Lithium-sulfur (Li/S) batteries offer great potential for efficient, safe and economic cell systems. Generally, the potential for commercialization of a cell system depends on the price, the safety of the device, energy density, longevity, cycle stability and rate capability. The reversible reaction in Li/S batteries is $\text{S}_8 + 16\text{Li} \rightarrow 2\text{Li}_2\text{S}$ and gives a high theoretical specific energy of approx. 2600 $\text{W} \cdot \text{h} \cdot \text{kg}^{-1}$, which is higher than the specific energies of Li-ion-batteries. This high specific energy density of Li/S batteries results from the high specific capacities of the elemental sulfur cathode with 1672 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$ for the reaction $\text{S} + 2\text{e}^- \rightarrow \text{S}^2-$ and the lithium metal anode with 3860 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$ for $\text{2Li} \rightarrow \text{2Li}^+ + 2\text{e}^-$. Nonetheless, Li/S cells also face several challenges such as a low sulfur utilization and low rate capability, which are caused by the insulating character of cyclo-$\text{S}_8$ and its slow redox-kinetics. Another issue is the polysulfide shuttle. Polysulfides ($\text{S}_x^2-$, $x = 3–8$) are formed as intermediates during charging and discharging. They dissolve in ether- and glyme-based electrolytes, migrate to the anode and form a passivating layer on the Li-surface. This results in a loss in capacity and decreases the cycle stability of the battery. In view of these issues, it is not surprising that commercialization of Li/S cells is still limited by poor rate capability and comparable fast degradation. In an effort to overcome these problems, several successful approaches have been presented and entail the incorporation of the insulating sulfur into a conducting framework as well as retention of sulfur in constrained geometries, porous organic frameworks, silicon-carbons and nitrogen-doped carbon-based composite materials. Also microporous, mesoporous or (hollow) carbonaceous materials have to be mentioned. Unfortunately, most, if not all of them, are too sophisticated to be of any real commercial usefulness.

Based on the system originally proposed by Wang et al., we recently presented sulfurized poly(methyl methacrylate)/poly(acrylonitrile) (PMMA/PAN) composite fibers, referred to as SPAN, which contain up to 46 wt-% sulfur and their high potential as Li/S cathode material. In combination with 3M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in fluoroethylene carbonate (FEC): 1,3-dioxolane (DOL; 1:1) as electrolyte, it allows for the highly reversible charging/discharging up to 8 C over >1200 cycles. This high cycle stability is related to the very unique structure of SPAN, which has been elucidated earlier by our group.

One of the most important structural features of SPAN is the presence of covalently bound sulfur in form of (vinyllogous) thioketones, which exist in their enolate form, thereby allowing for the formation of intra- and intermolecular oligosulfide chains. In turn, during charging, the enolic thioketones in their anionic form have been proposed to serve as “docking sites” for sulfur during recharge, which allow for the reversible reformation of the above-outlined oligosulfides. One drawback, however, is the comparable low sulfur loading of SPAN, which is limited to ca. 46 wt-%.

To shed more light on the very particular discharging and charging chemistry of SPAN, we carried out a comprehensive comparative study with SPAN and activated carbon fiber (ACF)-based sulfur cathode material containing up to 56 wt-% of elemental sulfur. Notably, this sulfur loading is significantly higher than the one of SPAN (up to approximately 46 wt-%). Investigations addressed differences in morphology, differences in cyclic voltammetry (CV) during charging and discharging as well as in discharge curves. A mechanism for the discharge/charge chemistry of SPAN is presented.

