Sodium Sulfide Cathodes Superseding Hard Carbon Pre-sodiation for the Production and Operation of Sodium–Sulfur Batteries at Room Temperature

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This study demonstrates for the first time a room temperature sodium–sulfur (RT Na–S) full cell assembled based on a pristine hard carbon (HC) anode combined with a nanostructured Na₂S/C cathode. The development of cells without the demanding, time-consuming and costly pre-sodiation of the HC anode is essential for the realization of practically relevant RT Na–S prototype batteries. New approaches for Na₂S/C cathode fabrication employing carothermal reduction of Na₂SO₄ at varying temperatures (660 to 1060 °C) are presented. Initial evaluation of the resulting cathodes in a dedicated cell setup reveals 36 stable cycles and a capacity of 740 mAh g⁻¹, which correlates to ≈85% of the maximum value known from literature on Na₂S-based cells. The Na₂S/C cathode with the highest capacity utilization is implemented into a full cell concept applying a pristine HC anode. Various full cell electrolyte compositions with fluoroethylene carbonate (FEC) additive have been combined with a special charging procedure during the first cycle supporting in situ solid electrolyte interphase (SEI) formation on the HC anode to obtain increased cycling stability and cathode utilization. The best performing cell setup has delivered a total of 350 mAh g⁻¹, representing the first functional full cell based on a Na₂S/C cathode and a pristine HC anode today.

1. Introduction

Stationary energy storage systems are crucial for the development of grid-reliability with the focus on renewable energy resources. In order to buffer the natural fluctuation of energy production from renewable energy resources, the demand for stationary energy storage devices is going to strongly increase in the near future. Current market reports project a tenfold increase of the overall annual battery capacity production until 2030. Lithium ion batteries (LIBs) as state-of-the-art technology may not be able to meet this rising requirement as rare elements such as lithium, nickel, and cobalt are needed for their setup. Additionally, most of them come from politically unstable regions of the world raising the chance for shortages in supply of the raw materials, thus potentially increasing the costs. Especially cobalt is discussed for its geopolitical unstable mining regions, and also lithium can be a critical element given to its price fluctuations and ecologic problems during mining.

The fast-growing market for electromobility will create great demand for LIBs and gather a high percentage of the available resources. Hence, other cell concepts need to be investigated from which the sodium–sulfur (Na–S) battery is a promising candidate. Both elements, sodium and sulfur, are available at very low cost due to their abundance, but show high theoretical capacities of 1166 and 1672 mAh g⁻¹, respectively.

The high temperature Na–S battery is already commercially available since 1980s. In this concept, the active elements sodium and sulfur are in the molten state but separated by a solid electrolyte. These conditions, however, lead to non-negligible safety risks and high running costs. Another drawback of this technology is the low utilization of the sulfur’s theoretical capacity as the electrodes need to be kept in a molten state.

To overcome these challenges, room temperature (RT) Na–S batteries are subject to current research in this field. Nevertheless, literature results show various limitations of RT Na–S batteries, which have to be overcome to create practical battery systems. These are mainly the low cycle life, low specific capacity, and insufficient coulombic efficiency (CE) which originates from the high reactivity of the sodium metal anode paired with its large volume changes and the intense polysulfide shuttle. Various improvements have been made by pioneering researcher groups to tackle the aforementioned issues, utilizing new electrolyte concepts, the implementation of an interlayer or separator coating, and varied cathode design and anode composition. A summary of these possible solutions is given in the reference. Another possibility to address these drawbacks is the utilization of a pre-sodiated hard carbon (HC) anode instead of a sodium metal anode. Carbonaceous anodes
are known to be safer than metal-based anodes being a special argument for their application in next generation all stationary energy storage devices.[12,13] The HC serves as a quasi-intercalation material for the sodium, resulting in much lower volume changes of the anode. For this reason, a stable solid electrolyte interphase (SEI) can be formed on the HC electrode surface during the pre-sodiation step preventing the polysulfide shuttle reaction.[13] The SEI is usually built of electrolyte salt residuals, which are ionically conducting but electronically isolating to block the contact of polysulfides with electrons from the anode.[14] This concept is one among various developed approaches to cope with the challenges of the RT Na–S battery system, which are well summarized in the reference.[11] Recently published results showed an RT Na–S cell with a stable performance over 1000 cycles on pouch cell level based on a pre-sodiated HC anode.[12] Nevertheless, the pre-sodiation step of the HC anode is laborious, time-consuming, and costly when transferred to larger scale production scheme because of the electrochemical treatment in an additional cell.

