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On The Mechanistic Role of Nitrogen-Doped Carbon Cathodes in Lithium-Sulfur Batteries with Low Electrolyte Weight Portion

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Abstract

The lithium-sulfur (Li-S) battery is a promising alternative to overcome capacity and specific energy limitation of common lithium-ion batteries. Highly porous carbons with nitrogen-doping as conductive host structure for sulfur/lithiumsulfide deposition are shown herein to play a critical role in reversible cycling at low electrolyte/sulfur ratio. The pore geometry is precisely controlled by an efficient, scalable ZnO hard templating process. By using an electrolyte volume as low as $4 \mu\text{l mg}^{-1}\text{s}$, the beneficial nitrogen functionality leads to a twofold increased cell lifetime turning our findings highly favorable for real applications. Stable cycling of up to 156 cycles (59 cycles with undoped carbon) with high sulfur loadings of 3 mg cm^{-2} is achieved. *Operando* X-ray diffraction patterns during cycling show the transformation pathway of the sulfur – polysulfide – Li_2S species. The observed intermediates critically depend on the nitrogen doping in the cathode carbon matrix. Nitrogen doped carbons facilitate polysulfide adsorption promoting the nucleation of crystalline Li_2S . These results provide new insights into the significant role of heteroatom doping for carbons in Li-S batteries with high specific energy.

Keywords:

cathode, conversion mechanism, lithium-sulfur battery, nitrogen-doped carbon, operando diffraction

1. Introduction

After identifying the lithium-sulfur (Li-S) battery as the candidate to overcome capacity limitation of common lithium-ion batteries and first prototyping series [1,2][2], several challenges still limit the competitive commercialization of the Li-S battery: The cycling stability of a practically usable Li-S cells with reasonable high sulfur loadings, low electrolyte weight portions, and a lithium metal anode is usually limited to less than 100 cycles due to dendrite formation and electrolyte decomposition. These degradation reactions at the anode

surface are significantly affected by soluble lithium polysulfides (LiPS), the cathode discharge intermediates, diffusing to the anode and leading to self-discharge and other side reactions. Goal of this work was to minimize and understand this effect by the development of easy-to-prepare hierarchical conductive carbon materials which are doped by nitrogen atoms using a facile and scalable process. These atoms support the adsorption of polysulfides and minimize their undesired transport to the anode. Several analytical and electrochemical methods were partially simultaneously applied to shed light on this complex process. Moreover, nitrogen doping is discussed to act as a redox mediator [3–5]. To the best of our knowledge, there is still a significant lack in understanding the beneficial effect of nitrogen doped carbons. Several groups showed that nitrogen-doped carbons, used either as carbon matrix for sulfur [6] or as a functional layer on the separator [7,8], significantly enhance the efficiency and lifetime of a cell. This is due to a reduced shuttle mechanism as a result of anchoring/adsorbing polysulfides at the cathode side. However, detailed mechanistic investigations on the role of the nitrogen are rare.

A crucial, but frequently ignored aspect is the electrolyte weight portion within the Li-S battery. Practical Li-S cells must operate under an electrolyte/sulfur ratio of less than 3 $\mu\text{l mg}^{-1}$ to achieve a high specific energy [9]. Up to now, the lowest reported values with acceptable cycling stability with standard DME/DOL LiNO_3 containing electrolyte on coin cell level are in the range of 5 $\mu\text{l mg}^{-1}$. However, other adapted electrolyte systems are recently published to result in lower electrolyte portions [10,11]. So far, lower values drastically reduce long term stability hampering a broad commercialization or implementation of published materials [12].

The integration of nitrogen atoms into graphene layers was reported to increase the electrical conductivity as well as the adsorption capability of polar species on the carbon surface [3,13]. The adsorption potential significantly depends on the amount of introduced nitrogen

containing functional groups. Due to their free lone pair of electrons electron pair, negatively polarized, pyridinic nitrogen atoms can function as Lewis-base. These pyridinic nitrogen atoms coordinate lithium cations and help to immobilize LiPS and Li₂S, respectively, as the discharging products. Carbon atoms in the electron rich proximity of quaternary nitrogen atoms also form anchor points. In contrast, pyrrolic nitrogen atoms are less effective for this purpose given that their free electron pair is preferentially integrated into the π -system of the five-membered ring in order to create an aromatic state. Therefore, the donor-acceptor interaction, necessary for the coordination/bonding of polar species, is less effective in that particular chemical environment. For example, graphene-sulfur composites with pyridinic nitrogen atoms (12.5 at%) show an increased capacity (compared with pyrrolic nitrogen atoms, 11.5 at%) after 100 cycles at C/10 [13], Both systems displayed superior capacities compared to the corresponding undoped graphene-based composite. However, graphene as a carbon scaffold for Li-S cathodes has no intrinsic porosity for the storage of ether-based electrolyte and sulfur, respectively. A certain ratio of micro- and mesopores is described to be beneficial for sulfur cathodes in ether-based electrolytes [14,15]. Hence, a nitrogen-doped, mesoporous carbon with an adjustable nitrogen content and chemical environment may show strongly positive influence on capacity. This material was successfully produced with the colloidal silica hard template method [16]. Silica nanoparticles are suitable and commonly used candidates for a precise tailoring of pores. Unfortunately, they can only be removed by hydrofluoric acid treatment. According to Sun *et al.*, 4 – 8 mass% nitrogen is sufficient for high conductivity. An acceptable immobilization of the LiPS only occurs above a heteroatom content of 8 mass% in their system. After 100 cycles at C/5, the optimized composite with 60 mass% sulfur and a nitrogen content of 8.1 mass% showed a coulombic efficiency (CE) of ~ 94 %. This result is recognized as rather high for a cathode/electrolyte system without LiNO₃, an electrolyte additive which is normally used to enhance the stability of the lithium anode.

To the best of our knowledge, there is still a significant lack of understanding the beneficial effect of nitrogen doped carbons. Analyzing nitrogen-doped carbon materials with a hierarchical mesoporous structure by XANES- and DFT-studies, Wang *et al.* found that oxygenated groups in α -position to pyridinic nitrogen atoms as well as pyrrolic N-atoms interact intensively with sulfur atoms [17,18]. At the same time, the coordination environment of the nitrogen atoms changed only marginally indicating an electron density transfer between adjacent carbonyl and carboxyl groups, respectively. This behavior leads to a highly negative polarization of the oxygen-containing groups, which effectively retained polar LiPS, coordinated at the positive partial charge located at the Li-side, *via* chemisorption on the carbon surface. Moreover, the precipitated Li₂S-particles were more homogeneously distributed. The (for ether-based electrolyte with high LiPS solubility) relatively high CE of >90% as well as the evaluation of the *ex-situ* adsorption behavior *via* UV/Vis-spectroscopy in our previous study [19] confirmed these results. Moreover, a nonpolar carbon surface tends to interact more preferentially with non-polar molecules such as S₈, whereas a polar nitrogen-doped carbon surface favors polar polysulfide species. Nitrogen-doping of carbons is an elegant strategy to create polar sites for polysulfide retention while maintaining a certain number of non-polar pores for sulfur adsorption.