**Experimental**

**Synthesis of active materials.**—Fibrous SPAN was prepared from PMMA/PAN-based nonwovens (1:3) in the presence of excess $\text{S}_8$ at 550 $^\circ\text{C}$ for 3 h in a nitrogen atmosphere. Excess sulfur was removed via overnight Soxhlet extraction with toluene. SPAN-based cathode material was synthesized by using a mixture of PAN/CNF-1603-20 activated carbon fibers (2000 $\text{m}^2 \cdot \text{g}^{-1}$; pores < 20 Å). Those were degassed at 100 $^\circ\text{C}$ in vacuum for 1 hour. $\text{S}_8$ was added to the carbon fibers in different ratios (Table S2). The sulfur was encapsulated into the carbon fibers under static vacuum ($p = 0.01$ bar) for 2 hours at 160 $^\circ\text{C}$. Residual sulfur was evaporated ($p = 0.01$ bar) at 250 $^\circ\text{C}$ under inert gas.

**Electrochemical characterization.**—Electrodes were prepared by coating a 70:15:15 wt-% mixture of fibrous SPAN or S/ACF: Super C65:PVDF in NMP on Al-foil (200 $\mu\text{m}$ thick). After drying of the electrode sheet at 60 $^\circ\text{C}$, electrode coins 12 mm in diameter were punched out and transferred to Swagelok T-type cells using a Freudenberg

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**Manuscript submitted August 21, 2017; revised manuscript received September 28, 2017. Published October 21, 2017. This paper is part of the JES Focus Issue on Lithium-Sulfur Batteries: Materials, Mechanisms, Modeling, and Applications.**

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Differences in Electrochemistry between Fibrous SPAN and Fibrous S/C Cathodes Relevant to Cycle Stability and Capacity

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Two different LiS cathodes are compared in terms of capacity (mA h g-sulfur$^{-1}$) and intermediates during discharge and charge. One cathode material is based on fibrous SPAN, a sulfur-containing material obtained via the thermal conversion of poly(acrylonitrile), PAN, in the presence of sulfur. In this material, sulfur is covalently bound to the polymeric backbone. The second cathode material is based on porous activated carbon fibers (ACFs) with elemental sulfur embedded inside the ACFs’ micropores. Cyclic voltammetry clearly indicates different discharge and charge chemistry of the two materials. While S-containing ACFs show the expected redox-chemistry of sulfur, SPAN does not form long-chain polysulfides during discharge; instead, sulfide is chopped off the polymer-bound sulfur chains to directly form Li$_2$S. The high reversibility of this process accounts for both the high cycle stability and capacity of SPAN-based cathode materials.
FS 2190 membrane and/or a Cellgrad separator 2325 and freshly prepared electrolyte. Electrochemical testing was performed on a BasyTec XCTS-LAB. Current density and specific were calculated based on the mass of sulfur in the cathode (1C = 1672 mA·h·g⁻¹ = 1 mA·h·cm⁻²).

Results and Discussion

Synthesis of cathode materials.—Fibrous SPAN was synthesized as reported.6,23–25 Elemental analysis (Table S1) revealed S-contents between 38 and 44 wt.-%. S/ACF-based cathode material was synthesized using Kynol ACF-1603-20 (2000 m²·g⁻¹; pores < 20 Å). ACFs were degassed at 100 °C in vacuo (p = 0.01 bar) for 1 hour. Next, various amounts of S₈ were added (Table S2). The sulfur was encapsulated into ACFs under static vacuum (p = 0.01 bar) for 2 hours at 160 °C.26,27 Residual sulfur was evaporated at 250 °C under nitrogen. The maximum amount of sulfur (56 wt.-% S) was reached with an S:ACF-ratio of 1:1. SEM images in combination with EDX (Figures S1 and S2, S.I.) revealed the absence of any sulfur clusters on the surface of the fibers. Notably, as revealed by XRD (Figure S3, S.I.), the small pore diameter of the ACFs effectively suppressed the formation of crystalline sulfur modifications (α-/β-S₈) inside the fiber.

