Influence of external stack pressure on the performance of Li-S pouch cell

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Abstract

The lithium-sulfur (Li-S) cell system is promising to satisfy the increasing need for cost-efficient energy storage with high theoretical energies due to the enormous theoretical gravimetrical capacity and the abundance of sulfur. Furthermore, the technology readiness level of Li-S batteries increased steadily in recent years due to extensive research, as well as the number of reported prototype cells. However, an often ignored test parameter is the application of external pressure to the cell stack. In this study, the influence of external pressure on the performance of Li-S cells is investigated. Therefore, five-layered pouch cells with solvent-free processed cathodes are assembled. These cells are tested under lean electrolyte conditions (electrolyte to sulfur ratio of 4.5 µl mg(S)⁻¹). To evaluate the influence of the used electrolyte system either the state-of-the-art 1,2-dimethoxynitane/1,3-dioxolane electrolyte or the sparing polysulfide solvating hexyl methyl ether/1,3-dioxolane electrolyte is deployed. The impact of pressure application is evaluated electrochemically as well as by post-mortem focused ion beam-scanning electron microscopy of the cycled electrodes. Moreover, a technique for infiltration of sulfur into the carbon host matrix is presented, discussed, and successfully implemented.

1. Introduction

In recent years, the number of lithium-sulfur (Li-S) demonstrator cells published at pouch cell-level has been steadily increasing. The ongoing interest in the Li-S system is justified by sulfur’s high theoretical gravimetrical capacity of 1672 mAh g(S)⁻¹ and specific energy of 2500 Wh kg⁻¹ [1–4]. Practical Li-S cells already achieved more than 470 Wh kg⁻¹ [5] and are considered to be the perfect candidates for lightweight and aeronautical applications. Moreover, sulfur is an environmental-friendly and more cost-efficient alternative to nickel-, manganese- and cobalt oxide containing cathode active materials [6].

In order to implement Li-S pouch cells into real-world applications and larger cell modules, it is crucial to investigate the influence of external parameters such as temperature [7–10] and/or external pressure on the performance. Especially for the external pressure, however, important information on the testing procedures of reported pouch cells is often not stated. Mostly it is not mentioned whether the pressure is applied [11–17] or the exact pressure is not given [18, 19]. This is especially problematic since it was demonstrated in the literature that the application of external pressure on the cell stack may have a beneficial influence on especially the cycle life of lithium anodes. The application of external pressure was shown by the group of Liu depending on the electrolyte, to prolong the lifetime of lithium anodes with variations depending on the electrolyte [20]. They applied pressure of 0.07 MPa and found that this alters the degradation mechanism of the lithium anode of their Li vs NMC cells [20]. In a comparable study by Yin et al, the pressure on the stack was increased to 1.1 MPa and they also demonstrated that the lithium growth...
mechanism is beneficially affected by the applied pressure [21]. Both demonstrated the lithium morphology upon plating to be less dendritic and voluminous. The voluminous growth of lithium is responsible for the depletion of active lithium as well as electrolyte decomposing on the steadily increasing anode surface area [22]. Hence, applying pressure on the cell stack might be one solution to tackle the fast capacity degradation caused by the degradation of the lithium anode without employing complicated protective lithium coatings [23, 24] as this fast capacity degradation and thereby poor cycle life are considered as the main challenge hindering the commercialization of the Li-S technology [6, 22]. However, from an application point of view, setups for pressure application on cell modules are controversially discussed. In addition, especially for state of the art Li-S electrolytes with high polysulfide solubility, certain porosity is needed for the effective conversion mechanism.

Consequently, there is a need for a better understanding of the role of stack pressure on multi-layered Li-S pouch cells and its impact on cell performance. The cells in such a study should be tested under realistic conditions, such as low electrolyte/sulfur ratios (E/S), adequate active material loadings, and limited lithium excess. Exercising lean electrolyte conditions is mandatory for achieving high gravimetrical energies since the electrolyte contributes to more than 40% of the cell’s total weight if an E/S ratio of 7 μl mg(S)⁻¹ is applied [6, 25, 26].

Other frequently disregarded factors are the scalability and sustainability of the electrode and cell manufacturing. In the literature, concepts are often presented which require complex material synthesis and/or toxic solvents such as N-methyl-pyrrolidone are used for slurry processing. Depending on the solvent employed, slurry processing can be generally detrimental since its less cost-efficient and environmentally friendly than completely solvent-free electrode coating techniques [27, 28]. Such a coating process should be linked to cost-efficient commercial carbon mass products to manufacture S/C cathodes via roll-to-roll (R2R) processing. In addition, prior to the mass-production of a large quantity of S/C cathodes, sulfur must be infiltrated into the conductive carbon matrix. Several infiltration approaches are described in the literature such as melt-diffusion, vapor-phase infusion, solvent evaporation, or chemical deposition [29], whereas solvent-free melt-diffusion is the easiest and most cost-efficient approach. Mostly, both components are dry-mixed and then heated up to the melting point or rather the point of lowest viscosity of sulfur. Since large quantities of S/C composite are needed for commercial electrode manufacturing the infiltration by melt-diffusion must be transferred from lab-scale and batch-wise to continuous processing.

