

Inert atmosphere protected pilot-scale extrusion of polyester-based solid polymer electrolytes for lithium metal batteries

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ABSTRACT

The advancement of solid-state batteries using dry processing represents a substantial milestone in the ongoing development and implementation of next-generation solid-state batteries. The extrusion systems in this study are designed to illustrate a proof of concept for the capabilities of compact downscaled extrusion systems integrated into glove boxes, employing star-shaped polyester-based polymers for evaluation. In addition to processing of pure polymers such as Bt-PCL, more complex hybrid polymer systems are also accessible for extrusion, where polycaprolactone grafted onto aluminum oxide (Al_2O_3 -PCL) is a representative example. This work demonstrates how research on solid-state electrolytes can be strongly complemented by application-oriented emphasis of processability. Extrusion denotes a manufacturing process that allows for straightforward large-scale production of high-quality polymer-based battery components, including solid-state electrolytes, artificial layers on the electrodes and interlayers. The equipment utilized in this study is capable of producing multiple square meters per hour of the respective membranes, affording a layer thickness of 35 μm in case of Al_2O_3 -PCL. Also, in case of Bt-PCL, membranes of 15 m in length and a layer thickness of 16 μm could be produced, demonstrating scalability of the process. Moreover, Bt-PCL underwent additional processing and was exploited as catholyte for higher mass-loading NMC_{622} cathodes to be operated in $\text{NMC}_{622}|\text{Li}$ cells in combination with Al_2O_3 -PCL as solid polymer electrolyte.

1. Introduction

Research and development in the field of solid-state batteries has made enormous progress in recent years, as demonstrated by the growing number of publications in the field and pilot-scale production efforts of numerous companies. Solid-state batteries have the potential to be the next milestone in battery technology, as they offer a number of compelling advantages. Unlike liquids, solid-state electrolytes do not leak out when the cell is damaged and they are in most cases thermally more stable than liquid electrolytes, though even solid electrolytes may burn [1–3]. Solid-state batteries may also enable unprecedented cell and battery concepts, including metallic electrodes such as lithium metal and new or optimized battery pack designs [4,5]. The employment of lithium metal and the associated reduction in cell weight can boost the available specific energy on cell level to over 450 Wh kg^{-1} [6,7]. According to the deployed electrolyte classes, solid-state batteries can be broadly categorized into several types: polymers, oxide- and

sulfide-based ceramics as well as hybrid electrolyte solid-state batteries, which combine elements from various classes, e.g. polymers combined with oxidic ceramic components [8–11]. The combination of individual material classes affords tailoring of desired properties of individual materials while compensating for potential weaknesses of the respective compounds [9,12,13]. Recently, a variety of polymer-based solid electrolytes were introduced, exploiting polymers such as poly(alcohols), poly(amines), poly(nitriles) or poly(caprolactones) [14–17]. These materials were utilized as pure polymer electrolytes, copolymers or in hybrid systems. Polymers are characterized by good chemical and electrochemical stability, good wettability and contact with the electrodes, particularly lithium metal, and enable large adaptability thanks to the rich possibilities offered by organic chemistry [9,10]. Nevertheless, polymer electrolytes also suffer from challenges such as limited ionic conductivity or mechanical stability, which can be improved by skillful adaption of hybrid electrolytes [12,13,18]. In view of application-oriented materials development, scalability, processability,

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applicability and, where feasible, sustainability of the selected materials should be carefully considered in addition to their electrochemical properties. Polymers have been industrially processed in large quantities for over 100 years [19]. In 2015, the global production volume of polymers was approximately 380 million tons, evidencing that polymers can be sufficiently scaled and processed for the development of potential solid-state electrolytes [20]. It is paramount to consider existing industrial machines and processes to be exploitable for the processing of introduced polymer-based electrolytes. Notably, on industrial scale, extrusion processes are suitable for mixing and production of polymer-based solid electrolytes [21]. Initial works exhibited the successful production of polyethylene oxide, polyethylene/polycarbonate and hybrid electrolytes made of polymer and ceramic constituents, which are for example mixtures of poly(ethylene oxide) (PEO) and lithium lanthanum titanate (LLTO) [22–25]. In particular, extrusion processes have the advantage that, compared to solvent-based processes such as solution casting, they do not require toxic solvents. Consequently, manufacturing costs are reduced at material level and energy- and cost-intensive processing steps such as drying are avoided [26]. In addition, the risk of incomplete solvent removal from polymer electrolytes during the drying process is eliminated. In contrast to discontinuous hot press production of polymer electrolytes, in which the starting materials of the electrolyte such as polymer, salt and fillers or additives are premixed and then pressed between two hot plates to form thin membranes, extrusion denotes a continuous, readily scalable process [27]. In a robust process environment, the polymer electrolyte can be produced in much more reproducible and greater quantities compared to batch manufacturing. The products that can be obtained from extrusion may be directly employed as solid electrolytes. However, mixtures can also be produced that are utilized, for example, as artificial solid electrolyte interphase (SEI) layers on lithium metal electrodes or as interlayer within the electrode/electrolyte stacks [28]. Herein, we present a proof of concept study with two extrusion systems, including a 9 mm and a 12 mm extruder. The pilot lines were designed to demonstrate the functionality of extrusion for the processing of solid-state electrolytes. As a reference material, we chose polyester-based solid electrolytes, particularly due to their higher electrochemical stability compared to state-of-the-art commercialized materials such as PEO and beneficial Li transport properties [12,29,30]. In addition, the material affords excellent physical properties conducive to extrusion, as elaborated in the subsequent sections. The presented extrusion systems are broadly applicable to other polymers and materials, and can be even further extended. For example, cross-linking the materials using ultraviolet radiation (UV) can be added as a finishing step. With a comparably small feedstock of 100–200 g, these systems are engineered to also facilitate research on novel and rather costly materials prior to larger scale-up.

2. Results and discussion

The present study evaluates the potential of dry processing by extrusion of star-shaped and hybrid polyester-based polymers. For this purpose, the polymer and hybrid polymer Bt-PCL and Al_2O_3 -PCL, respectively, are invoked as reference materials [12,29]. Furthermore, the extrusion systems that were already presented will be evaluated for their potential application for processing and production of dry polymer-based solid electrolytes. The work not only considers the production of solid-state electrolytes based on mechanically stable Al_2O_3 -PCL, but also manufacturing of artificial layers for solid electrolyte interphase (SEI) or cathode electrolyte interphase (CEI) functional layers by melt extrusion. In this case, Bt-PCL is used as interlayer between cathode and the electrolyte, effectively acting as catholyte. In addition to processing and characterizing the materials, the current work also involves assembly of full cells in pouch-type format, exploring the relevance of dry processing upon extrusion in the field of battery research.

Star-Shaped Polyester and Hybrid Star-Shaped Polyester

Polymers for Dry Processing via Melt Extrusion

Polyesters are particularly well-suited for the development of polymer-based solid electrolytes due to their diverse array of advantageous properties. These include good oxidative stability, which is important in view of higher voltage cathode materials that enable higher energy densities. However, polycaprolactone-based polymers are also suitable candidates due to their sufficient ionic conductivity and high lithium ion transfer number [12,17,30–32]. Customized, star-shaped polycaprolactones exhibit impressive properties that render them rather ideal for employment in lithium metal-based solid batteries [12,31]. Polymer Bt-PCL (Fig. 1) is an example of star-shaped polycaprolactones, comprising a benzene-1,3,5-triol core that is grafted with polycaprolactones. It was demonstrated earlier that this polymer system, when utilized in conjunction with a PE separator infiltrated with Bt-PCL, is compatible with NMC_{811} cathodes in lithium metal-based cells [31]. Another star-shaped polymer is Al_2O_3 -PCL (Fig. 1), in which polycaprolactone is grafted onto aluminum oxide nanoparticles. The resulting hybrid polymer electrolyte was successfully utilized in $\text{NMC}_{622}|\text{Li}$ cells, emphasizing favorable mechanical properties and exceptional reversibility during lithium dissolution and deposition [12].