Structural comparison.—Despite the fibrous structure of both cathode materials, these significantly differed from each other. Fibrous SPAN⁶ had a diameter around 15 μm compared to ACFs having a diameter of 9 μm. Also, SPAN had a specific surface area of 22 m²·g⁻¹ compared to ACFs, which had a specific surface area of 2000 m²·g⁻¹ resulting from a mostly microporous structure with pore diameters <2 nm (Table S1, S.I.). These small pores were used for infiltration with elemental sulfur, with the goal that the small pores would successfully impede the formation of large, crystalline sulfur entities, which in turn should improve redox kinetics of these cathodes. By contrast, as outlined above, SPAN-fibers consisted of a polymeric, aromatic structure with covalently bound sulfur.

Electrochemical characterization.—Cathodes were built from both active materials and consisted of 70 wt.-% SPAN and S/ACFs, respectively, 15 wt.-% Super C65 carbon black as conducting additive and 15 wt.-% poly(vinylidene difluoride), PVDF, as binder. Slurries were processed via doctor blading into coatings 200 μm in thickness on an aluminum foil. Coin type cells with a diameter of 12 mm were built using a lithium anode and 3M LiTFSI in FEC:DOL (2:1) as electrolyte.

Generally, short-chain poly(sulfide)s (Li₂Sₓ; x ≤ 3) that form upon discharge have a lower solubility in carbonates than in ethers.23,27–30 Vice versa, long-chain poly(sulfide)s are soluble in both carbonates and ethers. However, carbonates can react with the dissolved poly(sulfide)s via nucleophilic addition.28 Consequently, carbonates are usually considered incompatible with classical Li/S batteries based on S₈. As outlined earlier, the small pores in ACF fibers allow only for the presence of small, amorphous sulfur fragments inside the pores. These small amorphous sulfur fragments in ACFs but also the
covalently bound oligomeric sulfur units in SPAN should form short-chain but no long chain polysulfides. It therefore appeared beneficial to use FEC for both systems, not only to suppress polysulfide shuttle but also to form a stable solid electrolyte interfaces (SEI) on the anode and the cathode.

As can be seen in Figure 2, SPAN gives a high initial capacity of approximately 1370 mAh g⁻¹ while S/ACF delivers ca. 1400 mAh g⁻¹. Both cells show high cycle stability for at least 50 cycles with Coulomb efficiencies > 99% both for the SPAN- and ACF-based electrodes using an FEC-based electrolyte. Nonetheless, the SPAN cathode clearly outperforms the ACF-based one with the chosen electrolyte giving a reversible discharge capacity around 1200 mAh g⁻¹ compared to S/ACF with 260 mAh g⁻¹. With S/ACF, the substantial loss in discharge capacity between the initial and the second cycle can be attributed to the disability of ACFs to reintegrate all the Li₂S formed into to fiber during charging. By contrast, the formed Li₂S in the SPAN cathodes stays inside the porous fibrous network and can be reintegrated more easily and reversible. To understand the electrochemical differences between the two different cathode active materials, cyclic voltammetry (CV) was conducted, both with an FEC- and a 1,2-dimethoxyethane- (DME) containing electrolyte. Because CV curves did not change after the second cycle, only cycles 1 and 2 are shown (Figure 3).

Table S3 summarizes the different poly(sulfide)s formed during discharge together with the corresponding voltages at which they are formed. Upon discharge, S/ACF in 1M LiTFSI in DME/DOL as electrolyte shows a maximum in the range of 2.3–2.4 V, which correspond to long-chain poly(sulfide)s, i.e. Li₂S₈ and Li₂S₄, respectively. Another maximum at 2.05 V corresponds to the formation of Li₂S₂, which serves as an explanation for the lower discharge capacities.