The general observations for nitrogen atom doping in carbons are in agreement with the effects resulting from amphiphilic surface modification by polymers (e.g. PVP). Diverse metal oxides, chalcogenides and nitrides are also used to anchor polar polysulfides on the cathode side [20–23]. However, a crucial advantage of the nitrogen-doped carbons compared to amphiphilic surface modifications or additions of metal oxides lies in their high electrical conductivity. That guarantees electrochemical access to strongly adsorbed LiPS, optimal sulfur utilization, and reversibility of the transformation sulfur - polysulfides - sulfur. Hence, high overpotentials during discharge caused by insulating/nonconductive species are avoided.

Moreover, as already mentioned, nitrogen-doped carbons are known to act as redox mediators and may act as polar seeding sites for the heteronucleation of Li_2S . In summary, heteroatom doping is a suitable method to adapt sulfur cathodes in terms of their polarity as it allows controlled modifications of the basic properties of the carbon material like electron structure, wettability, adsorption capacity and surface polarity (alkalinity).

In this work, melamine and sucrose were chosen as nitrogen and carbon source, respectively, to create high performance but also scalable model materials for mechanistic investigations.

The N/C ratio in the hierarchical porous material was adapted and several analytical and electrochemical methods were partially simultaneously applied to shed light on this complex process. Melamine is cost-effective, has a high nitrogen to carbon atom ratio in its molecular structure, and enables a variety of possible chemical reactions between amine groups and oxygen functionalities. As a result, a homogenous network of a polymeric N/C-precursor that can be uniformly coated on polar ZnO nanocrystal surfaces is created. Moreover, by using a bottom-up approach and melamine, fewer pores are blocked because melamine pyrolysis occurs under generation of ammonia gas etching potentially blocked pores.

For stable cathode performance and high sulfur utilization, porous carbons with (up to 2.8 at%) and without nitrogen dopant as conductive host structure for sulfur/lithiumsulfide deposition are systematically developed and investigated in regard of their electrochemical and structure-property-relation. In contrast to the results by Sun *et al.* [16], approximately 2-3 mass% nitrogen doping was sufficient to reveal a clear impact of nitrogen doping on the cycling performance. The pore geometry is precisely controlled by an efficient and scalable ZnO hard templating process without using toxic chemicals such as HF or Cl_2 [14]. Additionally, high values for the total pore volume ($3.7 \text{ cm}^3 \text{ g}^{-1}$) as well as for the specific surface area ($1600\text{-}1800 \text{ m}^2 \text{ g}^{-1}$) are realized. The nitrogen content is controlled by varying the melamine:sucrose precursor ratios. Moreover, an *ex-situ* polysulfide liquid phase adsorption

method based on UV-Vis spectroscopy revealed that with increasing nitrogen content, higher surface polarities (water adsorption) and, higher amounts of polysulfides are adsorbed at the carbon materials. The cathodes show stable capacities of $>1000 \text{ mAh g}^{-1}_{\text{S}}$ in the first cycles at relatively low electrolyte volumes of up to $6.8 \mu\text{l mg}^{-1}_{\text{S}}$. Importantly, with increasing nitrogen content and constant electrolyte volume, more cycles are achieved which is crucial for the consideration of the material on full cell level. By using an electrolyte amount as low as $4 \mu\text{l mg}^{-1}_{\text{S}}$ sulfur, the nitrogen-containing functional groups lead to an increased cell lifetime (160 cycles) as it is highly desirable for real applications while non-doped carbon matrices lead to cell failure after 70 cycles. *Operando* X-ray diffraction patterns during cycling show that the transformation of the sulfur – polysulfide – Li_2S species critically depends on the nitrogen doping in the cathode matrix. Since both undoped and nitrogen-doped porous carbons exhibit similar structural characteristics (surface area, pore size distribution, pore volume), the critical role of surface functional group, which strongly affect the cycling stability at low electrolyte weight portions, is unambiguously identified.

2. Materials and Methods

Nitrogen physisorption / Mercury intrusion

Prior to physisorption measurements, the activated carbon samples were degassed for at least 24 h at 473 K. Nitrogen physisorption was measured at 77 K using a Microtrac BELSORB apparatus. Specific surface areas were calculated using the multipoint Brunauer-Emmett-Teller (BET) method ($p/p_0 = 0.05\text{-}0.2$). The pore size distribution was calculated according to the quenched solid density functional theory (QSDFT) adsorption model for the cylindrical/slit pore geometry at 77 K using the ASiQwin 3.01 software (Quantachrome). The specific micropore volume was also determined by the QSDFT method. The cumulative pore volume at a pore diameter of 2 nm corresponds to the micropore volume.

For the determination of the entire pore volume was carried out at $p/p_0 = 0.95$. The range recommended by the IUPAC at $p/p_0 = 0.99$ was not applied due to the lack of a plateau > 0.95 . The meso/macropore volumes (5 nm to 400 nm) as well as the pore size distributions were determined by Mercury intrusion porosimetry using AutoPore IV 9500 V1.07 according to the ISO 15901-1 standard.

Water vapor physisorption

The investigated sample was degassed prior to the measurements at 473 K. For the comparison of the adsorption tendency, the value at $p/p_0=0.02$ was used. Water physisorption was carried out on a Quantachrome Hydrosorb 1000 at 298 K.

X-ray photoelectron spectroscopy of nitrogen-doped porous carbons

XPS were performed with a Physical Electronics PHI 5600 CI spectrometer equipped with a 350 W Al X-ray source, a monochromator to produce $K_{\alpha 1}$ radiation and a hemispherical analyser for electron energy analysis. High-resolution spectra were recorded with a pass energy of 29 eV and a resolution of 0.1 eV. Before fitting with Gauss-Lorentz-type functions the spectra were background-corrected by a Shirley-type function with the help of the PHI Multipack software package (Physical Electronics) [19].

Ex-situ polysulfide liquid phase adsorption

PS solutions of Li_2S_6 were synthesized by stirring stoichiometric amounts of Li metal and S_8 in dimethoxyethane/dioxolane (DME/DOL) at 70 °C under Ar until no solid residues were observed and subsequently diluted from 2 M to 2, 4, and 8 mM [19]. Liquid phase adsorption isotherms were obtained from typical batch adsorption experiments. We recorded a low resolution isotherm with a low carbon:solvent ratio of $2.5 \text{ mg}_C \text{ ml}^{-1}$. For an isotherm, three samples of the respective adsorbent with a sample mass of 25 mg each were incubated with

Li₂S₆ solutions ranging from 2 to 8 mM c_0 in DME/DOL (50:50 V/V). After reaching an equilibrium state c_{eq} after 7 days, the carbon was filtered off the solution and the PS concentration was determined *via* UV-Vis spectroscopy. The adsorption excess Γ , i.e. the amount of PS adsorbed per unit mass of adsorbent, was determined by eq. 1

$$\Gamma = \frac{(c_0 - c_{eq})V}{m_{adsorbent}} \quad (1)$$

Plotting the isotherm showed a plateau for most adsorbents. Hence, polysulfide adsorption (PSA) was determined by calculating the average value of the three sample measurements.