In order to avoid the pre-sodiation step, a cathode implementing both active material components—Na and S—into the cell is necessary. The easiest way to implement both materials is to generate a cathode containing Na2S, the main discharge product of a Na–S full cell, which can be directly used for the initial charging of the cell. For this purpose, several requirements have to be met. First, the Na2S in the cathode requires close electronic contact to a conductive material like carbon to utilize the insulating Na2S. Coming along with the first point, the Na2S particles should be as small as possible and well dispersed in the carbon to avoid overpotential. Meeting both requirements, the carbothermal reduction of Na2SO4 to Na2S—is inspired by the Na2S production process—carried out in excess carbon is a promising approach that is already reported for Li–S battery research.[15,16] In this study, the carbothermal reduction is carried out partially below the melting points of Na2SO4 (Tm = 888 °C) and Na2S (Tm = 1180 °C) to prevent particle agglomeration due to melting. Using small particles of the raw material Na2SO4 thereby even smaller Na2S particles are expected to evolve and gain close contact to the carbon matrix during the carbothermal reaction.

For evaluation of these generated cathode materials, a stable cell setup should be used to minimize the influence of the other cell components on the cathode investigation through full cell performance. In the literature described cell compositions for the evaluation of Na2S cathodes typically employ an Na-metal anode, which is known to be unstable as stated above.[10,17,18] Wang et al. demonstrated the first RT Na–S full cell with Na2S-based cathode utilizing an Sn-doped carbon anode running over 50 cycles with an initial capacity of 550 mAh g−1.[10] Nevertheless, the capacity retention of their cell could not exceed 90%. In the following, we describe a novel approach toward stable full cell systems utilizing an HC anode with pre-built SEI by using a pre-de-sodiated anode. This concept is essential to select the best cathode material for full cell performance in a stable cell setup.

In the second part, we describe an in situ SEI formation concept for full cells based on HC anodes and Na2S/C cathodes. In this step, it is crucial to achieve in situ formation of the SEI on an HC anode, preventing the shuttle in the full cells with the developed Na2S/C cathodes. As the pre-sodiation step is usually executed in a carbonate-based electrolyte supporting the formation of a flexible SEI, we demonstrate a carbonate to aid SEI formation in the full cell electrolyte.[12,13] The challenge for the SEI formation in the first charging step of the cell arises from the evolving polysulfides, which diffuse into the catholyte and irreversibly react with carbonates.[19] This results in active material loss and needs to be prevented. Vizintin et al. described a procedure to suppress the development of polysulfides in the first charging step of a cell using a dedicated charging program.[20] Consequently, the idea herein was to build the SEI in situ by using a certain portion of carbonate additive, which is consumed during the first charging. Adapting the special charging program of Vizintin et al. to the herein described cell chemistry, the side reaction with polysulfides and the accompanied active material loss could be efficiently suppressed by the carbonate additive. With this concept, we were able to successfully demonstrate the feasibility of RT Na–S batteries based on pristine HC anodes and Na2S/C cathode without the necessity of HC pre-sodiation in the current work.