In this work, the influence of external uniaxial pressure on the electrochemical performance of pouch cells using carbon-black-based (Printex XE2-B, PTX) cathodes processed by a solvent-free R2R process is investigated. Additionally, the melt-diffusion infiltration is scaled-up to continuous processing by co-extruding the carbon and the sulfur. This facile infiltration process is then combined with a solvent-free R2R coating process to manufacture double-sided cathodes. Consequently, the impact of the infiltration method on the electrochemical performance of the dry-film cathodes is also investigated at pouch cell level. These pouch cells are tested under moderate E/S ratio of 4.5 μl mg(S)⁻¹ with the state-of-the-art (SOTA) DME/DOL (1,2-dimethoxyethane/1,3-dioxolane; DD) or the in-house developed sparingly polysulfide solvating electrolyte (SPSE) HME/DOL (hexyl methyl ether/1,3-dioxolane; HD) [30]. The average energy densities of the DD and HD-filled five-layered cells are 168 Wh kg⁻¹ and 197 Wh kg⁻¹, respectively. Post-mortem scanning electron microscopy (SEM) studies are conducted with the Li anodes as well at the cathodes. In the following, we demonstrate the significant influence of the applied pressure with a strong dependence on the electrolyte and the associated sulfur conversion mechanism, while effects of the infiltration method are negligible.

2. Experimental

2.1. Cathode manufacturing

The required sulfur/carbon composites are prepared by melt-infiltrating the sulfur (Sigma Aldrich, >99.5%) into the carbon black particles (Printex XE2-B; Orion Carbons). Both components are mixed in the ratio of 1.6:1 (S:C).

One composite is infiltrated batch-wise by standard melt-diffusion of pre-mixed carbon and sulfur. Therefore, the pre-mixed composite is infiltrated for 30 min at 155 °C under standard atmosphere.

The second composite is infiltrated by co-extrusion of sulfur and carbon nanoparticles. The infiltration by co-extrusion is conducted in a MKS-30 co-kneader (BUSS AG) at 140 °C with a single screw cross-head extruder, as shown in figure S1 (available online at stacks.iop.org/JPEnergy/4/014004/mmedia). The sulfur was dosed separately by a gravimetric dozer to adjust the required S:C ratio as exact as possible. The S/C composite throughput of more than 5 kg h⁻¹ is achieved and the resulting S/C pellets are ground by jet-milling afterwards.
Next, 3 wt% PTFE (Polytetrafluoroethylene) binder is added to both sulfur/carbon composites. The composition of both mixtures is S/PTX/PTFE 60/37/3. The as-prepared composites are used to manufacture solvent-free cathodes R2R via the DRYtrace® process (EP2820699B1; DE102017208220A1). This process generates electrode films by applying shear forces to the active material/binder composites. These electrode films are then instantly transferred to a primer-coated aluminium current collector (15 µm Al) foil. The double-sided cathodes (71 × 46 mm²) are cut via remote laser cutting directly from the resulting cathode coil. The average sulfur loading of the produced cathodes is 2.75 mg cm⁻², and their average density is 0.9 g cm⁻³.

2.2. Cathode surface characterization

The cathode morphology is characterized by SEM. These measurements are conducted on a SU8020 (Hitachi High-tech Corporation). Images are taken using 5 kV acceleration voltage and a working distance of 4 mm. The samples are fixed with an adhesive conductive carbon tape on the aluminium sample holder. To enhance surface conductivity, the samples are sputtered with gold in advance of the measurement.

2.3. Electrochemical characterization

The pouch cells are assembled by stacking five double-sided cathodes, 12 µm polyethylene (PE) separator, and double-sided lithium foil (2 × 50 µm; CEL China Energy Lithium Co., Ltd) in an argon-filled glovebox (MBraun, <0.01 ppm O₂ and H₂O). Prior to final sealing, the pouch cell stack is filled with a certain electrolyte volume. Either a mixture of DME, (battery-grade, Gotion) and DOL, (battery grade, BASF (v:v 1:1) with 1 M Lithium-bis(trifluoromethanesulfonyl)imide (LiTFSI, battery grade, BASF) and 0.5 M LiNO₃ (Alfa Aesar) or a mixture of HME (TCI Chemicals Deutschland GmbH) and DOL, (v:v 9:1) with 2 M LiTFSI is used as electrolyte. For cell assembly, an E/S ratio of 4.5 µl mg(S)⁻¹ is employed.