By contrast, the CV of SPAN (Figure 3b) shows only one maximum in the first discharge (U = 1.35 V), which is substantially less pronounced in the second discharge. There, weak signals in the range of ca. 2–1.6 V occur, which cannot be unambiguously attributed to a distinct sulfide species. Upon charging, a broad signal starting 2.1 V with one maximum at 2.2 V and a second signal at 2.45 V is observed. This lack of any pronounced signals at U > 2 V, which can in contrast to S/ACF not be assigned to individual sulfide species indicates the absence of any long-chain poly(sulfide)s such as Li₂S₈, Li₂S₆, and Li₂S₄ during discharge. The signal starting at 1.7 V is attributed to the formation of Li₂S, as outlined in Figure 1, the sulfur chains in SPAN are covalently bound to the polymeric backbone. The absence of the signals for long-chain poly(sulfide)s indicates a reduction mechanism, which neither starts from S₈ nor via the formation of S₆²⁻ with x ≥ 4. Instead, data strongly suggest that the polymer-bound sulfur chains in SPAN, whether intra- or intermolecular, are first reductively broken at some point to form terminal SPAN–S₄–S₈ moieties. These are then degraded stepwise from the chain end with concomitant formation of Li₂S until the sulfur chain is completely reduced according to SPAN–S₈ – Li⁺ + 2Li⁺ + 2e⁻ → SPAN–S₄–S₈ + Li₂S (starting from 2 ≤ x ≤ 7 and ending at x = 2). This is supported by the continuous discharge curve shown in Figure 6. The diffuse maximum during charging shows the reversible incorporation of sulfur into the polymer backbone. By contrast, S/ACF with the FEC-based electrolyte shows a broad maximum at 1.6 V during the discharge cycle (Figure 3c) indicating the formation of Li₂S. A small maximum at 2.35 V in the first cycle indicates the formation of long-chained poly(sulfides). These must react with the carbonate-based electrolyte since they cannot be detected in the second cycle. This proposed loss of sulfur is in accordance with the observed drop in capacity (Figure 2). The absence of long-chain poly(sulfides) leads to a short plateau in the discharge curves (Figure 5) leading to comparably low capacities (260 mAh g⁻¹).

Results for the SPAN cathodes in combination with FEC-based electrolyte are shown in Figure 3d. Only one signal can be detected at 1.35 V in the first cycle. In all further cycles, this maximum is shifted to 1.7 V. This indicates the improvement of the reversibility of the cell after the first cycle. The signal for the oxidation at 2.3 V corresponds to the signal for the formation of sulfur chains in SPAN according to SPAN–S₈ → Li⁺ + xLi₂S → SPAN–S₄–S₈ + Li⁺ + 2xLi (1 ≤ x ≤ 7). The broad signal clearly indicates the different lengths of the sulfur chains in SPAN (4 ≤ x ≤ 8).

Figure 3. CV of a) an S/ACF-based cathode with 1M LiTFSI in DME/DOL (1:1, see also Figure S4, S.I.) b) an SPAN-based cathode with 1M LiTFSI in DME/DOL (1:1), c) an S/ACF-based cathode with 3M LiTFSI in FEC/DOL (2:1, see also Figure S5, S.I.) and d) an SPAN-based cathode with 3M LiTFSI in FEC/DOL (2:1), all cycled between 3–1 V with 0.5 mV s⁻¹.

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**Table S3**

| S₈ | S₄ | S₂ |
|----|----|----|
| 207.2 | 241.2 | 231.8 |

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Journal of The Electrochemical Society, 165 (1) A6017-A6020 (2018) A6019
In summary, we have presented two fiber-based cathode materials for Li/S cells. The fibers strongly differ in the way the sulfur is integrated. CV clearly revealed differences in the discharge/charge behavior. Despite the good cycle stability of the S/ACF (50 cycles) with different electrolytes, cathodes based on this material show a substantially lower capacity than SPAN-based fibers, which gave better cycle stability and a higher rate capability with higher discharge capacities. CV clearly revealed the different discharge/charge pathways in these two cathode materials.

Acknowledgment

This work was financially supported by the Federal Ministry for Economic Affairs and Energy (project nr.: S50400). Dralon GmbH, Dormagen, Germany, is gratefully acknowledged for providing PAN-based fibers.

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