Bt-PCL is soft and adhesive, which complicates its handling. For the majority of amorphous polymer electrolytes, this aspect of processing represents the most notable challenge [12,33]. Al_2O_3 -PCL exhibits remarkable mechanical robustness, attributed to the presence of durable but abrasive aluminum oxide particles. Collectively, these two materials, each with its distinct properties, account for a considerable proportion of available polymer-based electrolyte systems. Consequently, they are well suited to serve as benchmark systems. The favorable one-pot synthesis of both polymers and associated high scalability make them particularly suitable for processing by extrusion. Here, the synthesis of both polymers was typically carried out in a 2-liter reactor, but a 5-liter reactor setup is also feasible, enabling the production of up to 1 kg of material per batch.

Pilot-Scale 9 mm Extrusion Line for Soft Polymers

Bt-PCL, which is employed in this work as a possible catholyte, is processed using a 9 mm twin-screw extruder with a downstream calender. The extrusion line is encased in a specialized glovebox, as illustrated in (Fig. 2 a). The glovebox enables the handling and processing of the starting materials under controlled conditions, with precise regulation of oxygen and water levels in the atmosphere. In addition to experiments conducted in dry N_2 environments with H_2O levels measuring below 0.1 ppm, experiments with different but defined water contents in the atmosphere are also feasible. The glovebox is divided into two sections, with the right-hand section serving as storage compartment and workspace for experiment preparation. All the materials are processed by the pilot line located in the left-hand box, which is equipped with an opening front panel, facilitating expeditious intervention in the event of complications while streamlining maintenance operations of the system. To prevent contamination of the storage box,

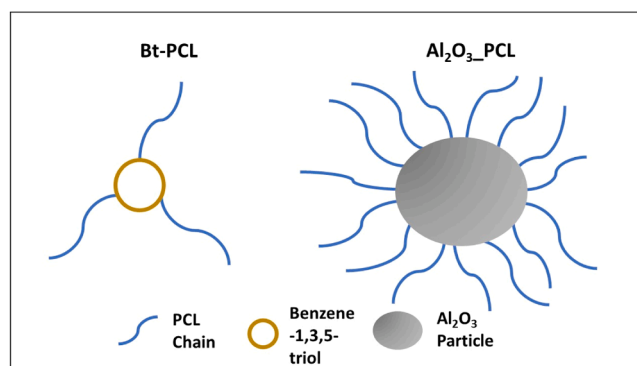


Fig. 1. Visual representation of the star-shaped polymer Bt-PCL and the hybrid polymer Al_2O_3 -PCL.

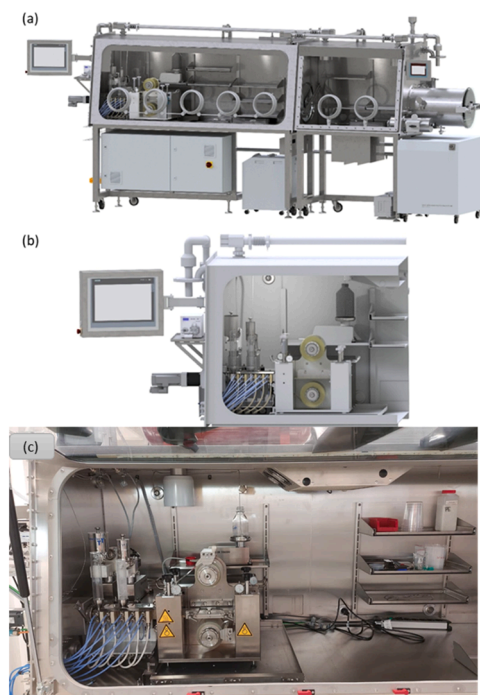


Fig. 2. a) Complete glove box of the Pilot-Scale 9 mm Extrusion Line, the right box is used for preparation and storage, while the left box is used for processing.; b) Detailed view of the extruder system in the left box compartment without the front panel; and c) a photo showing a close-up of the extruder system in the left glovebox without the front panel.

the two boxes can be hermetically sealed from each other.

Fig. 2 b and Fig. 2 c display an illustration and an actual photograph of the production line in more detail that comprises two solid dosing units, designated Feeder 1 and Feeder 2, and a liquid dosing unit. These components function to convey the raw materials into the twin-screw extruder. Also, a downstream heated film roller is positioned subsequent to the extruder. Feeders are positioned on precision scales, enabling gravimetric operation of the feeding devices, offering high accuracy in the composition of the materials to be extruded. The utilization of multiple feeders, as opposed to a single feeder, serves to eliminate the necessity for exhaustive premixing of materials and the potential for segregation of those materials within the feeder [22]. The screw diameter of the extruder is 9 mm, and the barrel length is 270 mm, resulting in a length-to-diameter ratio of L/D 30:1. The barrel is engineered as split barrel, subdivided into five zones that can be heated or cooled independently. The nozzle plate located at the terminal point of the barrel can be detached and substituted with alternative nozzles. The nozzle utilized in this experiment represents a slit nozzle, with dimensions measuring 40 mm in width and 0.2 mm in height. The screw is made from 1.4542 stainless steel, which has been precipitation-hardened to 42–45 HRC. The split barrel and nozzle are made from 1.404 stainless steel, both hardened via Hard-Inox-S to 65–67 HRC. Subsequent to the extruder, a film roller with heated calender rolls facilitates production of thin, homogeneous polymer films. Note that the extrudate can undergo calendaring in this instance to a width of up to 90 mm. Bt-PCL is melted and subsequently blended with conductive salt Lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI) in a ratio of $[C = O]:[Li]$ of 5:1, utilizing gravimetric feeders within the extruders. Then, the melt is calendered with a downstream film roller to thicknesses of 30–40 μm and widths of 60–70 mm. During the rolling process, the melt is situated between two release films, preventing the melt from adhering to the rolls of the calender. This process facilitates the production of membranes with lengths approaching several tens of meters, with theoretical capabilities extending up to 145 m, limited by the length of

the calender's release films. To illustrate the scalability of the extrusion process, a 15 m long Bt-PCL demonstration membrane was manufactured using the 9 mm extrusion line, as shown in Fig. 3. A secondary rolling step was invoked to reduce the layer thickness of the Bt-PCL membrane to 15–17 μm .

To investigate the mechanical impact and force transmitted by the extruder onto the polymer during processing, processing conditions were monitored and compared to data from size exclusion chromatography (SEC) measurements. To account for any influence of the screw geometries, two different procedures were utilized. Fig. 4 illustrates screws utilized: Screw (a) is a rudimentary screw composed exclusively of conveying elements, while screw (b) was equipped with a variety of kneading elements to increase the mechanical stresses exerted on the polymer [34,35].

Also, to account for the potential impact of variable conducting salts on SEC measurements, extrusion tests were performed with and without LiTFSI salt. No visible differences were observed. Bt-PCL revealed a molar mass of M_w : 49700 g mol^{-1} . Fig. 5 presents a graphical representation of the polymer's molar mass as a function of the measurement conditions, processed by screw (b). The polymer was characterized using SEC prior to the tests and was also measured after processing on the extruder at a screw speed of 80 RPM, identical to conditions exploited to yield Bt-PCL catholyte membrane in this work.

In a subsequent trial, the velocity was augmented two-fold to 160 RPM, with the objective of amplifying the shear forces exerted on the polymer. The results obtained in case of the screw geometry (a) are collected in the SI (see Figure S 1).

It is evident that even when employing screw (b) with its numerous kneading elements, no discernible changes in resulting molar polymer masses were noticed. Upon augmentation of the velocity to 160 RPM, no degradation effects of the polymer were detectable. Here, star-shaped PCL-based polymers are particularly well-suited for degradation-free processing by extrusion, reflecting its low melting point and low viscosity compared to other polymers such as PEO [12,29,36]. To further characterize the polymer films regarding homogeneity, cryogenic focused ion beam scanning electron microscopy (cryo-FIB-SEM) analysis was performed. A cross-section of Bt-PCL membrane reveals a uniform film thickness of 15–17 μm (Fig. 6 b). Furthermore, energy dispersive spectroscopy (EDS) of the cross-section images was done to elucidate the presence of homogenous salt distribution inside the films. As Bt-PCL mainly consists of carbon, it was monitored as "polymer distribution" (Fig. 6 c), while LiTFSI contains fluorine, which was evaluated as "salt distribution" (Fig. 6 d). Both carbon and fluorine element mappings demonstrated a uniform element distribution without element hotspots. Additional line scans were executed for validation (Figure S 2). Here, carbon and fluorine exhibited similar intensity trends during line scanning and therefore corroborate homogeneous salt distribution inside the extruded Bt-PCL membranes.