2. Results and Discussion

2.1. Carbothermal Reduction of Na2SO4 with Porous Carbon

The successful carbothermal reduction of Na2SO4 with porous carbon (ketjen black (KB) was proven via X-ray diffraction (XRD) measurements of the resulting composites Na2S/C-660, -760, -860, -960, and -1060. In the X-ray diffractograms of the composites Na2S/C-760, -860, -960, and -1060, no Na2SO4 peaks were detected after the treatment while the Na2S peaks appeared (Figure 1). However, in the measurement of Na2S/C-660, the Na2SO4 peaks were still observed and no Na2S peaks occurred (Figure S1, Supporting Information). Additionally, the typical Na2SO4 vibration bands in the Raman spectra[21] were exclusively observed for Na2S/C-660 (Figure S2, Supporting Information). Further the scanning electron microscope (SEM)

![Figure 1. XRD measurements of composites Na2S/C-760, -860, -960, and -1060 and relevant references with their peak patterns given at the bottom.](image-url)
image of Na$_2$S/C-660 shows structural features differing from that of the other composites (Figure 2), which were assigned to the remaining Na$_2$SO$_4$ particles via energy dispersive X-ray (EDX) mapping (Figure S3, Supporting Information).

Therefore, we can assume that the carbothermal reduction of Na$_2$SO$_4$ with KB can be effectually performed at temperatures of 760 °C and above.

To investigate the Na$_2$S ratio in the composites, two different methods known from the literature were used. One method was based on weight measurements and the other one on EDX spectra of the composites. For the first method, we measured the weight of the components Na$_2$SO$_4$ and KB before the treatment and the weight of the composite after the carbothermal reduction. Assuming that Na$_2$SO$_4$ completely reacts to Na$_2$S, we calculated the resulting amount of Na$_2$S in the composite and its mass (Table 1). This method can only be seen as a rough estimation for the Na$_2$S values. Underlining this, the calculated Na$_2$S percentage for the composite Na$_2$S/C-1060 shows a very high value of 90.6 wt.%, whereas the values for all the other composites (57–66%) fit in the expected range of about 71 wt.% Na$_2$S (see Supporting Information for calculation). To validate these calculations, EDX measurements were performed. Here we measured five EDX spectra from different spots of the composite probe and averaged the resulting mass percentages of the elements (Table S1, Supporting Information). Within this calculation, we observed that the Na–S ratio did not match the stoichiometry of Na$_2$S, but stays at values around 1.5 Na per S. This is in agreement with the observed metallic coating on the inside of the quartz furnace tube being used for carbothermal reduction. The Na evaporates during the process at high temperatures and leaves behind sodium-deficient Na$_x$S species in the composite.

The results of elemental analysis show less C mass (around 40 wt.%) compared to the EDX measurements (Table S2, Supporting Information). Hence, Na$_2$S amounts vary slightly from EDX to elemental analysis. However, given that EDX is not a quantitative method, those deviations should not be overinterpreted. Nevertheless, and more importantly, both methods result in values around 30% of Na$_2$S, which is far below from the expected values of 71 wt.% and the weight-based calculation. An additionally conducted analysis using lead (II) acetate led to a value of 30.6% Na$_2$S and with this is in the same range as the values gained through EDX measurement and elemental analysis. It therefore indicates the reliability of the other measurements.

For simplification of data interpretation, all electrochemical measurements were calculated based on the sulfur content according to the theoretical Na$_2$S mass derived by weight measurements. As a consequence, the actual capacities of the cells based on sulfur content should be higher than stated here. A calculation of the capacities based on the EDX-measured Na–S ratio is shown in Figure S4 in the Supporting Information.