The electrochemical characterization of the pouch cells is conducted at 25 ± 1 °C with a BASYTEC CTS system (BaSyTec GmbH). A constant uniaxial pressure was applied to the cells while testing by a pneumatic pressure control (Fraunhofer IWS). The pressure is varied between 0 and 0.31 MPa. The DD-filled pouch cells are galvanostatically cycled at 0.1 C in a voltage range from 1.9 to 2.6 V vs. Li/Li⁺, whereas 1 C = 1672 mAh g(S)⁻¹. The Coulombic efficiency (CE) is calculated by dividing the discharge (lithiation) capacity by the following charge (delithiation) capacity. The HME/DOL-filled pouch cells are discharged with 0.05 C in the first and 0.1 C in the subsequent cycles in a voltage range of 1.5–2.5 V vs. Li/Li⁺. They are charged with 0.05 C, whereby at the end of charge a constant voltage step at 2.5 V is applied until a current of 1/50 of the nominal capacity is reached.

2.4. Electrolyte characterization

2.4.1. Electrolyte preparation

Two different methods are used to prepare the polysulfide-saturated electrolytes. For preparing the DME/DOL electrolyte, Li₂S (Alfa Aesar GmbH + Co. KG) and S₈ (Sigma Aldrich, Inc.) are added in excess (molar ratio of 1:0.875) to the electrolyte and the mixture was then stirred for 2 weeks at 50 °C. For the preparation of the HME/DOL electrolyte, 0.5 M Li₂S and 0.4375 M S₈ are dissolved in pure DOL (stirring at 50 °C for 1 week). The mixture is subsequently added to a solution of LiTFSI in HME. The ratio is adjusted that a concentration of 2 M LiTFSI in HME/DOL (9:1) is finally achieved, and the mixture was stirred at 50 °C for two weeks. Both saturated electrolytes are filtered with a syringe filter (PTFE, 0.2 µm, Carl Roth GmbH + Co. KG) at room temperature to remove the excess solids.

2.4.2. Gravimetry

The maximum polysulfide concentration of an electrolyte was determined gravimetrically according to Dibden et al [31]. In an argon-filled glovebox a defined volume of the polysulfide saturated electrolyte is transferred into a round flask and sealed with a rubber septum. Outside the glovebox, an argon inflow and an outlet with needles are implemented to ensure pressure equalization during the following steps. The polysulfides are oxidized to sulfate by adding aqueous ammonia solution (28%–30% NH₃ in H₂O, Sigma Aldrich) and afterwards H₂O₂ (30%, Carl Roth GmbH + Co. KG) in excess. The mixture is stirred for 20 min at 40 °C and for 20 min at 80 °C to remove excess NH₃ and H₂O₂. Before the sulfate could be precipitated as BaSO₄, the solution is acidified with HCl (37%, Sigma Aldrich, Inc.) to a pH value below seven to prevent the precipitation of Ba(OH)₂. Afterwards, a solution of Ba(NO₃)₂ (Sigma Aldrich, Inc.) in deionized water is added in excess. The mixture is then centrifuged and the precipitate is washed twice with approximately 50 ml of deionized water. After drying for four days at 110 °C, the precipitate is weighed and the original concentration of polysulfides is determined.
2.4.3. Conductivity
The conductivity of electrolytes is determined with a four-pole graphite measuring electrode LF400 (including an internal temperature sensor) in combination with a measuring instrument GMH 5430 (GHM Messtechnik GmbH). The solution is heated with an external silicone oil bath in a temperature range between 20 °C and 50 °C and conductivities are measured in dependence on the temperature. The values given in the results section are calculated by using a linear fit.

2.4.4. Viscosity
The measurement of dynamic viscosity is performed by using a Haake Rheostress 1 instrument (Thermo Fisher Scientific Inc.) with a double cone measuring geometry (DC 60/1) at 25 °C. The volume used for measurement is 2.7 ml. The values given in the results section are determined at a shear rate of 62.1 s⁻¹.

2.5. Post-mortem analysis
After cycling the cells are disassembled in an argon-filled glovebox (Mbraun <0.01 ppm O₂ and H₂O). Samples are cut from the middle of the third cathode, as well as from the fourth anode. The cells tested under no external pressure as well as the ones cycled under 0.3 MPa are selected for post-mortem focused ion beam (FIB)-SEM. These samples are fixed with conductive carbon tape on an aluminium sample holder. The samples are transferred with an in-house developed transfer chamber to a FIB/SEM (JIB 4610 JOEL Ltd.) The FIB cross-sections are cut via a bombardment of the sample surface with Gallium ions. An acceleration voltage of 10 kV and a working distance of 14 mm is employed. The recording angle is 45°. The surface of the cycled electrodes is also characterized via SEM. These measurements are conducted with a JSM 7800 (JEOL Ltd), and an acceleration voltage of 2 kV is applied. The cathode is studied with a working distance of 4.5 mm, whereas 3.5 mm are employed as a working distance for studying the anodes.

3. Results and discussion
Two sulfur/carbon mixtures with the same composition and a sulfur mass of 60 wt% are produced via different melt-infiltration techniques. Cathodes are manufactured via a solvent-free process on a R2R scale using the as-prepared composites. These cathodes have an areal loading of 2.75 mg(S) cm⁻². Subsequently, they are morphologically studied and electrochemically analyzed at pouch cell level. In the following, the impact of the different infiltration techniques, as well as the applied stack pressure is investigated with two different electrolyte systems. Afterwards, the post-mortem FIB-SEM analysis of the cycled electrodes is discussed.