The data clearly emphasize successful fabrication of ultra-thin and homogeneous PCL-based membranes through the implementation of an extruder and calender. The employment of an alternative nozzle could potentially enable further reduction of the layer thickness, a necessity



Fig. 3. A 15 m long Bt-PCL membrane positioned between release films.

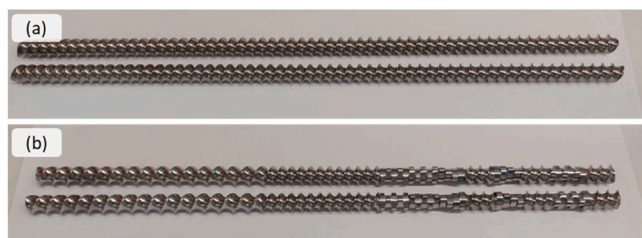


Fig. 4. a) Illustration of the 9 mm extruder screws with conveying elements only; and b) the extruder screw with conveying elements and various kneading elements.

for certain applications involving utilization of artificial layers such as CEI or SEI, respectively. Due to its mechanical properties, the 16 μm Bt-PCL membrane is no longer free-standing, so that for the manufacture of polymer layers of a particular fine thickness, the materials could be calendered directly onto the cathode sheets. This would eliminate a transfer process from the release film onto the ready-made cathode.

Pilot-Scale 12 mm Extrusion Line for Tough Hybrid Polymer/Oxide

A 12 mm extrusion line was implemented to explore scalability and processing of hybrid PCL materials upon cell manufacture. Al_2O_3 -PCL was processed to hybrid polymer membranes exploiting a modified pilot line situated within a glovebox. The glovebox of the 12 mm extruder is comparable in design to that of the 9 mm extruder, with the exception of an additional compartment to accommodate spatial limitations (see Fig. 7 a). The glovebox is divided into two sections, where the left and middle boxes are utilized for processing and operation of the pilot line. The right box is primarily utilized for storing educts, products and preparation of experiments for the extruder. A sealed door is positioned between the right-hand and middle box, permitting a hermetic sealing off the storage box from the boxes in which the materials undergo processing. The left-hand box is equipped with a front panel that could open quickly. This feature allows for rapid intervention in the event of

malfunctions and facilitates cleaning and maintenance of the pilot line. The 12 mm extrusion line exhibits a substantially more intricate design compared to the smaller 9 mm extrusion line, as illustrated in (Fig. 7 b and Fig. 7 c). The 12 mm extruder is equipped with five feeders, enabling independent introduction of five distinct materials into the system. Feeder 1 to 4 function as solid dosing units, while Feeder 5 allows for liquid dosing. Feeder 1 to 4 have an additional mixing barrel that enables premixing of the feedstock before its entry into the extruder barrel. The liquid dosing unit is directly connected to the extruder barrel. The feeders are positioned on precision scales, ensuring accurate gravimetric dosing of respective educts. The extruder barrel is engineered as split barrel with a screw diameter of 12 mm and a barrel length of 360 mm, resulting in a length-to-diameter ratio of L/D 30:1. The barrel is subdivided into six zones, each of which can be heated or cooled independently of the others.

In order to process the extremely mechanically hard oxide particles of the hybrid materials without causing damage, the mixing screws/barrels and the extruder screws/barrel are made of WC-Ni cemented carbide. In addition, the screw elements were also coated with titanium nitride, further improving abrasion resistance, reducing friction and hence screw wear. A slit nozzle with dimensions of 50 mm in width and 0.2 mm in height is mounted at the terminal point of the extruder barrel. It is made from 1.4404 stainless steel, which has been Hard-Inox-S hardened to 67 HRC. Subsequent to the extruder, a film roller is placed, which utilizes a heated calender to allow for rather uniform distribution of the hybrid membranes within the desired layer thickness. Al_2O_3 -PCL and conductive salt LiTFSI were introduced to the mixing barrel through two feeders and premixed. The materials were fed in a ratio of $[\text{C} = \text{O}]:[\text{Li}]$ of 5:1. Benzophenone was fed with a third feeder into the mixing barrel to function as a cross-linking agent. To verify the feed rates of the individual feedstocks, thermogravimetric analyses (TGA) were done on the extruded membranes (Figure S 4). The obtained results were consistent with the extruder's feed rates and demonstrated precise dosing, even when invoking multiple components. The educts were subsequently melted and homogenized within the extruder. In addition to the pure conveyor elements, kneading elements were also

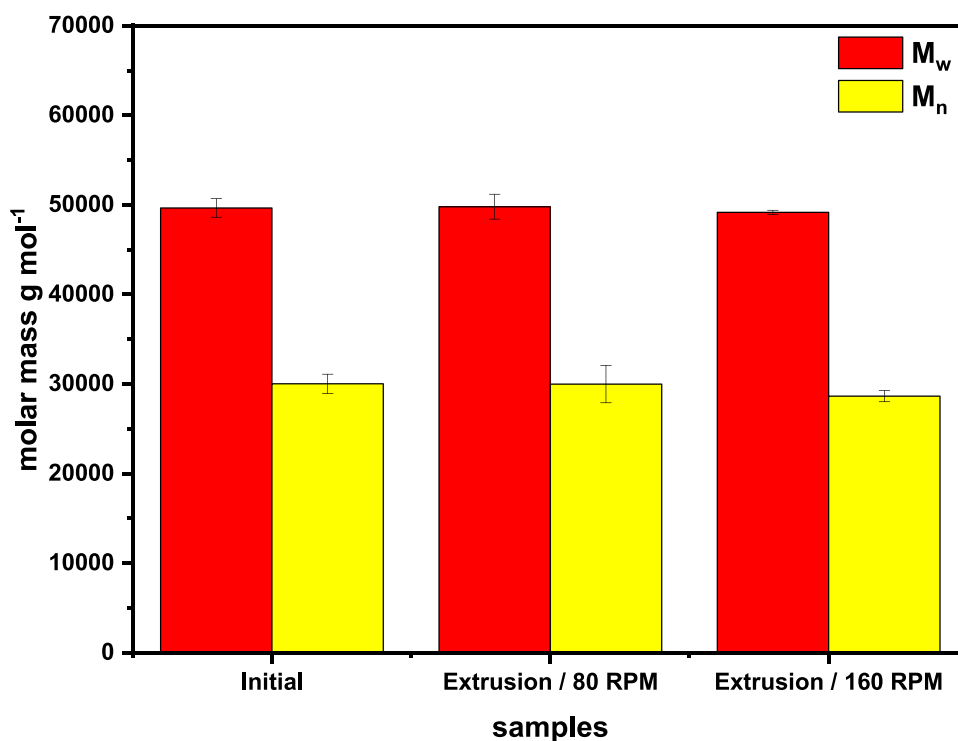


Fig. 5. Molar mass (g mol^{-1}) of Bt-PCL at the initial point and after processing at 80 RPM and 160 RPM, respectively. The results were achieved by processing with screw geometry (b).

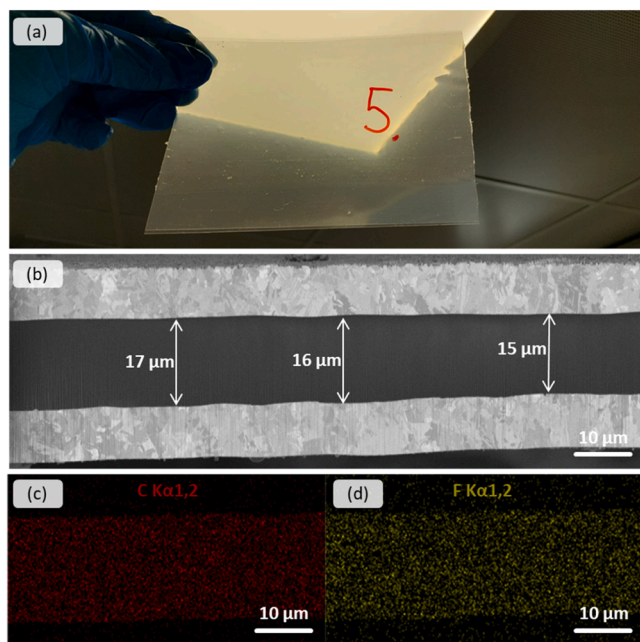


Fig. 6. a) Photo of the Bt-PCL membrane positioned between two release films; b) cryo-FIB-SEM cross section of Bt-PCL membrane (ETD Detector, SE mode); c) Carbon EDS mapping of Bt-PCL cross section; d) Fluorine EDS mapping of Bt-PCL cross section.