### Table 1. Calculated values for the Na–S ratio of the composites from the mass values before and after carbothermal reduction (column “Calculation”) and from EDX results.

|          | Calculation Na–S ratio | EDX Na–S ratio | Precipitation (Pb(Ac)$_2$) Na–S ratio |
|----------|------------------------|----------------|--------------------------------------|
| Na$_2$S/C-760 | 0.568                  | 0.320          | –                                    |
| Na$_2$S/C-860 | 0.618                  | 0.259          | 0.306                                |
| Na$_2$S/C-960 | 0.663                  | 0.353          | –                                    |
| Na$_2$S/C-1060 | 0.906                  | 0.261          | –                                    |

2.2. Electrochemical Investigation of Generated Na$_2$S-Based Cathodes in Dedicated Cell Setup

For the optimization of the carbothermal reduction temperature, all cathodes were examined with a specially designed cell setup. To minimize the effect of the anode on the cell behavior, we decided to use a pre-de-sodiated HC anode with pre-built SEI. With this setup, we expected a drastically reduced consumption of the active material of the cathode during first cycle due to anodic SEI formation. It should be pointed out that this step is as demanding as the pre-sodiation, but important to evaluate the cathodes in terms of their capacity utilization during cell performance without the blurring effects of unstable anodes.

Thus, the HC anode was pretreated/short-circuited in a cell setup known from pre-sodiation step to build up the SEI in a carbonate-based electrolyte. The pre-sodiated cells were then charged to a potential of 1 V to retrieve the Na from the HC structure, but establish a stable SEI. Subsequently, the sodium-free HC anode with preformed SEI was assembled against the Na$_2$S-based cathode and cycled in an ether-based electrolyte. Stable electrochemical cycling of the Na$_2$S-based cathodes in this designed cell setup could be demonstrated (Figure 3).

According to the discharge capacities (Figure 3, left), the best performing cells with the highest capacity utilization are achieved using cathode samples cath-860 and cath-960.
both cells perform equally with around 350 mAh g\(^{-1}\) at a theoretical C-rate of C/5, cath-860 shows slightly higher capacities at lower C-rates. This cell starts with 740 mAh g\(^{-1}\) in its first discharge, which is about three fourths of the literature value from Na\(_2\)S-based cathodes[18]. The capacity values based on EDX-measured Na–S ratio reach even higher values of up to 930 mAh g\(^{-1}\) at a theoretical C-rate of C/5 for cath-860 (Figure S4, Supporting Information) and exceed the theoretical capacity of sulfur in the first cycle with 1740 mAh g\(^{-1}\).

The standardized potential curves from first discharge of cells cath-860 and cath-960 have a similar appearance (Figure 3, right). Those profiles show the typical two-plateau shape of Na–S full cell potential curves, with one plateau at 2.2 V and the second one at 1.5 V where the electrochemical reactions from S\(_8\) to S\(_{82}^-\) and from Na\(_2\)S\(_4\) to the end products Na\(_2\)S\(_2\) and Na\(_2\)S take place.[4,13] The continuously decreasing potential even within plateau regions results from the influence of the desodiated HC anode. During discharge of the cell, the potential of the anode increases due to sodium extraction from the carbon (Figure 4). As a result, the full cell potential decreases faster since the difference of the anodic and cathodic potential decreases more rapidly than the cathodic potential itself does. The observation of the cathodic potential of cath-960 was conducted via three-electrode measurements using Na-metal as the third electrode.

The other cells of cath-760 and cath-1060 reach much lower capacities during cycling (Figure 3). In the potential curve of the lower temperature cell (cath-760), no plateaus can be detected, which gives evidence of almost no active material conversion during discharge. The reason for this poor electrochemical conduction of the active material was not obvious from the before mentioned composite characterization. The XRD patterns as well as the Raman spectra of Na\(_2\)S/C-760 showed successful conversion of Na\(_2\)SO\(_4\) to Na\(_2\)S since no peaks arising from residual Na\(_2\)SO\(_4\) after carbothermal reduction were observed as well as the characteristic Na\(_2\)S pattern occurred. However, a comparison of the SEM images for all composites combined with EDX mapping reveals the decisive characteristics. All measured SEM pictures showed two different kinds of textures consisting of spherical particles that can be clearly distinguished aside from non-compact and porous parts (Figure 2 and Figure 5). In accordance with the results from EDX mapping, the first ones were assigned to the defined salt structure of Na\(_2\)S and the second ones to the more undefined and less compact carbon structure (Figure 5).