3.1. Cathode morphology
The morphology of both cathodes is investigated by SEM. Both cathodes display S/C agglomerates with diameters in the range of several micrometers to more than 20 µm, as depicted in figures 1(a) and (d). In the cathode based on the co-extruded composite these particles are more prominent and appear to be less compressed as in the other cathode. As a consequence, the surface of this seems to be more porous than the one based on the standard composite, but the density of both cathodes is comparable. The stronger agglomeration of the co-extruded S/C is caused by the combination of pressure, temperature, and shear forces applied to the sulfur and carbon nanoparticles during the extrusion process. The standard melt-infiltrated composite is not subjected to such harsh conditions during the infiltration step. Thereby, it can be deduced that the infiltration technique and parameters influence the cathode morphology on the micrometer level. In figures 1(c) and (f) the single carbon nanoparticles of the utilized mesoporous carbon can be identified. As no significant differences between both cathodes can be detected, it can be concluded that the selected infiltration technique does not influence the cathode morphology on a sub-micrometer scale.

PTFE fibrils can be distinguished on the surface of both cathodes. These fibrils are characteristic of cathodes manufactured by the DRYtraec® process since they are formed by shearing the PTFE-binder containing electrode composite. As shown in figure 1, they form a network that interconnects the single S/C agglomerates and thereby ensures the cohesion of the cathode layer. These fibrils can bridge several hundred micrometres (figures 1(a) and (d)) as well as submicrometer distances (figure 1(c)) while exhibiting sub-micrometer diameters. These fibrils are often fractured while focusing the electron beam on them, as shown in figure 1(c).
3.2. Electrochemical evaluation at pouch cell level

The prepared cathodes are used in order to assemble five-layered pouch cells. These cell stacks are either filled with the SOTA DD electrolyte or the SPSE HD. A moderate E/S ratio of $4.5 \mu l \text{mg(S)}^{-1}$ is utilized. Constant pressure is imposed on the cell stacks by means of a pneumatic cylinder during the entire measurement.

3.2.1. Influence of stack pressure

Five-layered pouch cells are assembled using the cathodes based on the co-extruded S/C composite vs. 50 $\mu$m metallic lithium anodes. The applied pressure on the cell stacks is varied between 0 MPa and 0.31 MPa. A strong impact of the applied pressure on the discharge capacity of pouch cells assembled with DD electrolyte can be found; as depicted in figure 2(a). The uncompressed cell yields a discharge capacity of 1268 mAh g(S)$^{-1}$, whilst cells loaded with a pressure of 0.15 and 0.31 MPa retain capacities of 941 and 594 mAh g(S)$^{-1}$, respectively. This translates to a discharge capacity reduction of 27% and 73%, respectively. Both compressed cells exhibit a slightly reduced sulfur utilization during the first plateau at 2.3 V. In DD electrolyte, the first plateau is linked to the sulfur utilization by the formation of long-chain poly-sulfides (PS) such as $S_8^{2-}$ and $S_6^{2-}$ [32]. The end of this dissolution process is indicated by the so-called voltage dip, at which the viscosity of the electrolyte reaches its maximum due to the high concentration of solved polysulfides at this state of discharge [33]. The concentration of PS increases due to chain-length reduction reactions during the first plateau. A capacity of 365 mAh g(S)$^{-1}$ is achieved during this discharge step by the uncompressed pouch cells while both compressed cathodes deliver capacities of less than 340 mAh g(S)$^{-1}$. Interestingly, the sulfur utilization in the first plateau is only slightly affected by the pressure exertion, but a strong impact on the polysulfide precipitation during the second discharge is observed. During the second plateau at 2.1 V, a discharge capacity of 921 mAh g(S)$^{-1}$ is achieved by the pressure-less tested pouch cell, and the achieved discharge capacity of the pressed cells is severely reduced. The cell which is pressurized with 0.15 MPa reaches a capacity of 601 mAh g(S)$^{-1}$, while the cell exposed to maximal pressure yields only a capacity of 261 mAh g(S)$^{-1}$. After five cycles, both pressurized pouch cells deliver capacities of less than 340 mAh g(S)$^{-1}$.

Since both pressurized cells only utilize only a fraction of their cathode capacity, the stress on the lithium anode is also low since smaller amounts of lithium have to be stripped and plated. Thereby, the capacity degradation per cycle is lower than the one of non-compressed cells, as depicted in figure 2(c). The main reason for capacity degradation are the side reactions on the lithium anode surface. If the surface of the anode increases by extensive stripping and plating of lithium due to higher sulfur utilization on the cathode side, also the capacity degradation increases since more electrolyte reacts on the increased lithium surface [34]. After 40 cycles, the non-pressurized cell yields a capacity of 948 mAh g(S)$^{-1}$, whereas both compressed cells achieve capacities of 636 and 361 mAh g(S)$^{-1}$, respectively. The capacity degradation of the non-pressurized cells increases after 40 cycles, due to the depletion of LiNO$_3$. 