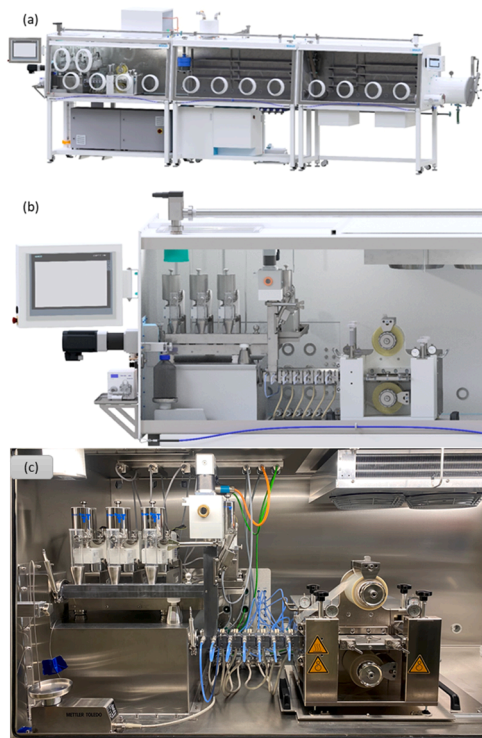


Fig. 7. a) Complete glove box of the Pilot-Scale 12 mm Extrusion Line, the right box is used for preparation and storage, while the left two boxes are used for processing. b) Detailed view of the extruder system in the left box without the front panel, and c) a photo showing a close-up of the extruder system in the left glovebox without the front panel.

installed in the screws to ensure more homogeneous mixing (Fig. 8). Subsequent to extrusion from the slit nozzle, partially molten Al_2O_3 -PCL hybrid material was fed between release films into the calender.



Fig. 8. Illustration of the extruder screw of the 12 mm extruders, showing two kneading zones.

In this instance, the hybrid electrolyte was meticulously calendered to a thickness of $\sim 35 \mu\text{m}$ and a width of over 70 mm. The membrane was cross-linked batch wise using ultra violet light after the calendering step. In the future, this process could also be carried out directly as a continuous process following calendering. The glove boxes were designed with the intention of accommodating a UV chamber and other equipment downstream from the current extruder system. After cross-linking, the membrane could be used as free-standing solid electrolyte membrane, see Fig. 9. The 12 mm extruder was demonstrated to facilitate the production of ca. 3.84 m^2 of solid electrolyte per hour. In comparison, standard dry processing in lab-scale for SPE, that is, hot pressing, allows for production volumes of up to 0.1 m^2 per hour with the same electrolyte. The high degree of automation in the production of solid electrolytes by extrusion enables larger quantities of membranes to be produced in defined quality. This reduces chances of operator impact, minimizing associated fluctuations in the quality of the prepared materials, a prerequisite for assembly of larger cells.

The mechanical stress experienced by a hybrid polymer mixture, such as Al_2O_3 -PCL, during the extrusion process is considerably larger than that of a pure polymer melt. In hybrid polymer blends, additional effects may occur, such as inhomogeneous stress due to locally increased shear forces at particle surfaces and limited mobility of polymer chains caused by interactions among polymer chains and particle surfaces. These and other phenomena may induce undesired degradation of the polymer chains and even full destruction of the polymer [37]. To verify this, the molar masses of the polymer Al_2O_3 -PCL were measured using SEC before and after extrusion, the measured molar masses are summarized in Fig. 10.

Even under conditions of rather extreme stress on the polymer in case of hybrid electrolyte Al_2O_3 -PCL during the extrusion process, no polymer degradation is evident. The molar mass M_w was determined as 61000 g mol^{-1} prior to the processing and as 60900 g mol^{-1} following extrusion at an RPM of 80, exhibiting almost identical results. In this instance, as with Bt-PCL, the material provides a distinct advantage due to its considerably lower melting temperature compared to PEO. This likely results in the presence of favorable rheological properties within PCL polymer, as characterized by its low viscosity in the molten state. Compared to batch wise hot-pressed materials, extrusion processing has no effects on the T_g or T_m of the materials. To confirm this, differential scanning calorimetry measurements (DSC) were performed on the extruded materials (see Figure S 5). Higher RPM values were not applied due to the elevated stress levels induced by the nanoparticles and the augmented external velocity of the extruder screws. Comparable reported extrusion processing and analysis based on PEO, particularly those involving PEO in combination with oxide particles, yielded substantial degradation of the polymer, with a maximum reduction in chain length of up to 30 % [22,24,38]. These findings unambiguously illustrate the advantages of PCL-based polymers compared to PEO-based

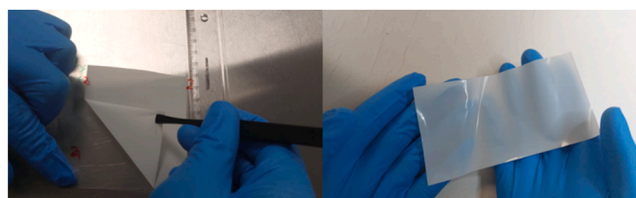


Fig. 9. Extruded free standing Al_2O_3 -PCL membrane with a thickness of $35 \mu\text{m}$.

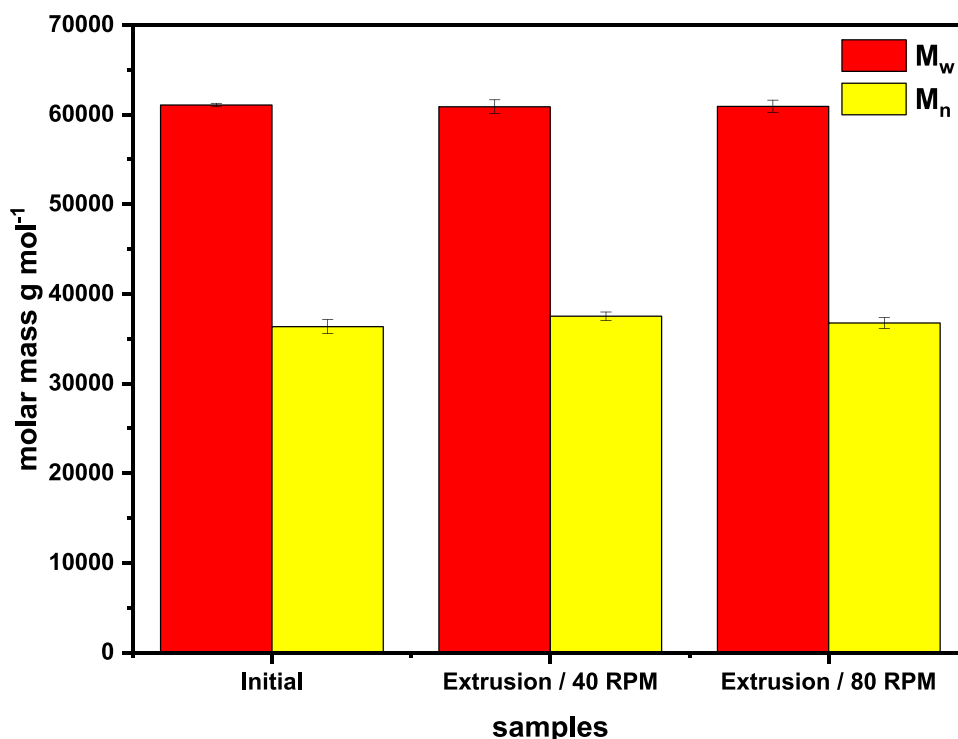


Fig. 10. Molar mass (g mol^{-1}) of $\text{Al}_2\text{O}_3\text{-PCL}$ at the initial point and after processing at 40 RPM and 80 RPM, respectively.