Synthesis nitrogen-doped porous carbons

The synthesis of nitrogen-doped hierarchical carbons was conducted in similar way to the hard templating route by using ZnO nanoparticles (Figure 1) described elsewhere [14]. As carbon precursor sucrose and as nitrogen precursor melamine were used. Typically, 5.25 g sucrose were diluted in 15 ml deionized water, and 100 mg of an aqueous 2.5 M NaOH solution were added. Subsequently, a defined melamine mass was added by heating the solution to 80 °C. For the exact concentration, it is referred to Table 1. The solution was dropped on 6 g ZnO nanoparticles (US Nano) and intensively blended. The white dispersion was then heated to 100 °C / 3 h and afterwards to 160 °C / 6 h in air. The final pyrolysis step was conducted at 950 °C / 2h with 5 K min⁻¹ heating ramp under argon (0.5 slm) in a quartz tube furnace (Gero). Three samples with no (HPC-N0) and two different nitrogen doping levels were synthesized and investigated (HPC-N1 and HPC-N2).

Structural characterization of nitrogen-doped porous carbons

The morphology of the samples was characterized by Transmission Electron Microscopy (TEM) on a JEOL JEM-2100. Samples were deposited on a Cu grid with a holy carbon film using an isopropanol dispersion generated by ultra-sonic treatment. The grid was dipped into

the dispersion for approximately 10 s, and the subsequent drying step took place at 70 °C on a heated plate.

Dryfilm electrode preparation

Dryfilm electrodes were prepared from the carbon/sulfur composites following a solvent-free roll-press procedure reported elsewhere. However, the weight ratio of carbon/sulfur composite, carbon nanotubes and PTFE binder was altered to 85: 12: 3. The $100 \pm 20 \mu\text{m}$ thick freestanding electrode film was further laminated on a primer coated aluminium foil in order to achieve a final active layer thickness of $100 \pm 10 \mu\text{m}$. The typical active material loading of the punched circular electrodes with a diameter of 15 mm is $3.5 - 3.8 \text{ mg}_\text{s} \text{ cm}^{-2}$.

Galvanostatic charge/discharge measurements

Dryfilm electrode, a porous polyolefin separator, and elemental lithium were stacked in a CR2016 coin cell in an argon filled glove box [14]. Before sealing, 4 or $6.8 \mu\text{l mg}^{-1}_\text{sulfur}$ of electrolyte was added. Ether-based electrolyte (1 M LiTFSI and 0.25 M LiNO₃ in 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 by volume)) was used. The cell assembly was slightly adapted for an electrolyte volume as low as $4 \mu\text{l mg}^{-1}_\text{s}$ as stated in Table 1.

The capacity and long-term stability tests were carried out by galvanostatic cycling with a BASYTEC CTS cell test system at varying rates ($1 \text{ C} = 1672 \text{ mA g}^{-1}_\text{sulfur}$). The cells with high polysulfide solubility in the electrolyte were cycled in a voltage range of 1.8–2.6 V vs. Li/Li⁺ at room temperature. The Coulombic efficiency (CE) was calculated by dividing the discharge (lithiation) capacity by the charge (delithiation) capacity.

Operando X-ray diffraction measurements

Operando XRD measurements were recorded at the beamline P02.1 of the synchrotron radiation source PETRA III at DESY in Hamburg. In an 8-fold coin cell holder described elsewhere [24], a modified CR2025 coin cell with a tightly sealed Kapton window on both electrode sides was used. In order to avoid detection of inactive parts of the cell, holes were cut out in the center of the stainless steel spacer and casing. Only the thin aluminum current collector on the cathode and the lithium foil are detected as inactive part of the cell. The aluminum foil was used as internal standard to normalize for intensity fluctuations. The modified S/C cathodes ($\sim 3.8 \text{ mg cm}^{-2}$ sulfur) with (HPC-N1) and without nitrogen-doped carbon (HPC-N0) were assembled *versus* lithium foil, Celgard 2500 separator and $7 \text{ } \mu\text{l mg}^{-1} \text{ s}$ ether-based electrolyte as described above (Table 2). The galvanostatic cycling was carried out in the range of 1.8 - 2.6 V at C/10. The beam energy was fixed to 60 keV, which ensures negligible polarization effects and very low mass absorption coefficients for most elements. A 16-inch two-dimensional flat panel detector of the XRD 1621 N ES Series (PerkinElmer, 2048×2048 pixels, pixel size $200 \text{ } \mu\text{m}$) was used for recording the diffraction patterns. The exposure time was set to 30 s with a 30 s dark image beforehand. Detector calibration and two-dimensional image integration were realized by a Si NIST standard and the software *Fit2D* [25]. Further details about the setup, the beam optics, the monochromators and experimental possibilities at the high-energy beamlines at P02 are reported elsewhere [26]. Signal areas were determined by fitting a Gaussian function. Structure refinement was carried out with the program *MAUD* [27]. A polynomial background and a Popa line broadening model were used for each structure type $\beta\text{-S}_8$ [28], Li_2S [29], Al [30], and Li [31]. In order to determine the instrument broadening of the synchrotron facility, LaB_6 (NIST standard) and a Caglioti pseudo-Voigt function was used.

3. Results and Discussion

The synthesis of hierarchical porous carbons was realized by a facile scalable method using ZnO nanoparticle hard templating in order to create well defined nitrogen doped hierarchical carbons with hierarchical pore structure (Figure 1). The nitrogen content was controlled by varying the melamine:sucrose ratios, and the resulting material is used as highly conductive scaffold in the LiS battery cathode.

3.1 Structural investigations by TEM, nitrogen and water physisorption, Mercury intrusion and XPS

The shapes of the nitrogen physisorption isotherms (Figure 2) for doped and non-doped carbon scaffolds indicate almost identical pore size distributions for HPC-N0 and HPC-N1. However, the melamine amount during the synthesis affects severely the absolute amount of adsorbed nitrogen, which is in particular pronounced comparing HPC-N1 and N2 (see red and blue curve, Figure 2). By using smaller melamine concentrations (150 mg/ 5.25 g sucrose), the specific surface area slightly decreases from 1757 m² g⁻¹ (HPC-N0) to 1689 m² g⁻¹ (HPC-N1). Further increase of the melamine concentration leads to a drastic reduction of the specific surface area and an increase of the pore size (965 m² g⁻¹; HPC-N2) (Table 3). In contrast, the carbon yield increases with increasing melamine concentration. The increased degree of crosslinking, due to the melamine addition, results in reduced formation of gaseous side-products during the pyrolysis. Additionally, the intense π - π interaction of the melamine molecules with the derived carbon surface shrinks the available surface area.

