



Nitrogen-doped carbons in Li–S batteries: materials design and electrochemical mechanism

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Li–S batteries have been considered as next generation Li batteries because of their high-theoretical energy density. Over the past few years, researchers have made significant efforts in breaking through critical bottlenecks, which impede the commercialization of Li–S batteries. Beginning with a basic introduction to Li–S systems and their associated mechanism, this review will highlight the application of one specific carbon family, nitrogen-doped carbon materials in sulfur-based cathodes. These materials will include nitrogen-doped porous carbon, carbon nanotubes, nanofibers, and graphene. The article will conclude with a summary of recent research efforts in this field as well as the future prospects for the use of nitrogen-doped carbon materials in Li–S batteries.

Keywords: nitrogen-doped carbon materials, Li–S batteries, sulfur cathodes, lithium sulfide cathodes, heteroatom effect

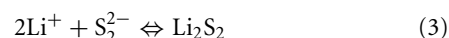
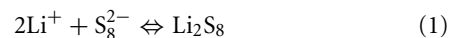
INTRODUCTION

The exponential consumption of fossil fuels has driven a large exploratory effort in the search for sustainable renewable energy sources and energy storage systems. Batteries as a powerful successor have taken a dominant role for the application of large electrical devices (Dunn et al., 2011; Goodenough and Kim, 2011). Since the introduction of Li-ion batteries (LIBs) by Sony in the early 1990s, these energy storage devices have been received extensive attention for the use in everyday-life portable devices, electrical grid, military, and electric vehicles (EVs) (Armstrong et al., 2013; Lee et al., 2013). Compared with other kinds of batteries, LIBs are competitive candidates owing to their high-energy density and long-cycle life (Rousse and Tarascon, 2014; Xu et al., 2014). However, the energy output of current commercialized LIBs still cannot meet the requirements for the development of EVs and hybrid electric vehicles (HEVs) with long-driving range (Gao and Yang, 2010). Owing to this inadequacy, the exploration of high-energy batteries is still critical for the development and application of Li-based batteries. Li–S and Li–air batteries are considered as next generation energy storage devices with superiorly high-theoretical capacity and energy density, and are well suitable for the use in EVs and HEVs (Song et al., 2013; Wang et al., 2013a; Zhang, 2013). In this review, a brief introduction of Li–S batteries with their advantages, challenges, and opportunities will be discussed. Following this, elaborations on the application of nitrogen-doped carbon materials, one specific family in Li–S systems, will be given.

MECHANISM AND CHALLENGES OF Li–S BATTERIES

The configuration of Li–S batteries is similar to LIBs, which is composed of sulfur-based cathode, Li metal anode, and electrolyte in

the middle to separate the two electrodes, as shown in **Figure 1**. The electrochemical reaction mechanism of Li–S batteries, however, is different from LIBs. Charging and discharging in layer-structured cathode and anode materials for LIBs are typically governed by a simple intercalation/deintercalation process (Evers and Nazar, 2013; Manthiram et al., 2013; Yin et al., 2013). Unlike LIBs, cathode materials for Li–S systems are composed of S_x molecules embedded within a host material, such as carbon, while the anode employs Li foil (Bruce et al., 2012; Song et al., 2013). During a typical discharge process, the S_8 ring is broken and forms an extended polysulfide chain. The long-chain polysulfides are then subsequently reduced down to shorter chain polysulfides, until their final form of either Li_2S_2 or Li_2S is obtained. This process is then reversed during the charge step. The overall electrochemical reactions have been proposed to occur in following manner (Wang et al., 2013; Yin et al., 2013; Zhang, 2013):



The most appealing advantage of sulfur cathodes in Li-batteries is the ultra-high-theoretical energy density ($\sim 2600 \text{ Wh kg}^{-1}$). Compared to the lithium metal oxide cathode materials typically used in LIBs, elemental sulfur has a much lower molar weight while also being able to undergo multi-electron reactions with Li metal. These advantages allow sulfur cathode materials to have an ultrahigh theoretical specific capacity, nearly 10