Consequently, we observed relatively large and compact particles of Na\(_2\)S for Na\(_2\)S/C-760 composite (Figure 5), which presumably causes a high overvoltage during the first cycles of the cells as it already was observed for Li\(_2\)S particles in the literature.[23] Hence, the gained capacity might be assigned mainly to capacitive effects of the carbon materials. For this reason, the used upper cut-off voltage of 2.5 V was too low to activate the Na\(_2\)S particles for electrochemical utilization in this case. Smaller particles were observed for the other composites.

The overpotential for both plateau regions in the potential curve (Figure 3, right) of cath-1060 indicates higher activation energy for the oxidation of the insulating Na\(_2\)S particles in this composite. This behavior seems to result from the slightly different and porous particle morphology of this composite (Figure S5, Supporting Information) as all other characterization measurements show similar results as the other composites. Hence, only a small percentage of the active
material can be electrochemically utilized resulting in lower capacities.

However, the highest addressable capacity was reached with sample cath-860 and all following cell experiments were conducted with this material.

### 2.3. Electrochemical Performance of Full Cells Based on Pristine HC and Na\textsubscript{2}S

The best performing Na\textsubscript{2}S-based cathode (cath-860) was tested in combination with a pristine HC anode in full cells. The cells were assembled with an adapted electrolyte containing 1 \textit{m} sodium perchlorate (NPC) in tetraethylene glycol dimethyl ether (TEGDME) and fluoroethylene carbonate (FEC) as SEI-building additive to achieve in situ SEI formation on the anode. In comparison to the cell setup with the standard electrolyte containing no additive, we could observe a clearly increased discharge capacity and higher CE of up to 70% (Figure 6). The very low CE in the first cycles is due to expected side reactions between the polysulfides and the carbonate additive from the electrolyte. To suppress these side reactions, a dedicated first charging step, defined as constant voltage (CV) step, was used similar to that proposed earlier for Li–S systems.\textsuperscript{[20]} Vizintin et al. discovered for Li\textsubscript{2}S-based batteries that with a CV of 3.2 V during first charge of the cell, almost no polysulfides develop in the cell. We adapted this strategy for the herein described Na–S system and the in situ SEI development as the suppression of polysulfides gives the possibility of complete consumption of the carbonate additive by

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**Figure 5.** SEM images and EDX mapping of a) Na\textsubscript{2}S/C-760 composite and b) Na\textsubscript{2}S/C-960 showing the elemental distribution of the contained C, O, S, and Na.

**Figure 6.** Discharge capacities and coulombic efficiencies of the assembled cells with cathode sample cath-860 against pristine HC in a coin cell setup at RT, cycled between 0.2 and 2.5 V with theoretical C-rate of C/20. Left: Comparison between two cells with different electrolytes consisting of 1 \textit{m} NPC in TEGDME with (red) and without (black) 1 vol\% FEC and cycled without special first charging step. Right: Comparison of the cell with 1 vol\% FEC in 1 \textit{m} NPC in TEGDME cycled without (red) special first charging step and the cell with 1 vol\% FEC and CV step (blue) with a cut-off current of C/20.
SEI formation during first charging step. Therefore, the loss of active material is diminished and almost doubled discharge capacities starting with 350 mAh g\textsuperscript{−1} were reached compared to the measurements without CV step (182 mAh g\textsuperscript{−1} in the first discharge) (Figure 6). Likewise, the CEs in the first three cycles of CV-treated cell show higher values of 17–45%. The composition of the in situ SEI built with 1 vol% FEC additive and a cut-off current of C/20 was determined via EDX measurement of the HC anode before and after cycling of the cell cath-860 (Figures S6 and S7, Supporting Information).