polymers and their options and potential offered for the extrusion thereof. Fig. 11 (a) presents a photograph of a manufactured $\text{Al}_2\text{O}_3\text{-PCL}$ membrane. Cryo-FIB-SEM analysis was performed to analyze the homogeneity of the hybrid polymer electrolyte. Fig. 11 (b) presents a cross section with uniform membrane thickness of 36 μm . $\text{Al}_2\text{O}_3\text{-PCL}$ hybrid polymer consists of grafted Al_2O_3 particles and PCL polymer and the resulting membranes contain LiTFSI as conductive salt. Al_2O_3 particles are distributed homogeneously throughout the cross section, as evident from a close-up of the left side (Fig. 11 c), demonstrating uniform distribution of the particles at various sizes. Energy-dispersive spectroscopy (EDS) mapping was additionally done (Fig. 11 d-f). Here, the aluminum (Al) signal was used as indicator for Al_2O_3 particles, carbon (C) for the polymer, and fluorine (F) for the incorporated Li salt. When comparing the Al (Fig. 11 d) and C (Fig. 11 e) mappings, there is no carbon signal detected inside the particle agglomerates, indicating that the particles were already agglomerated prior to synthesis. Similar to Bt-PCL membranes, a carbon and fluorine element mapping revealed uniform element distributions without any element hotspots (Fig. 11 e,f). To further verify uniform element distribution, line scans were executed (Figure S 3). Again, mappings of C and F show similar intensity trends during line scanning, while the Al signal is inversely proportional. In conclusion, all the extruded $\text{Al}_2\text{O}_3\text{-PCL}$ membranes clearly have high homogeneity in both particle and salt distributions.

In addition to $\text{Al}_2\text{O}_3\text{-PCL}$ membranes obtained from extrusion (see Fig. 11), an $\text{Al}_2\text{O}_3\text{-PCL}$ membrane produced in a batch process using a hot press was examined by SEM (Figure S 6). Here, similar agglomerates can be seen to be present within the membrane, suggesting that agglomeration of the particles occurred before or during synthesis and was not necessarily caused by processing, in agreement with the EDS mapping of carbon. It is conceivable that the agglomerates may be partially broken down by enlarging the kneading or mixing zones through additional kneading and mixing elements within the extruder screws. A potentially more promising alternative would be the incorporation of ultrasound during synthesis or exploitation of alternative mixing elements within the reactor. However, as this work does not address the optimization of material synthesis, but rather validates the

feasibility of extrusion processing of star-shaped PCL-based polymer and hybrid materials upon manufacture of battery components, this aspect falls outside the scope of this work and will not be further discussed.

Electrochemical characterization

To establish fundamental electrochemical properties of the extruded electrolyte membrane, $\text{Li}|\text{Al}_2\text{O}_3\text{-PCL}|\text{Li}$ cells were assembled. Electrochemical impedance spectroscopy (EIS) was performed to evaluate the overall ionic conductivity of the electrolyte membrane, the corresponding ionic conductivities are collected in the Arrhenius plot in Fig. 12 (a) and range from 0.00156 mS cm^{-1} to 0.088 mS cm^{-1} . All the measurements were conducted within the temperature range of 20 to 80°C. The $\text{Al}_2\text{O}_3\text{-PCL}$ membranes demonstrated slightly lower ionic conductivity compared to membranes produced by a batch process (hot pressing), which is most likely attributable to the alignment of the polymer chains and the subsequent alteration in polymer morphology. The polymer chains undergo elevated levels of mechanical stress upon extrusion, subsequently followed by calendaring, phenomena that were previously observed in other polymer-based systems manufactured by extrusion [22,39]. Subsequent investigations are planned to explore potential benefits of additional tempering steps for the membranes after calendaring or the use of elevated temperatures during the extrusion on the outcomes.

In order to assess the compatibility of the $\text{Al}_2\text{O}_3\text{-PCL}$ electrolyte with the lithium anode, the interphase resistances between the electrolyte and lithium metal were determined. For this, the $\text{Li}|\text{Al}_2\text{O}_3\text{-PCL}|\text{Li}$ cells were initially examined using EIS. Subsequently, the cells underwent cycling steps in which they were stripped and plated for 10 cycles at a current density of 0.1 mA cm^{-2} for one hour per half cycle. Following completion of the cycling process, interphase resistances of the cells were once again determined via EIS analysis. The measurement results are presented in the Fig. 12 (b). It appears that during the first 20 cycles, the interphase resistance remains relatively constant, but rise slightly thereafter, with a rise from 92 $\Omega \text{ cm}^2$ for "Initial" to around 109 $\Omega \text{ cm}^2$ "after 40 cycles". This slight increase is most likely due to the formation of the SEI, which is not ideally stable. In addition, a slight decrease in bulk resistance is evident after the first 10 cycles, suggesting that the

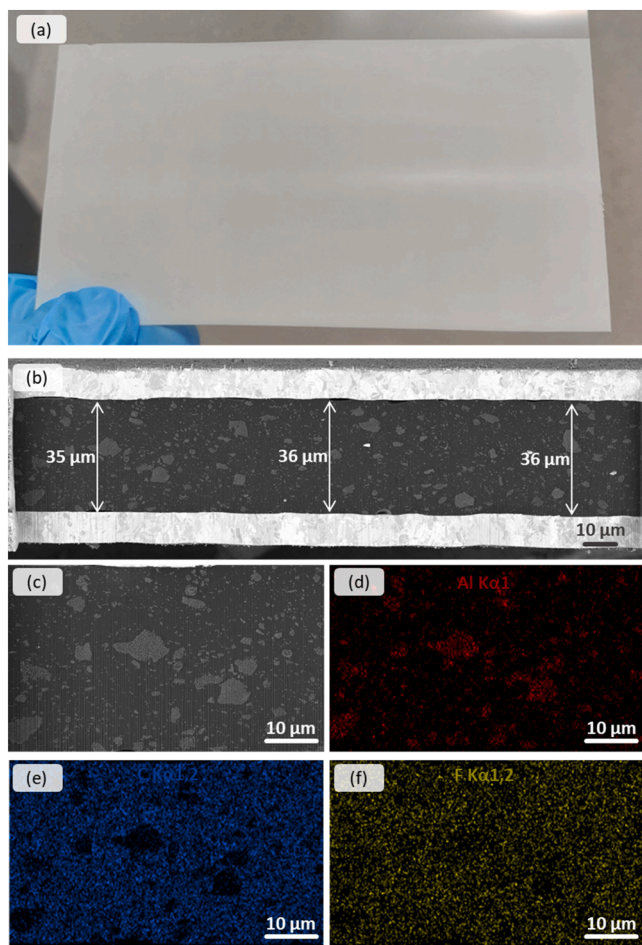


Fig. 11. a) Photo of the Al₂O₃_PCL membrane; b) 150 μm cross section (CBS detector, BSE mode); c) magnification of the cross section; d) Al EDS mapping; e) C EDS mapping and; f) F EDS mapping of the extruded Al₂O₃_PCL membrane.

contacts between the electrolyte and the electrodes may be enhanced by lithium deposition and dissolution or that the mechanical stress within the cell might lead to a minor adjustment in the layer thickness of the electrolyte. To enhance the interface between the electrolyte and lithium in the near future, the addition of additives such as lithium bis (fluorosulfonyl)imide (LiFSI) or other interface-stabilizing materials

may prove beneficial in further boosting the electrochemical performance [40–42]. To further derive the electrochemical properties of the electrolyte, linear sweep voltammetry (LSV) measurements were done. This method was employed to determine the electrolyte's electrochemical stability window (ESW). The results of this experiment are shown in Figure S 19. The ESW was determined to be ~5 V, as measured at a cutoff current density of 0.1 mA cm⁻². An ESW better than 4.5 V indicates the potential feasibility of PCL-based electrolytes to operate with higher-voltage cathodes, such as NMC [29,43,44].

In addition, a proof of concept study evaluated full cells using the extruded materials. For this purpose, NMC₆₂₂|Al₂O₃_PCL|Li and NMC₆₂₂|Bt-PCL/Al₂O₃_PCL|Li cells in coin and pouch cell formats were assembled, invoking extruded Al₂O₃_PCL as solid electrolyte and extruded Bt-PCL as catholyte interlayer. These are further subdivided into cells with medium cathode mass loadings (~0.4 mAh cm⁻²) and cells with comparatively higher cathode mass loadings (1 mAh cm⁻²) within the scope of this study. For the cells with cathodes with higher mass loading, the extruded Bt-PCL membrane was utilized as cathode interlayer infiltrated into the cathodes. Catholyte Bt-PCL was produced using the 9 mm extrusion line. In addition to the scalable production of catholytes and hybrid electrolytes, scalable solutions for preparing cathodes for infiltration were implemented. The cathodes were precisely cut to the required dimensions using a laser cutter (Fig. 13). Indeed, valuable insights were obtained benefitting subsequent application of extruded composite cathodes. The merits of laser cutting included the ability to achieve precise cuts with minimal mechanical stress of the material, resulting in rather clean edges, as confirmed by the SEM top view image (Fig. 13 e) as well as the FIB-SEM cross sections (Fig. 13 f) of the laser-cut edges [45].