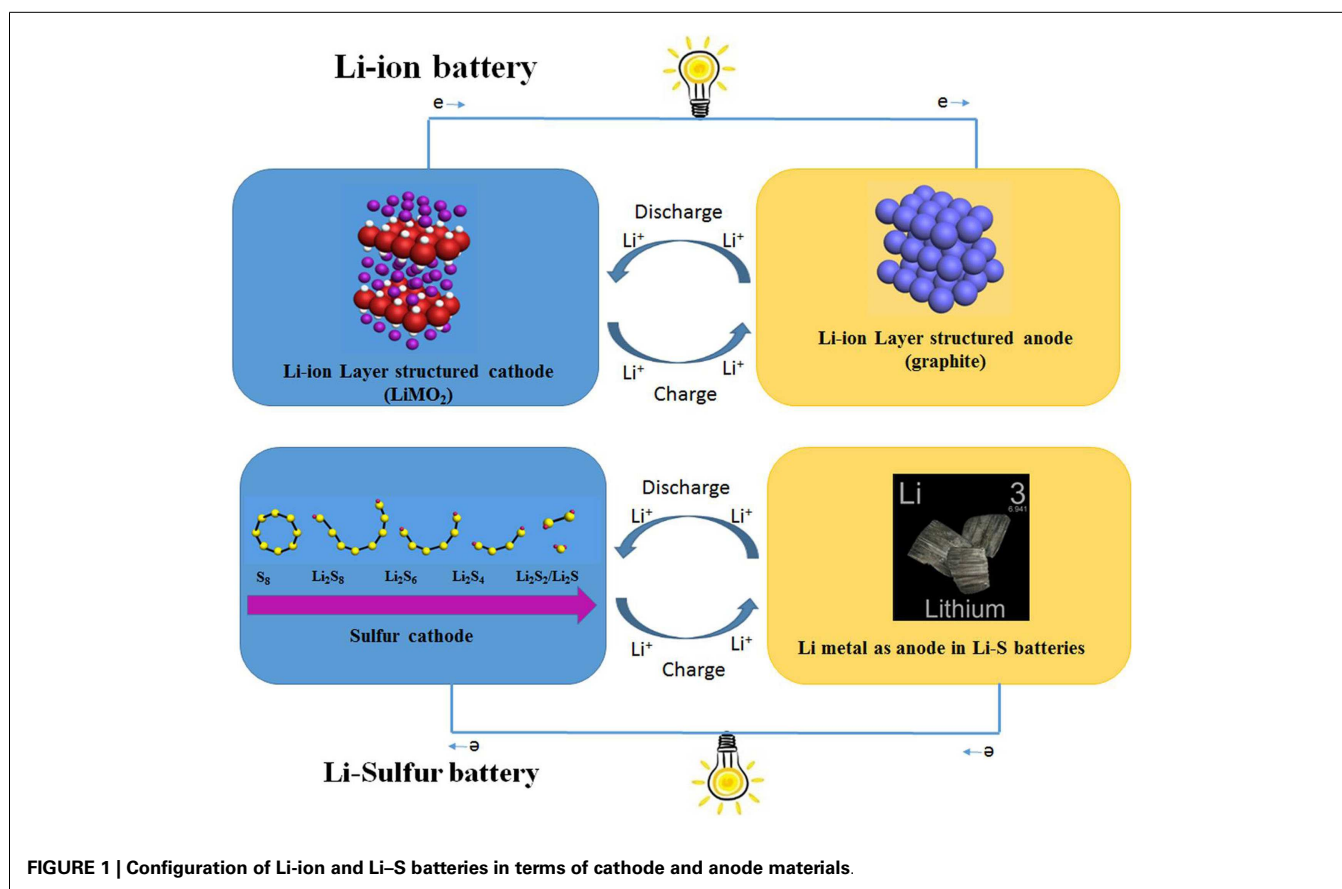


FIGURE 1 | Configuration of Li-ion and Li-S batteries in terms of cathode and anode materials.

Table 1 | Theoretical capacity, energy density, and working voltage of cathode materials.

Cathode material	Working voltage (V)	Theoretical capacity (mA h g ⁻¹)	Energy density (Wh kg ⁻¹)
Sulfur	2.2	1675	2566
Li-O ₂	3.0	3840	3505
Li-ion	3.0–5.0	100–270	400–700

times greater than current LIB cathode materials, as shown in **Table 1** (Hu et al., 2013; Zanghib et al., 2013; Islam and Fisher, 2014; Rouse and Tarascon, 2014). The working voltage of Li-S systems is mainly at 2.3–2.1 V and not as high as commercial cathodes of LIBs. However, this shortcoming is alleviated by the high-specific capacity, resulting in an energy density over five times greater than commercialized metal oxide cathode materials. Moreover, the abundance, low cost, and environmental benignity of sulfur make it an especially attractive material for use in next generation Li-based batteries (Zhang, 2013; Scheers et al., 2014).