The pore size distribution calculated from mercury intrusion shows the preservation of the pore system and the replication of the ZnO-templating to a certain degree. The identical pore size distribution of the carbon created without and moderate melamine concentration (HPC-N0 and HPC-N1) reveals the ideal combination of sucrose and melamine to form nitrogen-

doped carbon precursors. Nevertheless, with increasing melamine concentration (HPC-N2), other gaseous products such as ammonia lead to an etching and unfavorable pore widening and a broad pore size distribution [15].

Representative TEM images (Figure 3) substantiate the physisorption findings: The pores are located in the carbon scaffold, and the morphology of the material synthesized without and with moderate melamine concentrations is very similar. In contrast, the precursor with increased melamine content (HPC-N2) and higher nitrogen content, shows wider pores and slightly increased pore wall thicknesses. At most, a release of ammonia or methylamine during pyrolysis [32] and carbothermal ZnO reduction lead to a certain carbon etching on the one hand, but due to the increased π - π interaction of the melamine and carbon lattice to slightly thicker pore walls on the other hand.

According to XPS results (Table 4 and Figure S1), as expected, the highest nitrogen content is found in the sample prepared with the highest melamine concentration (2.8 at%). The chemical environment (pyridinic, pyrrolic, quaternary) of the nitrogen as retrieved from the N 1s binding energy data is comparable in both nitrogen-doped samples (HPC-N1 and HPC-N2). Small differences are observed for the carbon sample with moderate nitrogen content (HPC-N1). We found more pyrrolic (45 %) and less pyridinic (37 %) carbon – whereas less pyrrolic (36 %) and more pyridinic (44 %) carbon is calculated for the sample HPC-N2 (Table 4). For both nitrogen-modified samples, the amount of quaternary and N-oxide species is rather low. The relatively high concentration of pyrrolic groups in both samples suggests a variety of decomposition products during the synthesis [32,33]. According to the expectations, with increasing melamine amount, the number of pyridinic surface sites can be enhanced.

3.2 Polysulfide and sulfur ex-situ adsorption, water adsorption

The melamine concentration and therewith the nitrogen content in the carbon material also remarkably influences the surface polarity as revealed by water adsorption (Figure 4a). With higher nitrogen content, the water adsorption or rather water cluster formation in the lower relative pressure range $p/p_0 = 0.1 - 0.6$ increases (Figure 2). Moreover, the hysteresis is shifted to lower relative pressures implying pore filling at reduced pressures. Interestingly, for the absolute amount of adsorbed water, an inverse behavior was observed which is mainly attributed to decreasing micropore volumes. The higher amount of adsorbed water at low relative pressures underlines the high affinity of the material towards polar species resulting in an increased PS adsorption capability.

In this regard, we carried out adsorption experiments with 8 mM Li_2S_6 and sulfur solutions in DME/DOL (Figure 4) to demonstrate the effect of polar and nonpolar compounds on the tailored porous nitrogen-doped carbons. Considering the polysulfides, we observe the same trend as found for the water adsorption. With increasing nitrogen content, the adsorption capability for polar Li_2S_6 is enhanced. As a reference to our materials, a commercial supercapacitor carbon (Norit DLC) and a highly nitrogen-doped carbon material [34] were used in order to reveal the influence of the surface polarity on the adsorption behavior of highly polar polysulfides and nonpolar sulfur molecules (Figure 4b and Table S1). The results clearly show (Table S1) that a standard nonpolar activated carbon adsorbs only low amounts of Li_2S_6 (0.31 mmol g^{-1}) and high amounts of elemental sulfur (1.18 mmol g^{-1}). In contrast, a specifically tailored highly nitrogen-doped carbon [34] favors Li_2S_6 adsorption (1.08 mmol g^{-1}) and suppresses the adsorption of sulfur molecules (0.06 mmol g^{-1}). These findings clearly underline the expectations in terms of surface polarity and resulting affinity for sulfur vs. polysulfide adsorption. However, it should be noted that Li_2S_6 is only one

prototypical polysulfide species out of several other species, and that the polarity and viscosity of other polysulfides vary. Moreover, the polarization of the electrode will also influence the adsorption behavior being not taken into account within *ex-situ* studies without applying any potential. Nevertheless, for the comparison of different materials regarding their liquid phase adsorption properties, and their surface polarity, this method is rather sensitive.

3.3 Galvanostatic charge-discharge measurements of the carbon-sulfur composites in half cells vs. Li/Li⁺

In Figure 5 the electrochemical performance of the sulfur infiltrated carbons with (HPC-N1 and HPC-N2) and without nitrogen doping (HPS-N0) as a cathode vs. Li/Li⁺ is compared. All cathodes exhibit a sulfur content of 64 wt% (75 wt% in the composite without binder) and a sulfur loading of $3 \pm 0.1 \text{ mg cm}^{-2}$.

We highlight that these experiments were carried out at low electrolyte volumes of $6.8 \text{ } \mu\text{l mg}^{-1}\text{s}$ exceeding an electrolyte:sulfur ratio of ~ 2.3 as it is essential for high specific energy on cell level. In contrast to most studies, the electrolyte:sulfur ratios reach values of ≥ 12 as reported in the literature [35]. As known from previous studies, the electrolyte volume in the cell tremendously affects discharging behavior [36], sulfur utilization, and cycling stability. A higher electrolyte:sulfur ratio reduces the viscosity in the discharged state associated with a redistribution of polysulfides from the scaffold into the solution, in particular when ether based solvents are applied [37]. At the same time, electrolyte decomposition causing dry out and cell failure is masked due to a high electrolyte excess resulting in an apparently longer cycle lifetime but at the cost of decreased specific energy at cell level. For that reason, additional tests were carried out at an electrolyte volume of $4 \text{ } \mu\text{l mg}^{-1}\text{s}$. Theoretically, electrolyte volumes below $3 \text{ } \mu\text{l mg}^{-1}\text{s}$ are targeted in order to meet practically relevant cell conditions. However, to the best of our experience, $4 \text{ } \mu\text{l mg}^{-1}\text{s}$ is the

lowest electrolyte volume that can be reasonably handled with a constant concentration in a glove box atmosphere and quick evaporation of highly volatile ether based electrolyte solvents).