Figure 1. SEM micrographs of pristine dry-film cathodes. The sulfur infiltration is either conducted by (a)–(c) standard melt-infiltration or (d)–(f) melt-infiltration via co-extrusion.
It can be stated that the pressure application has no beneficial, but adverse impact on the performance of the studied DD (polysulfide soluble electrolyte) pouch cells, especially in regard to cathode active material utilization.

In contrast, no significant impact of the loaded pressure on the performance of the HD (sparingly polysulfide soluble electrolyte)-filled cells can be identified. The pressure-less tested cell yields an initial discharge capacity of 1195 mAh g(S$^{-1}$) while the cells tested with 0.15 MPa and 0.31 MPa show capacities of 1212 mAh g(S$^{-1}$) and 1176 mAh g(S$^{-1}$), respectively. The cells tested with 0 MPa and 0.15 MPa achieve capacities of approximately 420 mAh g(S$^{-1}$), while the cell tested with 0.31 MPa yields a capacity of 464 mAh g(S$^{-1}$) during the first plateau until the voltage dip at 2.1 V. In HD electrolyte, short-chain PS such as S$_4^{2-}$ are formed directly during the first plateau [30]. Possibly, this indicates that in cells with higher pressure, more short-chain PS are formed than in less compressed ones. Therefore, the viscosity of the electrolyte increases stronger, which explains why the cells tested with 0.31 MPa exhibit an overpotential of 0.1 V in each cycle. This effect has no significant impact on the overall discharge capacity of the cells. The increased overpotential can be invoked by an increase in the ionic resistance of the cell as the volume of electrolyte in the cathode is reduced by the compression. After five cycles, the cell tested with the moderate pressure shows a capacity of 1055 mAh g(S$^{-1}$) while the cell tested without pressure yields a comparable capacity of 1046 mAh g(S$^{-1}$). The cell tested with the highest pressure demonstrates still a capacity of 985 mAh g(S$^{-1}$). The long-time performance of the different cells is comparable, as displayed in figure 2(d). The cells tested without pressure exhibits a discharge capacity of 597 mAh g(S$^{-1}$) after 40 cycles. The cells tested with 0.15 MPa and 0.31 MPa retain capacities of 590 mAh g(S$^{-1}$) and 659 mAh g(S$^{-1}$), respectively. The cells tested under external pressure display a more pronounced decrease in CE than the non-pressurized cells. In the first 25 cycles, the CE of the pressurized cells decreased from approximately 95% to 87%, whereas the CE of the non-pressurized cell is still above 90% after 25 cycles. This could be linked to a more pronounced PS shuttle. Since the electrochemical reaction of the pressurized cell is stopped at a low state-of-charge, a higher concentration of PS remain in the electrolyte. Furthermore, the group of Manthiram demonstrated that at higher cycle numbers, the capacity degradation invoked by the depletion of addressable lithium is more prominent than the sulfur-related capacity degradation. Thereby, it can be concluded the increasing CE decrease of the pressurized cells might also be linked to side-reactions on the anode and the formation of dead lithium [35]. This illustrates that the results obtained with Li vs. NMC cells cannot be directly transferred to Li-S batteries since the lower CE indicates that more lithium-consuming

![Figure 2](image.png)

Figure 2. Voltage profiles of pouch cells with (a) DME/DOL and (b) HME/DOL electrolyte. Galvanostatic cycling of the respective (c) DME/DOL—(C/10) and (d) HME/DOL-filled (1st discharge: C/20, 1st charge: C/20 + CCV; subsequent discharge: C/10, charge: C/20 + CCV) five-layered pouch cells. An E/S ratio of 4.5 µl mg(S$^{-1}$) is employed.
Figure 3. Schematic illustration of the influence of external pressure application on the dry-film cathodes and their interparticular porosity. Darker electrolyte colors indicate higher PS concentrations in the electrolyte and thereby higher electrolyte viscosity.

side-reactions occur. In addition, it is known that sulfur and Li$_2$S agglomerates in the cathode and cannot be properly utilized over cycling [36].