Both images exhibited no signs of NMC particle cracking. The system's flexibility is also noteworthy. Geometries were modified promptly and without the need for tool adjustments, enhancing versatility and efficiency. Another advantage includes automation of the systems and associated scalability of the process. Cathodes exploited for infiltration were cleanly extracted from commercially available NMC₆₂₂ cathode sheets. The active material area was set to 12 mm in diameter for the coin cells or 25 × 20 mm for the pouch cells. The mass loading was 1 mAh cm⁻² / 6 mg cm⁻². The cathodes were precisely cut using a laser, taking less than a second per electrode. To allow for optimal contacts within the pouch cell and to attach a current collector, a 1 × 2 cm wide strip of aluminum was left as a contact surface on one side of the cathode, as illustrated in Fig. 13 (d). To assess the electrochemical performance of the produced materials, it is essential to integrate them into cells. In addition to coin cells commonly considered in research, it is equally important to demonstrate materials performance in larger

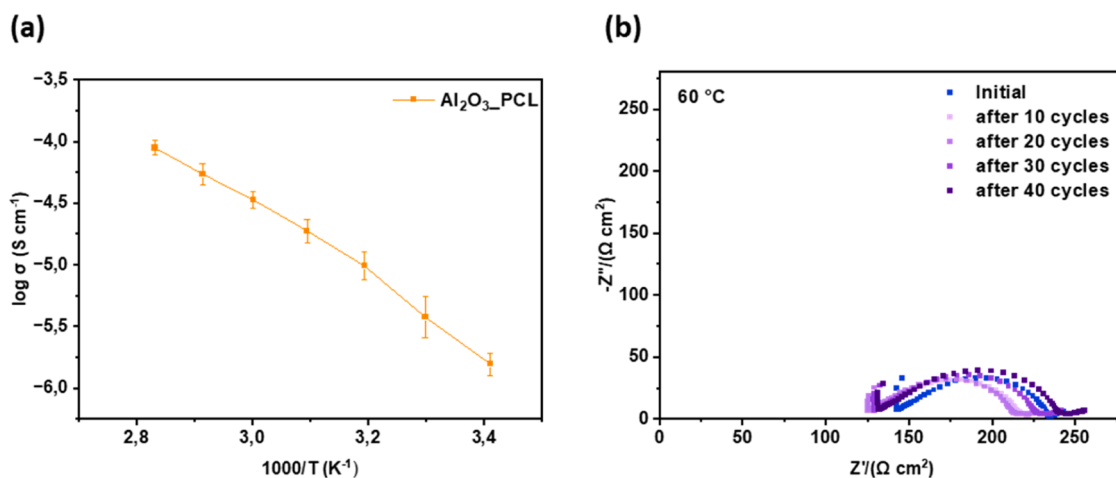


Fig. 12. a) Temperature-dependent ionic conductivity of extruded Al₂O₃_PCL electrolyte membrane. The drawn line is a guide to the eyes. b) Impedance spectra of Li||Li cells before and after stripping/plating experiments.

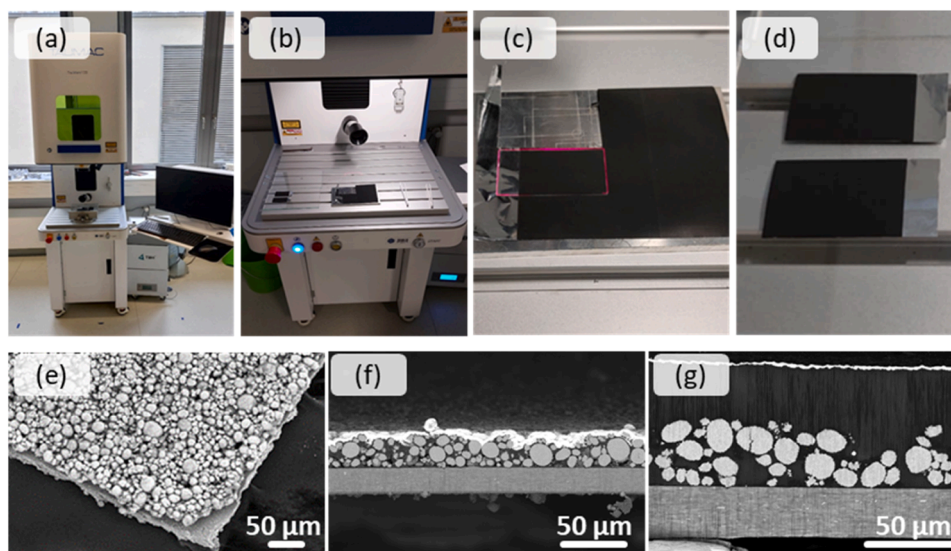


Fig. 13. a) Picture of the Taumac 100 M-TOP laser cutter used for preparing the cathode sheets; b) detailed view of the laser cutter's working area; c) commercial NMC₆₂₂ cathode sheets cut to size using the Taumac 100 M-TOP laser cutter; d) NMC₆₂₂ cathodes prepared for use in pouch cells; e) SEM images of laser cut cathode edge (ETD detector, SE mode); f) FIB-SEM cross section of the laser cut cathode edge (Pt/C layer sputtered for surface smoothing; CBS detector, BSE mode); g) FIB-SEM cross section of an infiltrated cathode (CBS detector, BSE mode).

pouch-type cells. However, the construction of larger cells necessitates the availability of substantial quantities of the respective battery components. Here, employment of extruders facilitates larger-scale production of catholyte and solid-state electrolytes, paving the way for assembly of multi-layered pouch cells. Bt-PCL membranes were infiltrated to previously cut cathodes by vacuum infiltration [46]. Furthermore, following the infiltration, the composite stack, comprising NMC cathodes and infiltrated Bt-PCL catholyte membranes, underwent post-treatment in a hot press, a step implemented to boost homogeneity of the stack. Illustrations of this process can be found in the Supporting Information (Figure S 7). FIB-SEM cross sections of a commercial and the resulting infiltrated NMC cathode are shown in Fig. 13 (f) and (g). After segmentation of NMC particles and carbon binder domains by imaging contrast (Figure S 10), a porosity of $\sim 37\%$ was determined for the commercially obtained NMC cathodes (Table S 1). Upon polymer infiltration, the Bt-PCL polymer infiltrates the cathode fully, until the current collector is reached as evident from Fig. 13 (g) as well as the EDS images of both cathodes in comparison (Figure S 9 and S 11) and the contrast segmentation of material (Figure S 12 and Table S 2). As a proof of concept, the cycling performance of NMC₆₂₂|Al₂O₃-PCL|Li and NMC₆₂₂|Bt-PCL|Al₂O₃-PCL|Li cells, in coin and pouch configuration, are displayed in Fig. 14. The charge and discharge curves of NMC₆₂₂|Al₂O₃-PCL|Li coin cells with moderate average areal loading of ~ 0.4 mAh cm⁻² / 2.4 mg cm⁻² afforded a capacity of ~ 175 mAh g⁻¹ (Fig. 14 a and 14 b). At this loading, it was possible to cycle the cathodes with the extruded solid-state electrolyte Al₂O₃-PCL without an additional catholyte. Note that the achieved discharge capacities correspond to the expected values [12].