Currently, a number of issues have hindered the realization of high-energy Li-S batteries (Bresser et al., 2013). These issues include the inherent insulating nature of sulfur and discharge products, as well as the dissolution of polysulfide species, leading

to a low utilization of sulfur in electrochemical reaction. During the discharge-charge process, dissolved high-ordered polysulfides diffuse through the separator and chemically react with Li foil, forming low-ordered polysulfides (Yang et al., 2013a). The reversed process occurs simultaneously as low-ordered polysulfide migrating back to the cathode, called “shuttle effect.” These side reactions give rise to serious consumption of active sulfur material and corrosion of anodic Li metal, leading to poor cycle life. Furthermore, the sulfur-based cathode material undergoes an over 80% of volume expansion during lithiating process, resulting in increased safety concerns (Yang et al., 2013a).

To achieve the practical use of Li-S batteries, carbon materials are seen as prevailing strategies in alleviating the issues mentioned above. Since Ji et al. (2009) reported highly ordered mesoporous carbon for Li-S batteries, various carbon materials have been employed in Li-S systems, including zero-dimensional mesoporous particles (Wang et al., 2012, 2014b), one-dimensional nanotubes and nanofibers (Hagen et al., 2012; Liang et al., 2012), two dimensional graphene (Wang et al., 2013b; Gao et al., 2014), and carbon paper (Su and Manthiram, 2012a; Chung and Manthiram, 2014). High conductivity, large pore volume, and desirable pore size of carbon materials are favorable to aid in improving the conductivity of sulfur cathodes while retaining an elevated amount of active sulfur material. Besides, it is widely accepted that the

sorption effect and specific morphology of carbon nanomaterials effectively retain polysulfides in carbon matrix and support to relieve the deleterious “shuttle effect.”

NITROGEN-DOPED CARBONS (N-CARBON) IN SULFUR CATHODE

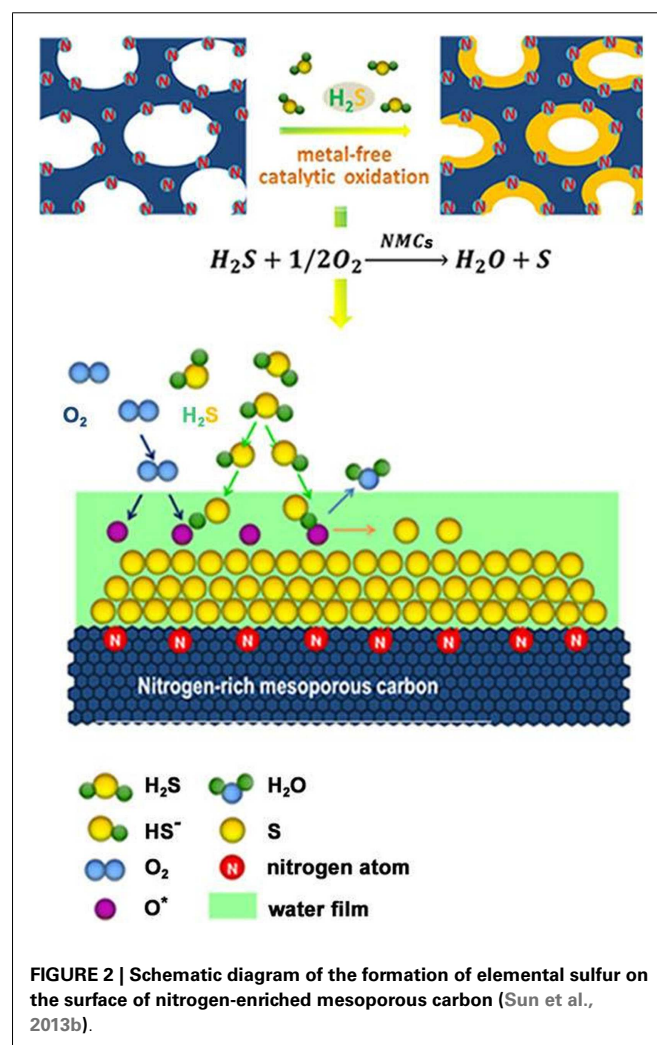
Nitrogen-doped carbon materials have extensively applied in energy storage devices including fuel cells (Geng et al., 2012; Cheng et al., 2014), LIBs (Li et al., 2012a; Chang et al., 2013), Li-air batteries (Li et al., 2012b, 2013), as well as many others fields (Lee et al., 2009; Xue et al., 2012). Their various applications in these fields are because of the metal free catalysis effect, high conductivity, distinct morphology, and specific surface properties. Two main synthetic routes are utilized for the production of nitrogen-doped carbon materials (Nishihara and Kyotani, 2012; Zheng et al., 2012). One method employed for the *in situ* inclusion of nitrogen into the carbon matrix is the use of a nitrogen containing precursor during pyrolysis (Meier et al., 2008; Sharifi et al., 2012; Shin et al., 2012). This method is predominantly used in the fabrication of highly ordered structures such as nitrogen-doped carbon nanotubes and nanofibers. Another strategy for the inclusion of nitrogen heteroatom is the use of a post-treatment method where nitrogen containing agents react with carbon materials to create various nitrogen-doping types, including pyridinic, pyrrolic, and graphitic nitrogen (Hao et al., 2010; Geng et al., 2011; Fellingner et al., 2012). Typically, this approach is generally conducted with ammonia gas under elevated temperature or with ammonium hydroxide in solvothermal process. The use of nitrogen-doped carbons in Li-S batteries can be categorized in three groups, including zero-dimensional porous carbons, one-dimensional CNTs and carbon nanofibers (CNFs), and two dimensional graphene.