The different influences of pressure application on the two electrolyte systems can be related to their different conversion mechanisms. It was demonstrated by the Kwade group that the secondary porosity of the cathode and thereby the interparticular pore volume is reduced by compaction, while the intrinsic porosity of carbon is not altered [37]. The volume of electrolyte in the cathode decreases proportionally, and therefore, the localized E/S ratio in the pores is altered by compaction. This is problematic for electrolytes with high PS solubility as depicted in figure 3 since their electrolyte viscosity increases fast due to the rising PS concentration. Moreover, the number of dissolved PS rises during the first plateau by PS chain-reduction reactions. This fast viscosity increase will reduce the amount of addressable sulfur. Due to high electrolyte viscosity and resulting low ionic conductivity plus hindered diffusion, the precipitation reaction in the second discharge step is hindered [38–40]. To confirm this finding, viscometry and conductivity measurements of the pristine DME/DOL electrolyte as well as with an saturated DME/DOL electrolyte with a PS concentration of 5.52 mol(S) l$^{-1}$ are conducted. The PS concentration is determined gravimetrically. The viscosity at 25 °C of the pure DME/DOL electrolyte is 2.1 mPa s, as depicted in figure 4(a). The viscosity increases to 122.9 mPa s, after PS addition. This corresponds to an increase in electrolyte viscosity of 5750%. The ionic conductivity decreases by PS dissolution, as shown in figure 4(b). The conductivity inclines from 12.6 to 1.5 mS cm$^{-1}$. Moreover, the reduction of active surface area by compaction must be taken into account [41]. A complete clocking of the active carbon surface is not likely due to the permeable nature of the formed Li$_2$S coating [42].

In contrast, the SPSE demonstrates no impact of the reduced electrolyte volume on the performance since the PS solubility is restricted. The maximum PS concentration in HME/DOL electrolyte is 0.36 mol(S) l$^{-1}$. Given that the short-chain PS are formed rather rapidly during the discharge process and long-chain PS barely diffuse out of the cathode, the electrolyte viscosity will be less affected by the PS chain-length reduction. Therefore, the viscosity increase of the HME/DOL electrolyte is less drastic, despite the reduced solvent volume, as shown in figure 3. This is confirmed by viscometry measurements of HME/DOL electrolytes with and without dissolved PS. The HME/DOL electrolyte viscosity increases from 5.5 to 6.7 mPa s, as shown in figure 4(a). This represents an increase in electrolyte viscosity of 21% by PS dissolution. The ionic conductivity decreases from 1.0 to 0.8 mS cm$^{-1}$, respectively.

Thereby, it can be concluded that the impact of the applied pressure on the performance of Li-S cells strongly depends on the employed electrolyte, its polysulfide solubility, and its accompanied conversion mechanism. Moreover, it can be stated that the HME/DOL is especially suited for cathodes with low intrinsic porosities, and due to this property and its low gravimetric density (1.1 g cm$^{-3}$) [25] especially qualified as an electrolyte for Li-S cells with high energy density.
3.2.2. Influence of sulfur infiltration

The cathodes based on standard melt infiltrated cathodes, as well as the ones based on co-extruded S/C, are used to assemble five-layered pouch cells. These cells are tested with a constant pressure of 0.31 MPa. Therefore, limited discharge capacities are achieved by both cathodes in DD electrolyte. In the 5th cycle, both cells yield a discharge capacity of approximately 440 mAh g(S)\(^{-1}\) as shown in figure S2. The discharge capacity of the standard cathode increases after the 10th cycle as displayed in figure S2(b), whereas the cathodes based on co-extruded S/C composite do not show such behavior. After 40 cycles, the standard cathode has a discharge capacity of 455 mAh g(S)\(^{-1}\), while the other cathode delivers a similar capacity of 381 mAh g(S)\(^{-1}\). No remarkable difference in capacity degradation can be distinguished between both cathodes.

As for the DD electrolyte, no significant impact of the infiltration technique on electrochemical performance of the cathodes is observed in HD electrolyte, as shown in figure S2(c). The cathodes prepared with the standard melt-infiltration technique provide a discharge capacity of 1202 mAh g(S)\(^{-1}\), whereas the cathodes based on the co-extruded S/C composite retain an initial discharge capacity of 1176 mAh g(S)\(^{-1}\). The cathodes based on the co-extruded S/C composite display an overpotential of 0.1 V compared to the standard composite, as depicted in figure S2(b). This increased overpotential could be linked to increased inner resistance of the cell [43]. After 25 cycles the cathode based on the standard composite achieves a discharge capacity of 840 mAh g(S)\(^{-1}\), while the cathode based on the co-extruded S/C composite retained a comparable capacity of 781 mAh g(S)\(^{-1}\). The CE of both cells decreases from approximately 96% in the first cycles to 88% in cycle 25. After 40 cycles, the standard cathode yields a capacity of 729 mAh g(S)\(^{-1}\), whereas the cathode based on co-extruded S/C composite reaches a capacity of 670 mAh g(S)\(^{-1}\). Both cathodes demonstrate comparable capacity degradation in the first 40 cycles.

It can be concluded that the sulfur infiltration technique has no relevant influence on the performance of the manufactured cathodes, and the industrially scalable extrusion process is a suitable candidate in order to generate the sulfur/carbon composite.