In order to reach better cell performance, the length of the first CV charging step was varied. Thereby, it was observed that the maximum discharge capacity fades with prolonged first charging while the cells gain more cycling stability visible in higher CE values (Figure 7). The longest first charging step until a cut-off current of C/100 shows a CE of 69% even in the second cycle, but has only very low capacity of 160 mAh g\textsuperscript{−1}. In its voltage profile, no distinct plateau regions could be observed. During a long charging step, there is more time for polysulfide shuttle, which is the reason why the active material loss in this case is relatively high.

In comparison, the voltage profiles of C/50 and C/20 cut-off current cells show the typical two plateaus achieving values of 297 and 350 mAh g\textsuperscript{−1}. Due to the small difference between those both cell capacities and the higher CE of C/50 cut-off current cell, the second one was chosen as an optimum charging duration. Compared to the original cell setup, the gained capacity is not much lower, which is why only a small amount of active material is lost.

Further on, three different amounts of carbonate additive in the full cell electrolyte were tested to enhance the capacity. Those cells were initially charged until the current in the CV step reached C/50 to give enough time for the controlled depletion of the additive. The best performance was gained with 1 vol% of FEC additive in the electrolyte, resulting in 297 mAh g\textsuperscript{−1} in the first discharge and stable cycling over ten cycles with a CE reaching 60%. The cells containing 2 and 5 vol% FEC additive, however, show lower capacities of 130 and 23 mAh g\textsuperscript{−1}, respectively (Figure 8). The initial coulombic efficiency (ICE) of 2 vol% FEC containing cell is 18% and therefore a little higher than the 1 vol% FEC one with 15%. However, the ICE of the 5 vol% FEC comprising cell is 0.5% underlining the low discharge capacity of the cell. This is assigned to the reaction of the carbonates with the polysulfides, consuming a lot of active sulfur-based material in the first few cycles. Hence, the amount of additive should not exceed a certain threshold to be consumed by the SEI formation in the first charging step. In the discharge profiles (cycle no. 1), no clear plateau region can be seen for the cells with 2 and 5 vol% FEC, showing almost no addressable active material for electrochemical reaction.

Summarizing these results, we obtained the best full cell performance with cells containing 1 vol% FEC electrolyte additive after charging them in the first step with a CV of 3.2 V until the current dropped below C/50.
3. Conclusion

In summary, we achieved for the first time the realization of sodium–sulfur full cells operating at RT based on pristine HC anodes and Na2S/C composites as cathodes. The Na2S/C composites were obtained via carbothermal reduction at varying temperatures and evaluated as cathodes versus HC anodes with defined SEI preformed by pre- and desodiation in carbonate electrolytes in order to minimize the anodic influence on the cathode evaluation. In particular, Na2S/C composites synthesized at 860 and 960 °C show a stable performance reaching highest discharge capacities of 740 and 615 mAh g⁻¹ and stable CE. This value of 740 mAh g⁻¹ correlates to ~85% of the maximum value in literature based on full cells with Na2S-based cathodes (860 mAh g⁻¹).[10] The results represent the first ever published Na2S/C|HC full cell, and the capacities achieved are promising for the development of RT Na–S batteries without a laborious and time-consuming pre-sodiation step.

The optimized cathodes enabled for the first time ever demonstration of a full cell system based on an Na2S/C cathode in combination with a pristine HC anode. Using a specifically adapted electrolyte system containing FEC as additive, we achieved an initial discharge capacity of 350 mAh g⁻¹ (first cycle) and 130 mAh g⁻¹ after ten cycles. Despite our achievements being certainly further improvable, these findings demonstrate the proof-of-concept for using pristine HC anodes in RT Na–S batteries without the need for pre-sodiation. The main promise of this new concept is compatibility with conventional production streams established for graphite anode processing and full cell lithium battery manufacturing.