NITROGEN-DOPED MESO- AND MICROPOROUS CARBON

Meso- and microporous carbon materials (MPCs) are widely used in Li-S systems. Nitrogen-doped MPCs (N-MPCs) are predominately prepared by the post-treatment methods. Compared with pristine MPCs, N-MPCs have enhanced conductivity due to the electron configuration of N atoms. Furthermore, N-MPCs have the additional advantages of high-surface area and large pore volume. These properties make N-MPCs ideal candidates as carbon hosts for sulfur cathodes. Research into the use of nitrogen-doped MPCs for Li-S systems was firstly reported in 2012, which proposed that N-MPCs may improve the conductivity of sulfur, resulting in high-sulfur utilization during Li-S cycling process (Sun et al., 2012). This study reported the use of nitrogen-doped mesoporous carbon (NC) as a host for sulfur cathodes. Compared with bare carbon-sulfur composite, NC/S composite showed a higher initial discharge capacity over 1400 mA h g^{-1} , indicating enhanced sulfur utilization. Furthermore, NC/S is demonstrated lower sulfur cathodic potential, higher redox current density in the CV profile, and smaller surface charge transfer resistance in EIS test. These results are strong indications of improved electrochemical activity of sulfur because of the inclusion of nitrogen.

More recent research has concentrated on the exploration of the nitrogen effects and different reaction mechanisms in Li-S systems. Sun et al. (2013a) reported the use of nitrogen-enriched

mesoporous carbon with tunable nitrogen content as host materials for sulfur cathodes. The nitrogen-doped carbon/sulfur composites delivered a reversible discharge capacity of 758 mA h g^{-1} at 0.2 C and 620 mA h g^{-1} at 1 C over 100 cycles. The authors proposed that nitrogen-doping facilitates the surface adsorption of polysulfide into mesoporous carbon, thus, preventing polysulfide dissolution. Another research has further determined the catalytic effect of nitrogen-doped carbon and demonstrated an economic strategy toward synthesizing sulfur/carbon composites via a bottom-up catalytic approach (Sun et al., 2013b). As shown in **Figure 2**, nitrogen-enriched mesoporous carbon acts as a catalyst and oxidizes H_2S down to elemental sulfur, allowing sulfur directly formed onto the carbon framework to produce a C/S composite. The authors stated that nitrogen inclusion increases the surface interaction between polysulfides and carbon framework, resulting in the improved performance. The composites exhibited a reversible capacity of 939 mA h g^{-1} after 100 cycles at 0.2 C and a rate capability of 527 mA h g^{-1} at 5 C after 70 cycles. These two reports clearly identify that nitrogen-doped carbon hosts can improve both capability and stability of Li-S batteries because of enhanced adsorption of polysulfides. However, there is still a lack