As elaborated from Figure 5 and Table S2, increased nitrogen content in the carbon material initially leads to a decreased sulfur utilization and a capacity of $1043 \text{ mAh g}^{-1}_{\text{S}}$ (94.6 % CE) for HPC-N2. The remarkable difference in sulfur utilization for the two nitrogen-doped materials HPC-N1 and HPC-N2 is attributed to the differences in porosity. Especially the higher micropore volume and surface area characterizing samples HPC-N0 and HPC-N1 lead to an enhanced number of sites for electron transfer from the conductive carbon scaffold to the active sulfur species. Thus, the initial sulfur utilization accounts to $1127 \text{ mAh g}^{-1}_{\text{S}}$ (97 % CE) in the 1st, and $1005 \text{ mAh g}^{-1}_{\text{S}}$ (98.9 % CE) in the 5th cycle for HPC-N1. Within the first 50 cycles, the capacity retention of the un-doped material is higher than for the doped materials (see Table S2). In this regard, after 50 cycles, 909 (98.4 % CE), 828 (96.4% CE) and $693 \text{ mAh g}^{-1}_{\text{S}}$ (93.9% CE) for HPC-N0, HPC-N1 and HPC-N2 were achieved, respectively. However, after 100 cycles severe degradation occurs for the HPC-N0 sample, and finally, after 148 cycles the cell failed most probably due to the low electrolyte amount. Before the cell dried out, a last capacity value of $685 \text{ mAh g}^{-1}_{\text{S}}$ (79.5 % CE) was obtained. In contrast, the cells with nitrogen doping could be cycled more often and with lower capacity degradation. Finally, 239 cycles with $502 \text{ mAh g}^{-1}_{\text{S}}$ and 81.8 % CE for the HPC-N1 material are realized. The longest cycle stability (262. cycle: $437 \text{ mAh g}^{-1}_{\text{S}}$ with a CE value of 79 % was observed for the HPC-N2 sample. However, due to its decreased microporosity, this sample cannot be directly compared to the other two samples. Based on the relatively moderate electrolyte amounts ($6.8 \text{ } \mu\text{l mg}^{-1}$), this finding is expected to be promising for cell designs on prototype level. Generally, the CE ranges between 98.7 and 96.4 % within the first 100 cycles for all samples, as the polysulfide shuttling continues unsuppressed due to the high solubility of polysulfides in the ether-based electrolyte.

The nitrogen-doped sample HPC-N1 showed promising results with $6.8 \mu\text{l mg}^{-1}$ sulfur electrolyte amounts, and the porosity is comparable to the corresponding undoped material. For that reason and higher suitability for practical application, the electrochemical investigations were repeated for the two samples HPC-N0 and HPC-N1, with $4 \mu\text{l mg}^{-1}_{\text{sulfur}}$, and an adapted experimental coin cell set-up. Figure 5 and Table S3 clearly reveal the aforementioned trend that the nitrogen-doped sample HPC-N1 outperforms the undoped one: The composite HPC-N1 is characterized by lower sulfur utilization in the first 20 cycles. In the subsequent cycles the capacity retention is higher than for the HPC-N0 material (see Table S3). In the first cycle, $972 \text{ mAh g}^{-1}_{\text{s}}$ (97.7 % CE) for the doped, and $1159 \text{ mAh g}^{-1}_{\text{s}}$ (103.4 % CE) for the undoped sample were obtained. After 50 cycles, for the nitrogen-doped carbon, $794 \text{ mAh g}^{-1}_{\text{s}}$ (94.7 % CE) and for the undoped scaffold, $579 \text{ mAh g}^{-1}_{\text{s}}$ (89.8 % CE) were achieved. Generally, the CE is typical for ether-based electrolytes with high LiPS solubility and ranges between 98.9 and 89.8 %, as related to polysulfide shuttling and high electrolyte dead volume for $4 \mu\text{l mg}^{-1}_{\text{s}}$. Both situations affect the discharge/charge efficiency much stronger than a higher electrolyte volume of $6.8 \mu\text{l mg}^{-1}_{\text{s}}$. Finally, 156 cycles with $600 \text{ mAh g}^{-1}_{\text{s}}$ and 77.3 % CE for the nitrogen-doped material are realized. In contrast, for the undoped sample, 59 cycles with $495.3 \text{ mAh g}^{-1}_{\text{s}}$ and 93.0 % CE were obtained before the cell failed abruptly.

The nitrogen content also influences the voltage level of the lower discharge plateau. With nitrogen, the value is slightly higher compared to the discharge profile of the undoped scaffold independent of the electrolyte:sulfur ratio (Figure 5). Using $6.8 \mu\text{l mg}^{-1}$ sulfur, the following results were obtained: For the nitrogen-doped sample, in the 5th, 10th and 50th cycle, a value of 2.12 V is observed. For the nitrogen-free sample, in the 5th and 10th cycle a value of 2.10 V is achieved, but in the 50th cycle that value is reduced to 2.09 V. This observation leads to the assumption that nitrogen doping reduces the overpotential, especially after 50 cycles. Nitrogen doping of the carbon surface clearly enhances the adsorption of polar

species such as polysulfides and Li_2S , where the nitrogen-doped sites may even act as Li_2S precipitation seeds. Moreover, they could support or rather catalyze electrochemical transformation of the sulfur – polysulfide – Li_2S species due to the direct bonding of nitrogen to the highly conductive matrix. For example, nitrogen-doped carbons are taken as metal-free catalysts for the oxygen reduction reaction in fuel cells [38] or for or partial oxidation of H_2S to sulfur [39,40], However, the catalytic mechanism is still under controversial discussion. A nitrogen content of 2 at% is rather low in comparison to other publications, and a calculation of the optimal nitrogen concentration for an ideal adsorption behavior for polysulfide species is challenging since polysulfides tend to disproportionate during cycling. Therefore, the concentration of species that can be adsorbed changes drastically at a certain depth of discharge. In order to analyze the influence of the nitrogen content during cycling, *operando* X-ray diffraction measurements were carried out at DESY synchrotron beamline facility and the effect of the reduced overpotential and Li_2S nucleation is discussed below, in more detail in the *operando* section.

These findings should be transferable to the lower electrolyte weight fractions of $4 \mu\text{l mg}^{-1}\text{s}$. Here, the nitrogen content also affects the voltage level of the lower discharge plateau. For the nitrogen-doped sample, in the 5th, 10th and 50th cycle, a value of 2.11 V is observed. For the nitrogen-free sample, in the 5th cycle, 2.10 V and in the 10th cycle, a value of 2.08 V is achieved. In the 50th cycle, that value is slightly more reduced to only 2.03 V. In comparison to our previously published data, the change in the voltage plateau level is relatively sensitive, and these data match well with the *operando* X-ray diffraction measurements discussed in the next subchapter. For that reason, these observations confirm the abovementioned hypothesis, that nitrogen doping reduces the overvoltage/polarization, especially with increasing cycle number and at a low electrolyte volume.