4. Experimental Section

The chemicals polytetrafluoroethylene (PTFE) and multi-walled carbon nanotubes (MWCNT) were vacuum dried at 120 °C for 12 h before inserting into the glove box (MBraun). NaClO4 was vacuum dried at 120 °C, and NaFSI at 100 °C for 12 h prior to use. Tetraethylglycol dimethyl ether (TEGDME) was purged with argon for 12 h and dried overnight. The circular electrodes with 16 mm diameter were punched out and were further dried for 12 h at 80 °C under vacuum before inserting into the glove box.

Carbothermal Reduction of Na2SO4 with Porous Carbon: Prior to carbothermal reduction, a saturated solution of Na2SO4 (Carl Roth, 99%) in deionized water was added dropwise to a 1:10-excess of acetone (Rotipuran, Carl Roth, 99.8%) that was cooled by an ice bath in order to precipitate homogeneous Na2SO4 microcrystals. The mixture was then stirred for 40 min and afterward filtered through a MN85/70 (Macherey Nagel) filter, washed three times with acetone, and the precipitate was dried at 80 °C overnight. For carbothermal reduction, the so obtained Na2SO4 microcrystals (250 mg, 1.76 mmol) were ground and then mixed with porous carbon (Ketjen Black [KB] EC-600JD; 140.7 mg, 11.71 mmol) via grinding. The carbothermal reduction of this mixture was carried out in a high temperature tube furnace under a constant Ar flow (0.5 sdm) at varying temperatures of 660, 760, 860, 960, and 1060 °C with a heating rate of 10 K min⁻¹ and 3 h dwell period. The obtained composites were transferred to a glove box with H2O and O2 levels below 0.1 ppm and kept under inert conditions for all further handling.

Electrode Preparation: The Na2S-based cathode sheets were dry film processed (under inert gas). Therefore, 7 wt.% of MWCNTs (Nanosyl SA, 90% C-purity) were thoroughly blended with 90 wt.% of the Na2S composite in a mortar with 3 wt.% of PTFE (Daikin, F-104 additive) were evenly added to the mixture and then grinded at 120 °C until a free-standing cathode film with a thickness of ~200 µm is formed. The film was then laminated onto a carbon-coated aluminum foil sheet (Exopack) and circular cathode electrodes with a diameter of 15 mm were punched out. The resulting cathodes were named cath-temperature referring to the temperature of the carbothermal reduction of the employed composite.

HC anodes were prepared via wet film coating/doctor blading technique. A 15% solution of styrene-butadiene-rubber (SBR)-100 (under Targray) in water (1852 mg) were mixed with deionized water (3 mL), Carboxton P (Kureha Battery Materials Japan Co. Ltd., 99%, 5000 mg, 416 mmol), and carbon nanofibers (CNF, Pyrograf Products Inc., PR-25-XT-HHT; 277.8 mg, 23.1 mmol) in a 50 mL grinding beaker. The mixture was milled for 10 min in a vibration mill MM400 from Retsch GmbH. The generated slurry was then casted onto a carbon-primer-coated aluminum foil (Pi-Kem) with a doctor blade (300 µm wet film thickness) and dried overnight. The circular electrodes with 16 mm diameter were punched out and were further dried for 12 h at 80 °C under vacuum before inserting into the glove box.

Cell Assembly and Electrochemical Measurements: All cells were assembled using CR2016-casings (MTI Corp.). For the pretreatment of the anode electrodes, a pre-sodiation cell setup was used as described in Pampel et al.[12] A sodium metal electrode was (freshly) prepared by scratching off the oxide layer of calendered sodium from both sides of the sheet and pressing it onto a steel spacer with a thickness of 1000 µm (d = 16.7 mm). The HC anode was placed in the bottom part of the coin cell casing and electrolyte (30 µL) was added consisting of 1 M sodium bis(fluorosulfonyl)imide (NaFSI, Solvionic, 99.7%) in a solvent mixture consisting of DEC (Sigma Aldrich, 99.9%) and ethylene carbonate (EC, Alfa Aesar, 99%) in a volume ratio of 6:4, and 3 vol% of FEC (Alfa Aesar, 98%) were additionally added. Further, a polyethylene separator (thickness: 12 µm, d = 19 mm) and the prepared sodium metal electrode adhered to the spacer were placed on top, and the cell was cramped with a pressure of 500 psi. The cells were short-circuited for 2 d and afterward charged until 1 V with an electric current of 0.2 mA cm⁻². Thereafter, the cell was disassembled, the excess sodiation electrolyte was gently removed from the HC anode with Kimtech precision wipes, and the electrode was washed in full cell electrolyte for 5 min. The standard full cell electrolyte was obtained by addition of 1 M sodium perchlorate (NaClO4, Alfa Aesar, 98.0–102.0%) to TEGDME (Sigma-Aldrich, >99%). Subsequently, excess electrolyte was removed by a Kimtech precision wipe, washed with fresh standard full cell electrolyte (30 µL), and dried again to reveal the pretreated anode electrode.