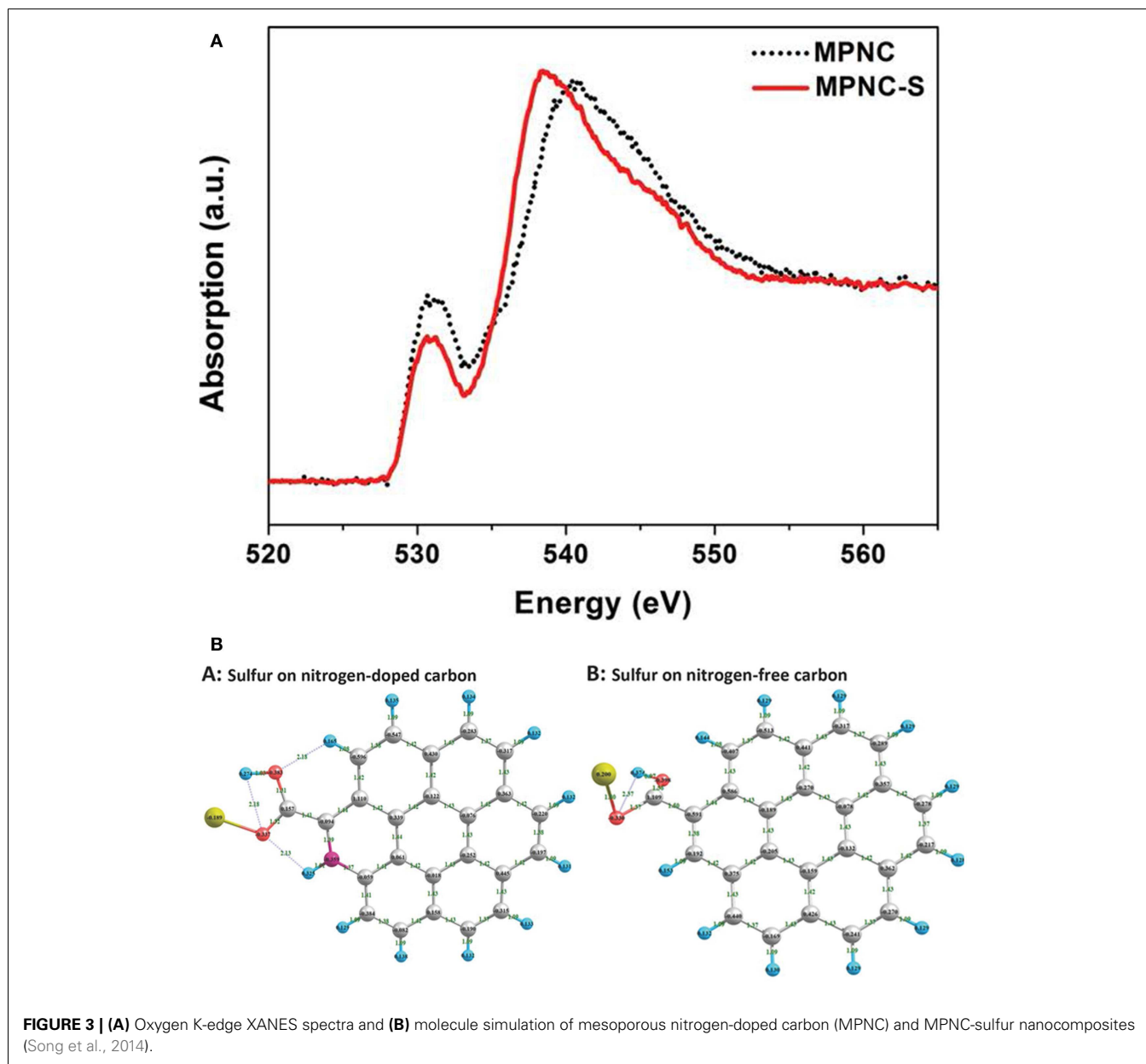
of understanding behind the exact mechanism that exists between doped nitrogen species and polysulfide species.

Except of “adsorption effect,” recent research has confirmed the presence of chemical interactions between N-doped carbon and sulfur-based species. Song et al. (2014) reported the interaction between nitrogen, oxygen, and sulfur in sulfur cathodes. With the use of X-ray absorption near edge structure spectroscopy (Figure 3), the authors determined that nitrogen-doping enable more sulfur accessible to oxygen functional groups on carbon, which is considered as a key role in sulfur immobilization. Recent research conducted by Li et al. (2014a) also demonstrated the presence of chemical interactions between discharge products of lithium sulfides and N atoms from mesoporous carbon host by synchrotron-based X-ray photoelectron spectroscopy (XPS). The favorable interaction results in a uniform distribution of

discharge products and drastically improves the electrochemical performance (Figure 4).