3.3. Post-mortem analyses

The cells cycled under varying external pressure are disassembled after cycling. To conduct post-mortem FIB-SEM analysis, samples are obtained from the third cathode of the five-layered pouch cells as well as from the fourth anode. The cells filled with DD-electrolyte demonstrate a degradation trend, as shown in figure S3. The S/C cathodes of the cells cycled without any external pressure exhibit a strong formation of wrinkles. Partial delamination of the cathode coating occurred while disassembling the cells. No delamination is detected investigating the pressurized cathodes. The formation of wrinkles decreases with increasing external pressure. It was found that the dry-out of the cells tested with lower pressure is more advanced. The degradation trend is more pronounced for the Li anodes than for the cathodes as illustrated in figures S3(b), (d) and (f). The anodes of the cells tested with 0.3 MPa exhibit a discoloration on the surface as well as an increase in surface roughness as depicted in figure S3(f), whereas the anodes of the non-pressurized cells have completely deteriorated. These anodes do not longer exist as foils, but they are completely fragmented into powder-like lithium, as shown in figure S3(b). The anodes of the cells tested with 0.15 MPa demonstrate pitting corrosion as shown in figure S3(d). It should be pointed out that the decreased anode corrosion with
increasing external pressure is less a result of the pressure impact on the lithium, it is more likely a result of
the drastically reduced capacity utilization of the cathode and thereby the reduced amount of required
lithium on the anode side. The latter causes less corrosion of the lithium anode since less lithium is stripped
and plated in every cycle. The separators of the cells demonstrate an increased discoloration with increasing
external pressure. This results from an increased PS content in the separator, due to an increased PS
concentration in the electrolyte since the complete electrochemical conversion of dissolved PS to Li₂S
terminated prematurely.

The cycled anodes, as well as the cathodes, are studied via SEM and FIB-SEM, as shown in figure 5. The
surface of both cathodes, tested without or with 0.31 MPa, is fractured. These fractures can be appointed to
the swelling and expansion of the dry-film cathodes just after electrolyte contact [44]. The length of the
fractures approaches several hundred micrometers, while the width is in the μm-scale. The fractures formed
on the surface of the cathodes tested with maximal pressure are more pronounced. The cathodes tested
without pressure show stronger delamination from the current collector, as demonstrated in figure 5(c). The
coating thickness is 14 μm, whereas the nominal value is 108 μm. The nominal value is calculated from the
cross-section of the pristine cathode, shown in figure S5(a). The increased delamination can be appointed to
the higher stress in the cathode since more sulfur is utilized in these cathodes. Furthermore, the cathodes are
not pressed against the current collector foil with external pressure facilitating delamination. However, the
cathode tested under pressure also displays delamination, as shown in figures 5(f) and S6(c), (d). The
thickness of the pressurized cathode is 50 μm. The FIB cross-section in figure S6(c) reveals that the dry film
cathode tested under pressure is highly compacted with nearly any bigger transport pores left. The thickness

Figure 5. SEM micrographs of (a)–(f) cathodes and (g)–(l) Li anodes cycled in DD-filled pouch cells. A constant external pressure
of (a)–(c); (g)–(i) 0 MPa or (d)–(f); (j)–(l) 0.3 MPa is exercised while testing.
of the cathode is reduced by 54%, and due to the applied pressure, only submicrometer pores can be observed in figure S6(d). This is in accordance with the literature, demonstrating that the application of external pressure on the cathodes drastically reduces their macro-porosity [44] Contrarily, the pressure-free tested one does not show such compaction. In figures S6(a) and (b), macropores with a length and width of several micrometers can be observed as well as submicrometer pores. On a nanometer-scale, no significant impact on the cathode structure can be distinguished as shown in figure S4. It can be concluded that the pressure application has a limited influence on the surface morphology of the cathode. This is also demonstrated in figures 5(b) and (e). Both cathode surfaces are comparable to each other, as well as to the pristine state, depicted in figure 1(e). However, it has a strong impact on the porosity of the cathodes, as can be seen from the cross-sections. These results support the theory described above. It has to be noted that the sample morphology might be altered by the impact of the fast gallium ions, all samples show a strong ‘curtaining-effect’. Especially the sulfur might evaporate during the cutting process in the vacuum chamber. Moreover, it must be taken into account that partial delaminations of the electrodes occurred during the disassembly of the cells.

Contrarily to the cathodes, the pressure application does have a strong impact on the morphology of the Li anodes as displayed in figures 5(g)–(l). The lithium forms rod or dendrite-like structures during cycling when no external pressure was applied during cycling, as shown in figure 5(g). The length of these structures is between 10 and 50 µm, while their diameter is below 10 µm. These rods have a high surface area since they consist of smaller rods and pillar-like structures. The anodes tested with an external pressure of 0.3 MPa exhibit another surface morphology as depicted in figures 5(j) and (k). Grains with a diameter of 10 µm are visible on the anode surface, as shown in figure 5(j). The surface of these grains shows the formation of 3D structures which consist out of smaller grains. The formation of compact Li structures after cycling under external pressure was already described in the literature [15, 16]. However, the different Li morphology might be linked to the reduced lithium utilization of the anodes tested under pressure. Since the lithium anode of the pressure-less tested DD cells completely deteriorates, no FIB cuts could be conducted. The anodes disintegrated into millimeter-scaled particles, as shown in figure S3(b). The cross-section of the pressurized anode reveals that the anode thickness has increased during cycling from 50 µm to 64 µm, due to the voluminous growth of lithium, as displayed in figure 5(l). The copper current collector is visible in figure S6(e). Next to the current collector, a gap between both Li foils can be observed. Inside this gap, the formation of lithium grains, similar to the one on the surface, can be distinguished as displayed in figure S6(f). In addition, the formation of µm-scaled pores inside of the anode foil can be observed.