Full cells were assembled using the Na2S-based cathodes and either pairing them with the pretreated HC anodes (dedicated cell setup) or with pristine HC anodes for the aimed full cell concept. The special electrolytes for the aimed full cells were obtained by addition of 1, 2, or 5 vol.% of 4-fluoro-1,3-dioxolan-2-one (FEA, Alfa Aesar, >98%) to the standard full cell electrolyte of 1 M NaClO4 in TEGDME. For all full cells, the amount of electrolyte was set to 10 µL mg⁻¹+ 5 µL. The cells were assembled with a porous polypropylen membrane (Celgard 2500, thickness: 25 µm, d = 19 mm) separator and a 1000 µm spacer.

For three-electrode measurements, the cells were assembled in a three-electrode cell (EC-Ref, EL-Cell GmbH). As reference electrode, calendered Na with freshly scratched off oxide layer was pressed into a pinhole, lateral to the cell setup. The pretreated anode and the cathode were assembled in the cell with a glass fiber separator (thickness 1.55 mm, EL-Cell GmbH) and the standard full cell electrolyte of 1 M NaClO4 in TEGDME (350 µL).

Materials Characterization: Galvanostatic cycling tests were conducted with a BaSyTec Cell Test System at 24 °C (± 2 °C). SEM images and EDX mapping were performed by a JEOI JSM-6610LV. For the mass ratio investigation via EDX, the Point & ID method of the Oxford Instruments software connected with the JEOI JSM-6610LV was employed and five spectra from different points of the powder.
probes were collected, which were averaged afterward. Ag-varnish was used as adhesive for probe preparation on the Al sample holder. The precipitation experiments were conducted in double determination with the Na2S/C-860 composite (50 mg each). After stirring the Na2S/C-composite in a 0.3 M NaOH solution (1.5 mL) for 36 h to solve the Na2S, the carbon was separated from the solution via filtration (sartorius stedim filter, grade: 1288) and washed three times with few milliliters of the NaOH solution. Lead acetate (Pb(Ac)2), Carl Roth, ≥99.5% was added from a 0.1 M solution in deionized water (3 mL). The precipitate was centrifuged for 10 min at 4500 rpm in a Centrifuge (Laborzentrifuge Sigma, 2-16P). Afterward the solution was removed, and the precipitate was washed three times with NaOH solution (4 mL), respectively, and centrifuged to gain the pure precipitate. After drying overnight at 60 °C, the weight of the lead sulfide precipitate was determined (57.6 and 36.0 mg) and the underlying amount of sodium sulfide was calculated (18.8 and 11.8 mg, respectively). The average of both masses was used to calculate the Na–S ratio (Table 1).

For XRD measurements, an X-RAY Diffractometer D5005 (Siemens AG) was used. The elemental analyses were executed with a CHNS elemental analyzer (EuroEA Elemental Analyzer). Raman measurements were performed by a Renishaw inVia microscope with an excitation wavelength of 514 nm.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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carbothermal reduction, hard carbon anodes, pre-sodiation, sodium–sulfur batteries, stationary energy storage

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