As illustrated in Figs 14 (c) and (d), the effect of the catholyte is evaluated using cathodes with areal loadings of 1 mAh cm⁻², labeled in this study as comparatively "higher mass loading". Utilizing the Bt-PCL catholyte (NMC₆₂₂|Bt-PCL|Al₂O₃-PCL|Li) enabled better contacts with the cathode active material (see Fig. 14 (c)), as reflected by the provided capacity of 175 mAh g⁻¹. In contrast, Fig. 14 (d) shows charge and discharge curves of (NMC₆₂₂ (1 mAh cm⁻²)|Al₂O₃-PCL|Li) cells that do not incorporate additional Bt-PCL cathode interlayer. Merely a fraction of the theoretical cathode capacity could be achieved, emphasizing benefits of cathode interlayers as well as catholytes being present in case of solid-state cells. As the number of cycles was increased, the discharge capacity concomitantly rose. This observation suggests that the

Al₂O₃-PCL electrolyte may establish stronger contact with the cathode over time. However, this effect was limited to a discharge capacity of ~ 75 mAh cm⁻², which underscored the necessity for a supplementary Bt-PCL interlayer at comparatively higher mass loadings. A relatively rapid fading phenomenon was observed in all cells, a state of health (SOH) of 80% was reached for the majority of cells after 70-100 cycles, as illustrated in Figures S 20-S 22. In addition to the capacity fading, isolated drops in the charging voltage occurred during lithium deposition within the cells. The 35 μ m thin electrolyte layer may be a potential factor contributing to lithium metal dendrite-induced micro-penetration, thereby facilitating micro-short circuits within the cells. It can be assumed that the hybrid membrane Al₂O₃-PCL reaches its limits at this particular layer thickness (35 μ m) and that further mechanical reinforcement appears necessary for facilitating even thinner membranes. Fig. 14 (e) illustrates the charge and discharge curves of (NMC₆₂₂ (1 mAh cm⁻²)|Bt-PCL|Al₂O₃-PCL|Li) pouch cells, where the overall capacity of the cell amounted to 5 mAh, and its dimensions are 25 $\times$ 20 mm of active material (Figure S 8). The specific capacity of the pouch cell is approximately 100 mAh g⁻¹ after formation, which is below the theoretical specific capacity of the cathode material. The observed decline in specific capacity can be attributed to the not yet ideal configuration of the pouch cells setup and the lower cell pressure of ~ 0.1 MPa, compared to the coin cells ~ 0.2 MPa [47]. The exact assembly of the pouch cell was demonstrated to have a noteworthy impact on the achievable performance of pouch cells or other larger cell geometries that operate on the basis of solid-state electrolytes. The present study does not encompass complete optimization of cell setup for pouch cell or their assembly, rather, the objective of this work was to illustrate that the availability of well-defined reproducible, high-quality SPEs facilitates construction of application-specific cell geometries and enables a better comparison to conventional lithium-ion technologies. To further optimize the cell setup, finetuning of the assembly process steps of cells is required, particularly in view of achieving application-oriented cell capacities. Here, almost continuous, large-scale production of polymer materials (including SPE; artificial layers and interlayers) via extrusion will be beneficial, likely facilitating the integration of automated cell assembly machinery, such as stacking or Z-folding robots. This proof of concept work demonstrated that the Al₂O₃-PCL and Bt-PCL materials are suitable for processing via extrusion systems, and could be operated in NMC||Li cells, thereby successfully illustrating the capability of the

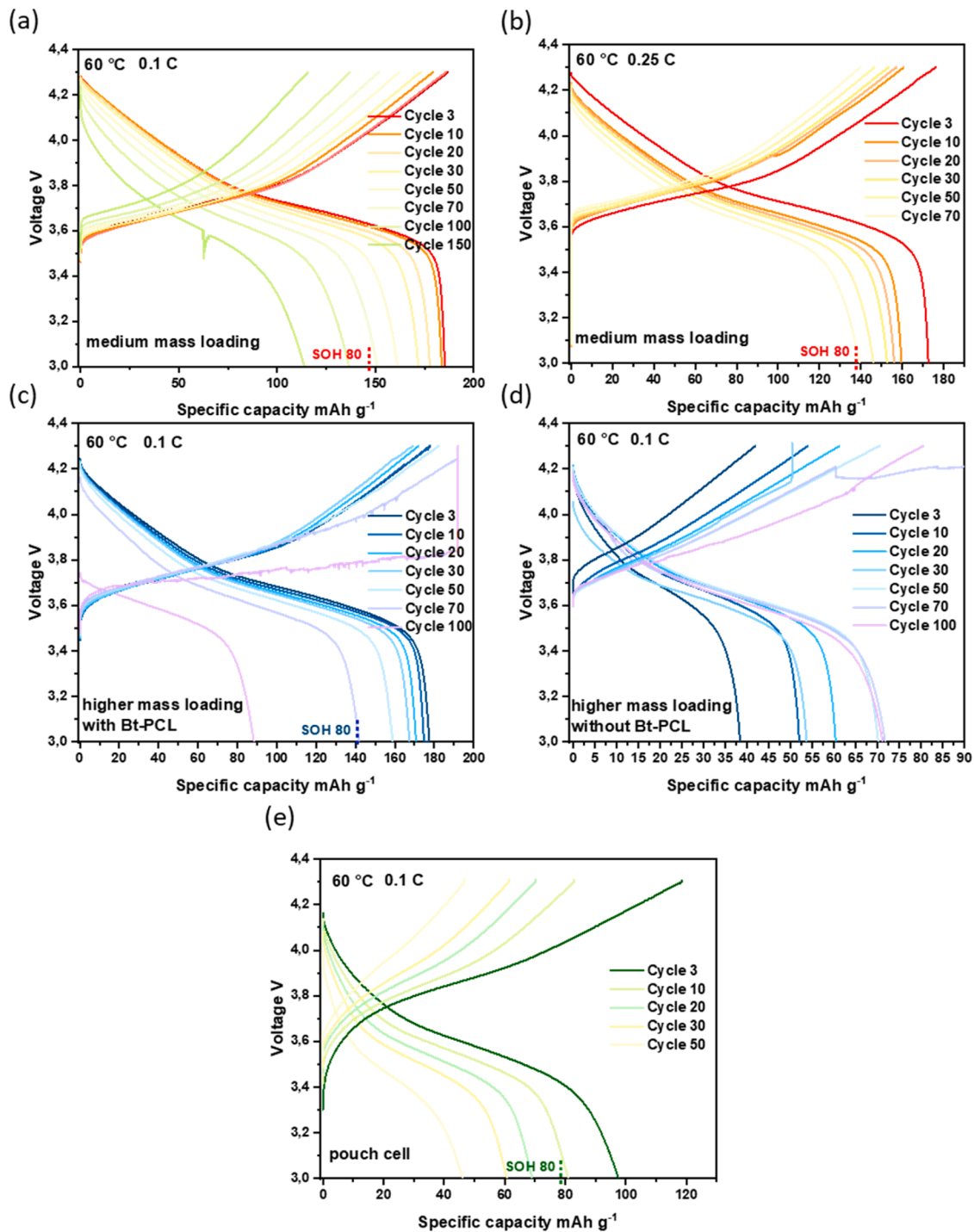


Fig. 14. (a) Charge and discharge curves using moderate cathode mass loadings of $\sim 2.4 \text{ mg cm}^{-2}$ at 60°C and 0.1 C in coin cell setup ($\text{NMC}_{622}/\text{Al}_2\text{O}_3\text{-PCL}/\text{Li}$); (b) charge and discharge curves of moderate cathode mass loadings of $\sim 2.4 \text{ mg cm}^{-2}$ at 60°C and 0.25 C in coin cell setup ($\text{NMC}_{622}/\text{Al}_2\text{O}_3\text{-PCL}/\text{Li}$); (c) charge and discharge curves of higher cathode mass loadings of $\sim 6.0 \text{ mg cm}^{-2}$ loadings at 60°C and 0.1 C in coin cell setup ($\text{NMC}_{622}/\text{Bt-PCL}/\text{Al}_2\text{O}_3\text{-PCL}/\text{Li}$); (d) charge and discharge curves of higher cathode mass loadings of $\sim 6.0 \text{ mg cm}^{-2}$ at 60°C and 0.1 C in coin cell setup ($\text{NMC}_{622}/\text{Al}_2\text{O}_3\text{-PCL}/\text{Li}$) and (e) charge and discharge curves of higher cathode mass loadings $\sim 6.0 \text{ mg cm}^{-2}$ at 60°C and 0.1 C in pouch cell setup ($\text{NMC}_{622}/\text{Bt-PCL}/\text{Al}_2\text{O}_3\text{-PCL}/\text{Li}$).

implemented pilot lines for processing of both soft polymers and mechanically abrasive hybrid polymer-based electrolytes. Optimization of grafted hybrid polymer materials will continue, taking frictional stresses or any other materials impacts upon extrusion processing into account, in this way not only boosting their cell performance but also advancing scalability and processability of hybrid polymer electrolytes suitable for lithium metal batteries.