3.4 Operando X-ray diffraction measurements of Li₂S/S₈ during cycling

3.4.1 Mechanism and qualitative phase identification over cycling

In order to understand the enhanced long-term cycling behavior and lower overpotential of nitrogen-doped carbons in Li-S batteries, *operando* X-ray diffraction of the Li-S cells was carried out. *Operando* XRD of Li-S cells was already proven to be a powerful technique to track the phase changes and elucidate the mechanism in the cells [41–47]. In Figure 6 the galvanostatic cycling of the two Li-S cathodes HPC-N0 and HPC-N1 (2 at %) at C/10 are displayed. Both cells show the typical voltage profile for Li-S cells with two main plateaus at about 2.3 and 2.1 V vs. Li/Li⁺. We determined a discharge capacity of 1190 mAhg⁻¹_s in the first cycle for both cells. Over three complete cycles the capacities of all three samples are comparable with a discharge capacity of more than 1000 mAh g⁻¹_s. Importantly, the electrochemical results are in the range of the in-house measurements (Figure 5). Several proposed discharge mechanisms are found [48], and we will focus on that one published by Cuisinier *et al.* [49] given that this mechanism seems to be well-accepted in the scientific Li-S community due to their detailed in-situ X-ray absorption and diffraction studies. The discharge process is governed by three steps in a reaction scheme [50].

In the first upper plateau (I), the solid sulfur is reduced to soluble polysulfides in a solid-to-liquid reaction:

UV-Vis spectroscopy and electrochemical methods revealed a subsequent disproportionation of S₈²⁻ to S₆²⁻ under re-formation of S₈

The voltage drop is attributed to a viscosity maximum due to the higher molarity of short-chained polysulfides in the solution. In the second lower plateau, a liquid-to-solid disproportionation reaction of S_4^{2-} to S_6^{2-} and Li_2S takes place (d).

The S_6^{2-} is again reduced according to equation (c) which predominantly contributes to the overall capacity.

It should be noted that the Li_2S may initially be present as dissolved S^{2-} and Li^+ ions [49]. There are references describing the reaction mechanism *via* a Li_2S_2 intermediate [48]. However, the Li_2S_2 phase is neither visible nor observed during our measurements. Similarly, Cuisinier *et al.* [49] did not demonstrate the presence of insoluble Li_2S_2 . This phase was once described by *operando* XRD but only at very low C-rates (C/50) and high conductive salt concentrations [51]. Both parameters strongly deviate from our experimental conditions, since these parameters seem to kinetically support the formation of Li_2S_2 . At our conditions, a crystalline Li_2S_2 is absent. We verified the Li_2S_2 absence in our data which enables us to omit this compound in the following discussions.

During the 45 hours of cycling, at every 10 min, a diffraction pattern of each cell was recorded accounting to total number of about 240 patterns per cell. A chronological representation of all patterns is available in the supporting information including a view of representative patterns at the end of a discharging and a charging half-cycle of each cell (Figure S2 and Figure S3). Interruptions of the analysis are due to sudden X-ray beam turned off caused by technical issues at the synchrotron facility.

In principle, two crystalline allotropes of sulfur (α - and β -sulfur) and Li_2S are observed (Figure 7). The diffraction patterns of the fresh cells reveal the presence of the monoclinic β -sulfur phase (space group $P2_1/c$ [28]), independent of the nitrogen content (Figure S4). At this stage orthorhombic α -sulfur (space group $Fddd$) was not detected. A phase analysis was

carried out in order support the presence of β -sulfur and the results are shown in Figure S5. However, the signal-to-noise ratio of the pattern is too low to extract reliable information. For that reason, laboratory XRD measurements were used to analyze the sulfur-infiltrated porous carbons and the patterns undoubtedly proof the presence of β -sulfur already in the initial state of the cell (Figure S5) with crystallite sizes ranging from 50 – 100 nm. The presence of monoclinic β -sulfur in the fresh cell was originally not expected as the thermodynamically stable phase is the orthorhombic α -sulfur. Indeed, to the best of our knowledge all groups consistently report the presence of α -sulfur in uncycled cells. β -sulfur was only observed after cycling of a Li-S cell [42,43,45–47,52]. In contrast to other references, where the pristine α -sulfur was only milled and blended with the porous carbon, we used a melt infiltration technique. Apparently, according to the Ostwald's step rule β -sulfur as the less stable polymorph crystallises first from a melt. Our results suggest that the stability range of different sulfur phases may depend on the pore size of the carbon and the method of sulfur incorporation into the porous scaffold (i.e. melt infiltration at 155 °C).

Over the first discharge, the β -sulfur peaks decrease irrespective of the nitrogen content of the carbon scaffold, and completely disappear by the end of the first plateau due to reduction of sulfur to soluble polysulfides. Within the second plateau an intense reflection at 3.57° 2θ occurs in both cells corresponding to the (111) lattice plane of the cubic Li_2S structure ($Fm-3m$). The maximum intensity of this reflection is obtained at full depth of discharge (DOD). We determined a crystallite size of 6 - 7 nm for Li_2S in the HPC-N1 sample and 3 - 4 nm in the HPC-N0 sample, suggesting that the Li_2S crystallites within the HPC-N1 cell are able to reach larger crystallite sizes compared to the HPC-N0 sample. During charging, the intensity of the Li_2S 111 reflection decreases in both cells and vanishes at the end of charging (~ 2.6 V vs. Li/Li^+). The disappearance of Li_2S is followed by the subsequent formation of a new phase most likely $\beta\text{-S}_8$ ($P2_1/c$) again. Following the next two cycles, we observed a reversible appearance or disappearance of the $\beta\text{-S}_8$ and Li_2S phases at usual potentials. Note that the

proportions of the multiple β -S₈ reflection areas change considerably after each cycle. For example, the ratio of the 310/211 reflections in the nitrogen-doped sample at the end of each cycle ranges from 0.7 to 1.7 without any apparent correlation. This observation suggests that the texture of the sulfur phase and the orientation of the formed sulfur crystallites vary for each cycle.

3.4.2 *Semi-quantitative analysis over cycling*

An exact quantification of crystalline sulfur fractions by XRD is challenging. We therefore focused on the change of certain reflections during cycling as applied by other groups to obtain information about the reaction progress [44,47]. Considering the most intense sulfur reflection 310 at $2\theta = 3.45^\circ$ in both cells, we observe a linear correlation between reflection area and time. Obviously, the time is also in linear correlation to the capacity and SOD/SOC. This gradual behavior is in line with the observations of Canas *et al.* [47] and Waluś *et al.* [44]. However, considering the HPC-N1 sample, the sulfur reflection disappears faster and completely vanishes already within the upper plateau (I) at a DOD of 17 %. In contrast, for the cell with the HPC-N0 sample the sulfur reflection persists nearly to the beginning of the second lower plateau (25 % DOD) and covers the regions I and II. Considering the re-formation of sulfur at the end of charge, the reflection areas are decreased compared to the beginning and close to the detection limit, especially for the undoped sample. Thus, sulfur appears rapidly for the HPC-N0 sample at the end of charging probably due to precipitation from a supersaturated solution and disappears slower when it is reduced due to the limitation by the current flow. This behavior indicates that the formation of the solid sulfur phase is inhibited compared to the HPC-N1 sample. As already mentioned, the appearance of the Li₂S phase at the second plateau is followed by the most prominent 111 distinct (111) peak of Li₂S at $2\theta = 3.57^\circ$. We found that the Li₂S precipitation follows a non-linear behavior and the rate

of Li_2S formation is best ascribed with an $f(x) = Ae^{Rx}$ function (values for each cycle are summarized in Table S5). However, the investigation of the exact kinetics is beyond the scope for this work.