It is demonstrated that the anode deteriorates severely when a high discharge capacity is yielded over several cycles, as a large quantity of lithium is shifted between both electrodes as depicted in figure 3. By limiting the discharge capacity extracted, the lifetime of the cell can be extended at the expense of energy density. The severe degradation of the lithium anode indicates that the anode must be stabilized either by an artificial SEI or other protective coatings if a high capacity utilization should be reached. These findings underline that the lifetime of Li-S cells is mainly limited by the unstable lithium anode.

The cells tested with HD electrolyte demonstrate that there is no remarkable impact of the pressure on the post-mortem morphology, as depicted in figure S7. Like the S/C cathodes of the DD-filled pouch cells, the cathodes tested with HD electrolyte show wrinkle formation due to the swelling of the cathode. Increasing pressure increases the delamination of the S/C cathodes since the active material coating is partially pressed into the separator, as demonstrated in figures S7(a) and (e). The HD pouch cells cycled without pressure do not show such strong degradation of the Li anode (figure S7(b)) as their DD counterparts, as depicted in figure S6(b). Nonetheless, the anode exhibits strong corrosion, hence, the anode is still present as foil and not as a powder. It can be distinguished that larger and brittle plates delaminated from the anode. Moreover, pitting corrosion and discoloration of the anode surface is visible. The anodes of the cells tested under external pressure demonstrate a comparable degradation, as shown in figure S7(f). As for the cathodes, more pronounced electrode delamination can be found.

Similar to the electrodes of the DD cells, the electrodes of the HD are also examined by post-mortem SEM or rather FIB-SEM analyses. The cathodes, however, delaminated from the current collector while FIB-crosssection preparation. During the SEM measurement, a complete disintegration of the cathode occurred. Due to the severe corrosion of the anodes no FIB cuts could be performed since the brittle anode is destroyed while cutting and measuring.

4. Conclusion

In this study, the influence of constant external uniaxial hydraulic pressure, varying from 0 MPa to 0.31 MPa, on the performance of multi-layered Li-S pouch cells filled with either the SOTA DME/DOL electrolyte or the SPSE HME/DOL was investigated. A lean E/S ratio of 4.5 µl mg(S)−1 was employed for the pouch cell
testing. Additionally, the sulfur melt infiltration was upscaled to an extrusion process to meet the requirements of R2R cathode processing. The influence of the co-extrusion infiltration technique on the performance of the solvent-free processed S/C cathodes was evaluated on pouch cell level and compared to a conventional lab-scale melt-infiltration. No significant influence of the sulfur infiltration technique on the cathode performance could be identified, hence, it can be concluded that the up-scaling of the sulfur infiltration from a discontinuous lab-scale process to a continuous co-extrusion process, with a throughput of more than 5 kg h\(^{-1}\), is promising for future industrialization.

It is demonstrated that the impact of compressing Li-S pouch cells depends strongly on the sulfur conversion mechanism controlled by the respective electrolyte. While a pronounced sulfur utilization reduction with applied pressure is found for cells filled with the highly PS solvating DME/DOL electrolyte, for SPSE HME/DOL, the utilization remains high even at high applied pressure. This stark contrast could be caused by pressure-induced cathode porosity reduction lowering the electrolyte volume in the cathode which is expected to affect the highly PS solvating electrolytes more detrimentally than the performance of the SPSE HME/DOL as it can be used with lower E/S ratios. Moreover, the stronger increase in electrolyte viscosity by the dissolution of PS must be taken into account as shown by viscosity measurements of the two pristine electrolytes in comparison with their PS saturated versions. This demonstrates that SPSEs are particularly well suited for Li-S cells with compacted highly-densified cathodes.

The post-mortem studies found that the lithium growth on the anode side is affected by the applied pressure. Increased pressure has a beneficial influence on the deposition behavior of lithium and invokes the formation of less dendritic and compact structures. Pressure application on the S/C cathodes causes densification eliminating the macropores in the cathodes, thus affecting the above mentioned electrochemical conversion mechanism.

Moreover, it is demonstrated that the deterioration of the lithium anode is particularly pronounced when desirably high capacity utilization is achieved. Since a high capacity utilization is mandatory for Li-S cells with high energy densities, the lithium must be perspective stabilized by applying electrolyte additives or a protective layer.

Future studies on pouch cell level should be conducted in which the external pressure and the operation temperature are varied as the complex conversion mechanism of Li-S cells and its undesired side reactions strongly depend on the temperature.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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