ONE-DIMENSIONAL NITROGEN-DOPED CARBON NANOTUBES AND NANOFIBERS

One-dimensional multi-walled carbon nanotubes (MWCNTs) and CNFs have been investigated as conductive additives in Li-S systems (Su and Manthiram, 2012b). The one-dimensional structure of MWCNTs and CNFs has been confirmed to effectively encapsulate sulfur and prevent polysulfides dissolution (Zheng et al., 2011; Moon et al., 2013). As a result, nitrogen-doped CNTs or CNFs recently have attracted greater attention. Owing to the highly ordered structure of CNTs and CNFs, the most common method for nitrogen inclusion is the use of *in situ* nitrogen-doping approach (Lee et al., 2011; O’Byrne et al., 2011; Lepró et al., 2012).



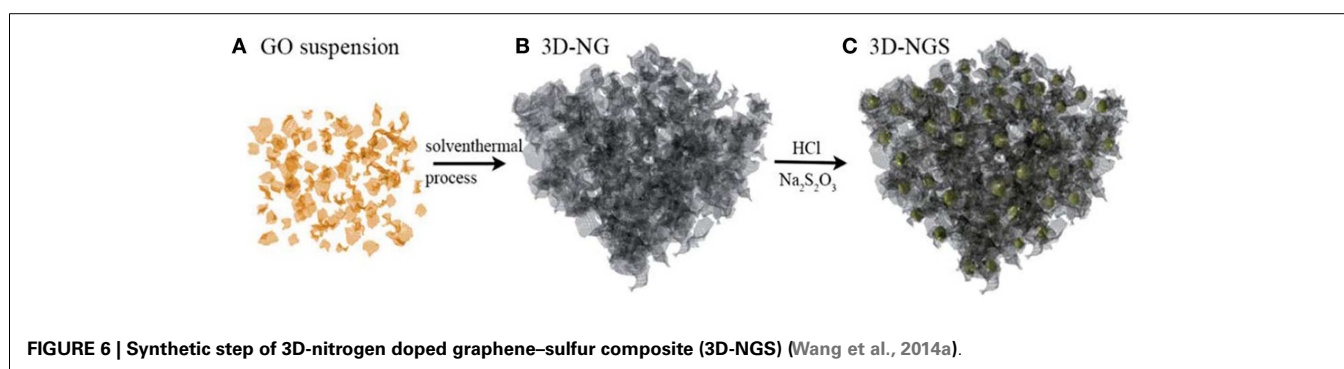
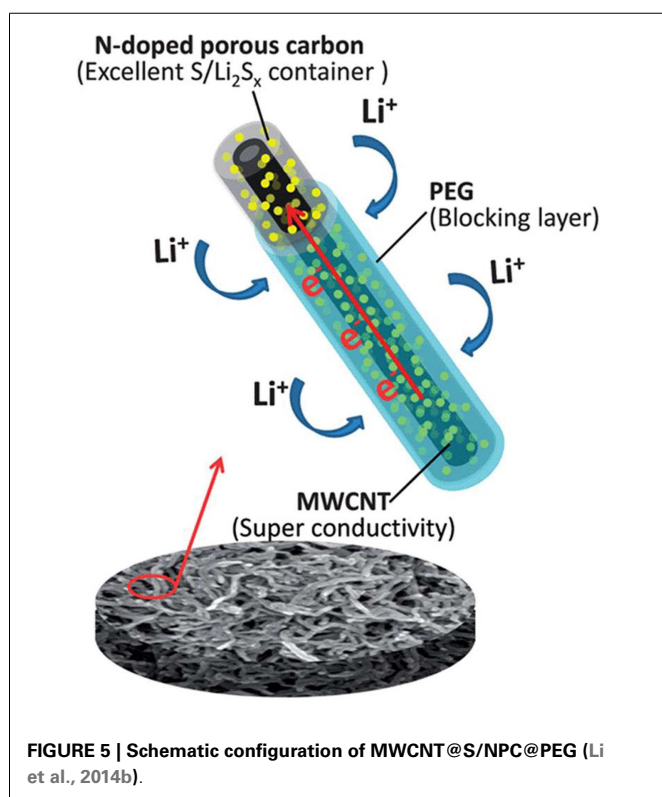
research of nitrogen-doped graphene in sulfur cathodes is very limited. Wang et al. (2014a) reported the use of a porous three-dimensional nitrogen-doped graphene (3D-NG) for sulfur cathodes. The nitrogen-doping process was conducted via solvothermal process with ammonium hydroxide as a nitrogen-doping agent (shown in Figure 6). The 3D-NG-sulfur composite (3D-NG/S) had a high-sulfur loading content of 87.6 wt% and exhibited a specific discharge capacity of 792 mA h g^{-1} after 145 cycles under 600 mA g^{-1} . The authors proposed that N-doping graphene facilitates fast Li-ion transmission and simultaneously traps polysulfide. Moreover, 3D structured graphene can accommodate volume expansion while allowing electrolyte penetration. Compared with other carbon materials, the layer-structured graphene and N-doped graphene have their specific 2D morphology, electronic, and ionic conductivity, considering as new superstars in carbon materials. Application based on nitrogen-doped graphene

in Li-S systems is still insufficient and further detailed research is necessary.