Without nitrogen doping, no Li_2S formation is observed almost over the entire second plateau, but grows exponentially close to the end of discharge. The first Li_2S peak is observed at about 85 % DOD for the undoped cells. The delayed appearance and exponential growth of Li_2S are in good agreement with the *in-situ* XANES studies of Cuisinier *et al.* [49] using also melt-infiltrated porous sulfur-carbons as cathode. In contrast, Waluś *et al.* [44] used a simple ball-milled sulfur-carbon composite as well as lower current rates and observed fast Li_2S growth at the beginning of the lower plateau, but the rate decelerated to the end. These results suggest that also cathode design, preparation and charging rates strongly influence the Li_2S precipitation. Indeed, when using nitrogen-doped carbons, the formation of Li_2S which is already detected immediately after reaching the second plateau at about 50 % DOD, and the intensity increases similarly in an exponential way. However, the slope is less steep compared to the samples without nitrogen. Interestingly, the Li_2S 111 reflection area is only half as much compared to the nitrogen-doped sample although the overall capacity and sulfur loading is comparable suggesting the presence of sulfides in the solution or amorphous Li_2S . However, for nanocrystallites in the observed magnitude, differences in regards of the reflection area should not be over-interpreted.

The different behavior of Li_2S precipitation in dependency of the nitrogen content may be explained by an interfacial energy barrier between polar sulfide and nonpolar carbon scaffold as recently proposed by Fan *et al.* inhibiting nucleation [53]. Reaching the lower plateau, S^{2-} may exist in a supersaturated state according to Cuisinier *et al.* [49] and Li_2S precipitates in a well-defined structure when the nucleation barrier for nucleation is surpassed. In order to overcome the interfacial nucleation barrier and to initiate the precipitation of Li_2S , certain overpotential exists for porous carbons which need to be overcome to allow Li_2S precipitation.

According to Fan *et al.* [53] low interfacial energy, as a result of low overpotential and an increase of the binding energy between carbon substrate and Li_2S as precipitate, needs to be provided to allow precipitation as well as a heterogeneous nucleation site. Both requirements are fulfilled by the N-doped carbons. In contrast, for nitrogen doped carbons, the energy barrier for Li_2S nucleation is significantly decreased probably due to a more polar carbon surface and Li-N interactions - as already confirmed using water adsorption isotherms and Li_2S_6 physisorption - acting as heterogeneous nucleation site (Figure 8). A higher overpotential is observed for the undoped carbon and a higher supersaturation of the S^{2-} solution is required to allow precipitation. We can further confirm that the overall growth kinetics do not change as we observe an exponential growth independent of nitrogen doping which is also underlined by the conclusions of Fan *et al.* [53] Interestingly, significantly less Li_2S precipitates in the absence of nitrogen-doped carbons suggesting still either amorphous Li_2S or more likely still supersaturated S^{2-} in the solution as inferred from the discussion above. The latter one explains the longer cycle life with nitrogen-doped carbons as the amount of sulfur within the solution and therewith, the contamination of the lithium metal anode is significantly reduced over the period of cycling. This is caused most likely due to faster withdraw of the sulfides from the electrolyte solution. It is also possible that nitrogen-doped carbons may catalyze the disproportion reaction of Li_2S_4 to Li_2S (equation d), and hence, accelerate Li_2S precipitation and growth.

Considering the second and third cycle, the precipitation of Li_2S is shifted to a higher state of discharge in both cells. For the HPC-N1 sample, Li_2S is observed at 50 % in the 1st, at 62 % DOD in the 2nd and at 68 % DOD in the 3rd cycle. The Li_2S 111 reflection area after each complete discharge (100 % DOD) of the cell with nitrogen-doped carbon scaffold remains nearly constant and reaches a value of 97 % after three cycles. In contrast, almost no Li_2S is determined from XRD after the second cycle in the cell for HPC-N0. Instead, we observe a growing background noise at the Li_2S 111 reflection position with increasing time

independent of SOC. This background noise may be caused by increasing concentration of an inactive deposition of (amorphous) sulfidic species on the lithium metal anode due to shuttle effect that is in good agreement with the CE being lower than 100 % (see section 2.3). We believe that the nucleation barrier increases over cycling due to a coating of the carbon substrate surface with insulating sulfidic species that increase the required overpotential and, hence, hinder the precipitation and especially crystallization of Li_2S from the S^{2-} -containing solution. The active sites are blocked by strongly bonded S-species and the catalyst is poisoned.

The oxidation of Li_2S (charge) follows a linear behavior which is in good agreement to other studies using XRD [44] and XANES [49]. However, the rate of Li_2S consumption seems to be slightly lower at the beginning than at the end. Importantly, the Li_2S oxidation rate is independent of nitrogen-doping suggesting that the nitrogen-doped seeding sites only play a crucial role for the precipitation process of S^{2-} . In Table S3, we summarized the average slope of each cycle and cell.

Fan *et al.* recently [53] proposed that the nucleation potential drastically depends on the interfacial energy barrier between Li_2S and carbon. Herein, we proved that the overpotential of Li_2S nucleation, most likely from supersaturated S^{2-} solutions are influenced by the use of heteroatom-doped carbons lowering the interfacial energy barrier and therewith the overpotential, but the overall growth mechanism of Li_2S is not affected (Figure 8). Fan *et al.* further revealed that the growth significantly depends on the current which may explain differences in the formation kinetics of Li_2S in our cells compared to other *operando* investigations of Li-S batteries by Waluś *et al.* [44] We showed that nitrogen doping of carbons reduces the interfacial energy on the carbon substrates for Li_2S and therewith provide selective and homogeneous nucleation sites for at least crystalline Li_2S growth. There is a negligible overpotential needed to initiate the Li_2S nucleation, and therewith provides selective and evenly distributed heterogeneous nucleation sites for crystalline Li_2S nucleation

and growth. In contrast, for undoped carbons, the interfacial energy barrier between carbon substrate and Li_2S is very high and nucleation is suppressed within the second plateau. As another possibility for the nonappearance of a Li_2S nucleation may be found in the inaccessibility of seeding sites, e.g. defects in the undoped carbon, as they are poisoned by S-species. However, once the cell potential drops further, the required overpotential is provided and nuclei are immediately formed which cause subsequent Li_2S precipitation.

