Table S3).

In summary, we examined a new synthetic route for the production of \( \text{Li}_2\text{S-C} \) composite materials for Li-S batteries. The combination of aerosol spray pyrolysis and sulfurization has been shown to be a robust method for the conversion of various lithium salts including nitrate, acetate, and carbonate to \( \text{Li}_2\text{S-C} \) nanocomposites using sucrose as the carbon precursor. Furthermore, the cycling performance of the \( \text{Li}_2\text{S-C} \) composite has been found to be closely correlated to its precursor-derived microstructure. The combination of \( \text{Li}_2\text{CO}_3 \) and sucrose results in the \( \text{Li}_2\text{S-C} \) composite with the best electrochemical performance, which has a non-hollow composite structure with \( \text{Li}_2\text{S} \) uniformly embedded in the carbon matrix. The detailed mechanism of aerosol spray pyrolysis and the optimization of the composite’s structure and electrochemical performance will be further investigated in our future studies.

**AUTHOR CONTRIBUTIONS**

NH completed most of the experiments. JS, JZ, and CF helped with the experiments and data analysis. JG designed the experiments. All authors co-wrote the manuscript.

**ACKNOWLEDGMENTS**

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2018.00476/full#supplementary-material

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Hart et al. Lithium Sulfide Cathode


Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Electrochemical potential window of battery electrolytes: the HOMO-LUMO misconception

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1. Thermodynamic cycle to estimate the absolute redox potential of Fe(III)/(II) couple

Figure S1. Thermodynamic cycle to estimate the absolute redox potential of Fe(III)/(II) couple considering the work to remove the solvation shell upon transfer of the Fe$^{2+}$ into the gas phase, ionization energy and the solvation energy of Fe$^{3+}$, resulting in the absolute potential of 5.20 V. The alternative approach is to utilize the standard redox potential of Fe(III)/(II) couple of 0.77 V vs. SHE and the definition of the SHE at the absolute vacuum scale of 4.44 V, resulting in the absolute potential of 5.21 V.
2. The correlation of the experimental ionization energies (HOMO) and tabulated standard reduction potentials of aqueous transition metal

Table S1. Experimental vertical ionization energies (VIE) of some hexaqua complexes of transition metal ions\(^2,3\) and the corresponding standard oxidation and reduction potentials.\(^4\)

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<th>Species</th>
<th>VIE, eV</th>
<th>Redox pair</th>
<th>(E_{\text{red}}, \text{~V})</th>
<th>Redox pair</th>
<th>(E_{\text{ox}}, \text{~V})</th>
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<td>Ti(^{3+})</td>
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<td>Cr(^{3+})</td>
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<td>Cr(^{3+})/CrO(_2)</td>
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<tr>
<td>Cr(^{2+})</td>
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<td>Cr(^{3+})/Cr(^{2+})</td>
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<td>Mn(^{2+})</td>
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<tr>
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<tr>
<td>Co(^{2+})</td>
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<tr>
<td>Cu(^{2+})</td>
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<td>Cu(^{3+})/Cu(^{2+})</td>
<td>2.4</td>
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Figure S2. Correlation of the experimental HOMO energies (vertical ionization energy) and standard reduction potentials (black) and oxidation potentials (red) of the transition metals.
3. References