NITROGEN-DOPED CARBON IN LITHIUM SULFIDE CATHODES

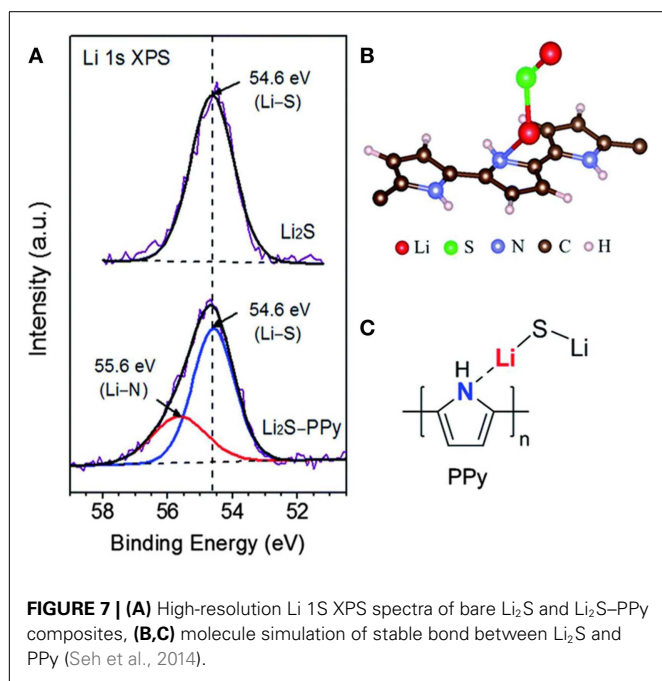
Recently, lithium sulfide (Li_2S) has gained attention as a promising cathode material because of its potential to avoid the use of Li metal and the unsafe formation of lithium dendrite (Seh et al., 2013). Furthermore, Li_2S cathodes can avoid volume expansion issues because they are already in a fully lithiated state. Besides, Li_2S also has an ultrahigh theoretical capacity of 1166 mA h g^{-1} (Yang et al., 2012, 2013b). However, research of Li_2S is still in its infancy due to many critical issues that currently exist. The non-conductive nature of Li_2S and dissolution of intermediate product polysulfides plague the use of Li_2S , similar to sulfur cathodes, leading to poor cycle life and reduced coulombic efficiency (Han et al., 2014). Especially of the dissolved polysulfides, they will chemically react with cathode and anode parts, called “shuttle effect.” Another perilous issue impeding the use of Li_2S is its high sensitivity to water and oxygen (Jeong et al., 2013). These issues cause considerable challenges for the application of Li_2S , requiring elaborated protection of Li_2S in order to avoid contact with ambient environment from synthesis to battery assembly (Lin et al., 2013; Seh et al., 2014).

To overcome these issues, carbon materials have been employed for use in the development of Li_2S cathodes. These materials include graphene, polymers, as well as mesoporous carbon. Nitrogen heteroatom inclusion in carbon matrix is favorable to the encapsulation of Li_2S and allows the carbon material to cover the surface of Li_2S . Guo et al. (2013) introduced a mechanism outlining the interaction of Li-ions and nitrile groups from polyacrylonitrile (PAN). The authors suggested that this interaction can be exploited to build carbon- Li_2S composites and fabricate a uniform distribution of Li_2S on carbon, leading to an improved cycle performance. Research conducted by Seh et al. (2014) further confirmed the mechanism of interaction between Li-ions and nitrogen groups. The Li_2S -polypyrrole composite was synthesized via an *in situ* polymerization process. Using high-resolution XPS, it was determined the interaction between N atom from polypyrrole and Li-ion from Li_2S , which enables polypyrrole to cover the surface of Li_2S particle tightly (Figure 7). This uniform coating layer can prevent polysulfides dissolution during cycling. Furthermore, the conductive polypyrrole coating enables fast electron transmission, ultimately leading to elevated utilization of Li_2S .