4. Conclusion

The mechanistic role of nitrogen in porous carbon cathodes in the lean electrolyte regime, as it is relevant for industrial applications, was analyzed electrochemically and by *operando* XRD techniques comparing doped and non-doped carbons with almost identical pore size distribution. The high performance of hierarchical porous model carbons with high specific surface area and pore volume were produced using a facile, scalable carbon synthesis based on a ZnO template with precise and independent control of porosity and surface polarity, i.e. well defined nitrogen containing surface functional groups. The increasing carbon polarity as quantified by water adsorption isotherms correlates with a higher affinity for polysulfide adsorption in the electrolyte. Even if the issue of a highly reactive lithium anode could not be solved, galvanostatic charge/discharge measurements show that the nitrogen-doped version of the hierarchical porous carbons outperform undoped hierarchical porous carbons - even at low electrolyte fraction as it is crucial for a high specific energy on cell level. As observed in the *operando* diffraction experiments, the nitrogen doped carbons facilitate the heteronucleation of Li_2S on the conductive substrate during cycling due to the enhanced LiPS and Li_2S adsorption. *Operando*-experiments revealed a reversible Li_2S dissolution and precipitation with nearly 100 % retention over three cycles. In contrast, non-doped carbons inhibit Li_2S nucleation and growth. Hence, a high over-potential is required to initiate the Li_2S precipitation from supersaturated S^{2-} solution and reversible Li_2S reformation is suppressed.

These results fully explain the extended cycle life for nitrogen-doped carbons in the lean electrolyte regime. However, the growth mechanism itself seems to be largely independent of the modified carbons since we observe an exponential growth of Li_2S in both cases. We could further show that the metastable β -sulfur phase, often observed after cycling, may appear before cycling if a melt-infiltration technique is used. Our results are in excellent agreement with investigations by Fan *et al.* [53] and Cuisinier *et al.* [49].

For the first time, we reveal the crucial mechanistic role of nitrogen functional groups in hierarchical porous carbons at low electrolyte weight fractions to realize Li-S batteries with high specific energy.

Supporting Information

Acknowledgements

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Figure 1. Synthesis scheme of the hierarchical porous carbons using melamine and sucrose as carbon and nitrogen precursor, respectively, and ZnO nanoparticles as mesopore template. Micropores are created by in-situ carbothermal reduction of ZnO to Zn vapor and CO finally etching the carbon.

Figure 2. (a) Nitrogen physisorption isotherms, (b) Pore size distribution generated from the mercury intrusion (C) Water physisorption isotherms of hierarchical porous carbons without (HPC-N0) and with two different nitrogen contents (HPC-N1 and HPC-N2).

Figure 3. Transmission electron microscope images of the porous carbon material scaffolds: (a) HPC-N0, (b) HPC-N1 with 2at% N, and (c) HPC-N2 with 2.8 at% N.

Figure 4. Water adsorption amounts at $p/p_0 = 0.2$ (a), amounts of adsorbed Li₂S₆ amounts (b) for carbon materials without (HPC-N0) and with 2 (HPC-N1) and 2.8 at% nitrogen (HPC-N2), respectively.

Figure 5. (a) Galvanostatic cycling and discharging capacities of carbon materials without (HPC-N0), with 2 (HPC-N1) and 2.8 (HPC-N2) at% nitrogen contents for $6.8 \mu\text{l mg}^{-1}\text{s}$ electrolyte volume at C/10 and the corresponding discharging profiles for the 5th, 10th and 50th cycle (b) galvanostatic cycling and discharging capacities of carbon materials without and with 2 at% nitrogen content using $4 \mu\text{l mg}^{-1}\text{s}$ electrolyte at C/10 and an adapted coin cell assembly to reduce the dead volume in the coin cell for the 5th, 10th and 50th cycle.

Figure 6. Galvanostatic cycling (1.8 - 2.6 V) of the *operando* XRD Li-S coin cells at C/10 (a) HPC-N0 and (b) HPC-N1.

Figure 7 a) *Operando* XRD of a Li-S cell with HPC-N0 (black) and HPC-N1 (red). The reflection areas of the most distinct lattice planes of β -sulfur and Li_2S were plotted against the cycling time of the cells. The first cycle with a linear fit for sulfur reduction, Li_2S dissolution and an exponential fit for the Li_2S formation. For the determined values it is referred to the supporting information in Table S4 – S6. b) all cycles of the undoped carbon-containing cell and c) all cycles of the nitrogen-doped carbon containing cell

Figure 8. Proposed mechanism of the inhibited Li_2S formation on the conventional carbon (a) and the fast formation on the nitrogen-doped carbons (b) The nitrogen atoms (blue) act as seeding sites for LiPS adsorption and precipitation of crystalline Li_2S

Table 1. Battery parts used for the galvanostatic charge/discharge measurements with corresponding electrolyte volume and $3.5 - 3.8 \text{ mg}_\text{s} \text{ cm}^{-2}$ sulfur loading

diameter cathode	separator thickness	spacer	Li chip	electrolyte volume
12 mm	25 μm	2 x 500 μm 15.5 mm	15.6 mm	6.8 $\mu\text{l mg}^{-1}_{\text{sulfur}}$
15 mm	5.5 μm	1 μm 16.7 mm	16.5 mm	4 $\mu\text{l mg}^{-1}_{\text{sulfur}}$

Table 2. Selected parameters of each *operando* coin cell for galvanostatic cycling between 1.8 – 2.6 V vs. Li/Li^+ in ether-based DME:DOL/ $\text{LiTFSI}+\text{LiNO}_3$ electrolyte.

sample	C-rate _{discharge}	C-rate _{charge}
HPC-N0	C/9	C/10
HPC-N1	C/10	C/10

Table 3: Collected and extracted physisorption data (specific surface area, total pore volume and micropore volume) of the three synthesized carbon samples

description	melamine concentration / 5.25 g sucrose	SSA ^{a)} / $\text{m}^2 \text{ g}^{-1}$	$V_{\text{tot}}^{\text{b)}}$ / $\text{cm}^3 \text{ g}^{-1}$	$V_{\text{micro}}^{\text{c)}}$ / $\text{cm}^3 \text{ g}^{-1}$
HPC-N0	0 mg	1750	3.69	0.54
HPC-N1	150 mg	1689	3.5	0.55
HPC-N2	300 mg	965	3.7	0.33

a) specific surface area calculated by using MBET-Theorie ($p/p_0 = 0.05-0.2$)

b) total pore volume calculated from nitrogen physisorption isotherm at $p/p_0 = 0.95$

c) micropore volume calculated from nitrogen physisorption isotherm by estimation of the cumulative pore volume for pores $< 2 \text{ nm}$ aus QSDFT (slit /cylindric pores, adsorption branch)

Table 4. Total nitrogen content and nitrogen species within the porous carbon samples determined from the N 1s spectral data by XPS

description	N-content / at %	Pyrrolic N / area%	Pyridinic N / area%	Quaternary N / area%	N-Oxide / area%
HPC-N1	2	45	37	7	11
HPC-N2	2.8	36	44	12	8

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