SUMMARY AND OUTLOOK

Li-S batteries are considered as promising high-energy storage devices for the application of long-distance EVs. Two key challenges currently facing the realization of Li-S batteries are the improvement of cathode conductivity and the dissolution of polysulfides. The use of carbon as a host material is clearly an excellent strategy toward these issues. This review highlighted a new family of carbon materials, nitrogen-doped carbon, and its application in sulfur and sulfide cathodes, including the use of zero-dimensional mesoporous carbon, one-dimensional carbon nanotubes and nanofibers, and two dimensional graphene. Nitrogen-doped carbon materials are well suited for this application because of their high conductivity, featured morphology, and modified surface properties. The review presented here on nitrogen-doped carbon demonstrates the improved electrochemical performance of these materials and provides a detailed discussion on mechanisms through which nitrogen significantly improves these systems, as



shown in **Table 2**. The previous researches have demonstrated clear evidences of the presence of chemical interactions between N-doped carbon and sulfur or sulfide cathodes, enhancing the immobility of polysulfides.

The use of nitrogen-doped carbon for sulfur cathodes has undergone tremendous development, but further improvements in this field need to be established. Understanding of nitrogen-doping effects in Li-S systems should be further studied. Two main effects of N-doped carbon have been proposed in literature. One is the improved conductivity of N-doped carbon, leading to high utilization of sulfur. The other is the immobility of polysulfides, resulting in stable cycle life. However, not enough work has been done to address the mechanisms governing these phenomena. Detailed research on the correlations between the nitrogen-doping and sulfur cathode performance remains a challenge. Advanced characterization methods, such as synchrotron radiation analysis, can reveal the mechanisms behind the electrochemical performance. Synchrotron-based X-ray spectroscopy is a very powerful tool that can be used to understand the chemical structure of composites in Li-S systems. It has been confirmed by synchrotron radiation analysis: (1) the presence of interactions between graphene and sulfur via XAS spectroscopy (Ji et al., 2011); (2) the polysulfides transformation via operando XAS (Cuisinier et al., 2013); and (3) the dissolution effect of polysulfides via operando X-ray diffraction (soft X-ray) and transmission X-ray microscopy (hard X-ray) (Nelson et al., 2012). The research of synchrotron radiation on N-doped or other heteroatom-doped carbon in Li-S batteries will shed light on the doping effect on electrochemical performance.

Furthermore, developing high quality and economic N-doped carbon materials is another challenge for applicable Li-S energy storage systems in future: (i) developing methods to synthesize mass-production of N-doped CNTs with low cost; (ii) identifying N doping types (pyridinic, pyrrolic, and graphitic nitrogen) on which is favorable for battery performance and developing approaches to control the percentages of desirable N doping type; (iii) understanding surface properties of N-doped carbon and finding ways to reduce the irreversible capacity loss of batteries, resulting from doping effect (Xiao et al., 2013); (iv) improving other heteroatom-doped carbon materials for Li-S, LIBs, and other energy storage systems.

Table 2 | Summary of nitrogen-doped carbons in Li-S system in terms of synthetic method, sulfur load, and electrochemical performance.

Material	Nitrogen-doped method	Sulfur/sulfide load	Capacity	Reference
Nitrogen-doped mesoporous carbon-sulfur	Post-treatment (high-temperature ammonia treatment)	70 wt%	800 mA h g ⁻¹ over 100 cycles under 0.7 mA cm ⁻²	Song et al. (2014)
Nitrogen-doped carbon nanotube-sulfur	<i>In situ</i> growth (C, N contained precursor)	53.9 wt%	791 mA h g ⁻¹ over 50 cycles under 0.5 C	Li et al. (2014b)
Nitrogen-doped carbon nanofiber-sulfur	<i>In situ</i> growth (C, N contained precursor)	77.01 wt%	749.8 mA h g ⁻¹ after 180 cycles at 0.2 C	Yang et al. (2014)
Nitrogen-doped graphene-sulfur	Solvothermal treatment	87.6 wt%	792 mA h g ⁻¹ over 145 cycles at 600 mA g ⁻¹ (0.37 C)	Wang et al. (2014a)
N-involved polymer-Li sulfide (Li_2S)	<i>In situ</i> growth (N contained carbon monomer)	86 wt%	785 mA h g ⁻¹ over 400 cycles at 0.2 C	Seh et al. (2014)

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