3. Conclusion

In the context of solid-state batteries, it is imperative that research and development efforts consider critical practical factors such as scalability and processing during early stages of materials development. By addressing these factors, researchers may optimize the development of these materials, thereby achieving a substantial enhancement in their applicability. In this context, extrusion was demonstrated as an effective

method for the processing and manufacturing of polymer-based solid-state electrolytes. In the present study, the viability of dry processing of solid polymer-based battery materials, including electrolytes and artificial CEIs for polyester based polymers, was assessed. To this end, two pilot lines consisting of feeders, extruders, and calenders were presented and evaluated invoking promising polymers as well as hybrid polymer mixtures. As demonstrated, highly compact, yet also highly complex pilot extrusion lines for polymer based solid-state electrolytes can be integrated into gloveboxes. Their compact design necessitates only minor quantities of feedstock for processing, rendering them especially well-suited for exploitation with novel and relatively costly materials in R&D contexts. The integration in gloveboxes renders them a potential alternative to conventional extruders operated in a dry room, thereby enabling application-oriented research and give the advantages of affording processing of sensitive materials, which require handling under an inert gas atmosphere. Compared to available extrusion systems described in the literature, the pilot systems presented here are more technologically advanced and better suited to practical applications, as illustrated based on data collected in Table S 3. Despite their compact nature and integration within a glovebox, feedstocks can be metered gravimetrically and automatically. In addition, utilization of very soft and sticky materials and the processing of highly abrasive hybrid materials is also feasible, thereby reflecting a wide range of potential application scenarios. The integration of film rollers within the manufacturing process enables a direct conversion of extruded materials into thin membranes. In addition, extrusion was shown as suitable method for the production of potential artificial CEIs or SEIs, or as functional thin interlayers in solid-state batteries. Also, scalability was demonstrated using Bt-PCL, a candidate material as a relatively soft polymer. Here, a 15 m long demonstrator membrane with a thickness of 16 μm was successfully produced and exploited as interlayer on NMC₆₂₂ cathodes. In addition, hard and abrasive Al₂O₃-PCL hybrid polymer was successfully processed by extrusion, obtaining free-standing 35 μm thin solid electrolyte membranes. Extrusion processing yielded high-quality, reproducible membranes even with materials that pose challenges for the equipment. As proof of concept, the extruded materials were shown to be successfully incorporable into solid-state coin and pouch cells. The insights acquired during the processing and production of the dry polymer electrolytes and application-oriented cells could be integrated into the material development process, which is considered as crucial for further advancement and optimization of solid polymer electrolytes, with the objective of expediting the practical application of these promising materials. In summary, this work demonstrated the potential of extrusion processing to further catalyze research and materials development for application-oriented cell configurations, including multi-layered (pouch) cells.

Experimental

Material

Aluminum Oxide Nanoparticles (99.999%, MSE Supplies), Tin(II) 2-ethylhexanoate (96%, Thermo Scientific Chemicals), ϵ -Caprolactone (99%, Thermo Scientific Chemicals), Methanol (99.6%, Honeywell), Toluene (99.8%, Sigma Aldrich), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) (Sigma Aldrich), 1,3,5-Trihydroxybenzol (TCI, 99.0%), Lithium metal (20 μm , Honjo Chemical Corporation), LiNi_{0.6}-Co_{0.2}Mn_{0.2}O₂ (NMC₆₂₂, CustomCells), NMC₆₂₂-Powder (BASF TODA Battery Materials LLC), Carbon Black (Super C65, Imerys Graphite & Carbon), PVdF (Solef® 5130, Solvay), NMP (99.5%, Sigma Aldrich).

Synthesis

The reactor system comprises an IKA EasySyn 2000 reactor with an IKA Eurostar 100 control stirrer using a paddle mixer. The system is equipped with a reflux condenser and connected to a Schlenk line using dried nitrogen gas. All the work at the reactor was carried out under nitrogen counterflow. The reactor was pre-dried under vacuum and nitrogen flushed.

Synthesis of Bt-PCL

250 g of ϵ -caprolactone and 16.15 g of trihydroxybenzene were

placed in a round bottom flask and stirred under nitrogen counterflow, until all solids are dissolved. This mixture was then added to the reactor. Additional 250 g of ϵ -caprolactone and 200 ml (173.4 g) of toluene (dried) were added and stirring was started. The mixture was then heated to 110°C. 1 h after reaching the target temperature, 1.4 ml (1.8 g) of tin(II)ethylhexanoate was added. The mixture was left to stir for 22 h while the viscosity increased. Then, the mixture was cooled to 60°C and 1 L of toluene was supplied, and the mixture was stirred for 2 h. Upon completion of the reaction, Bt-PCL was precipitated in methanol batch wise, adding 500 ml of reaction mixture to a volume of 3.5 L methanol. The polymer, which precipitates as small pieces of size below 2 mm was then vacuum filtered and dried in a vacuum oven at 40°C and 4 hPa.

Synthesis of Al₂O₃-PCL

500 g of ϵ -caprolactone was added to the reactor at room temperature. Under strong stirring and using a long funnel, 150 g of aluminum oxide nano-particles (dried under vacuum at 110°C for 72 h) were added. The mixture was stirred for 5 minutes, then a vacuum was applied for 1 minute to remove gas out of the particles and break up agglomerates. The mixture was heated to 110°C, after reaching that temperature, it further stirred for one hour. 20 ml of tin(II)ethylhexanoate were added to the mixture. The mixture underwent 20 hours of stirring at this temperature, following which 750 ml of toluene were added dropwise to the still-hot mixture. After doing so, the mixture was cooled to 60°C and a further volume of 750 ml toluene was added in the same manner, increasing the stirring as the viscosity decreases. The mixture was left with strong stirring for three hours. Afterwards, using two dropping funnels and a 5 L beaker, 500 ml of reactor content were added to 3.5 L of strongly stirred methanol. The polymer, which has formed irregular, fluffy pieces about 5 mm in size, was vacuum filtered and dried in a vacuum oven at 40°C and 4 hPa. Before the polymer could be used, further drying was required.

Processing by Extruder and Calender

The processing of the materials and production of the Bt-PCL and Al₂O₃-PCL membranes were carried out in a dry glovebox that was filled with nitrogen.

Bt-PCL catholyte membrane preparation: The Bt-PCL was placed in the solid feeder 1 of the 9 mm extruder, while the conductive salt, LiTFSI, was placed in solid feeder 2. The extruder barrel underwent the following tempering process: Zone 1: 55°C, Zone 2: 100°C, Zone 3: 100°C, Zone 4: 85°C, Zone 5: 80°C, with Zone 5 representing the final zone prior to the barrel nozzle. Zone 0 was cooled using an IKA RC 2 basic circulating cooler, with a liquid coolant (silicon-based oil), and the cooling medium temperature set to -15°C. The extruder was operated at a speed of 80 rpm. It was established that feeder 1 supplied Bt-PCL with a mass flow of 120 g h⁻¹, while feeder 2 supplied LiTFSI at a mass flow of 60 g h⁻¹, respectively. The film was processed at a speed of 600 mm per minute and subjected to a calender temperature of 120°C. The melt was extruded through a slit die with dimensions (H: 0.2 mm, W: 40 mm). The extrudate was compressed between the two release films of the film roller, resulting in a membrane thickness of 30 μm and width of 70 mm. Subsequently, the membrane underwent a process of rolling up or cutting into strips with approximate length of 80 cm. The strips were stored and subsequently processed for further investigations.

Al₂O₃-PCL electrolyte membrane preparation: The Al₂O₃-PCL hybrid polymer was loaded into solid feeder 2 of a 12 mm extruder line. The extruder barrel underwent a process of tempering, which is outlined as follows: Zone 1: 80°C, Zone 2: 100°C, Zone 3: 140°C, Zone 4: 140°C, Zone 5: 120°C, Zone 6: 120°C. Zone 6 is located at the terminal point of the barrel. Zone 0 was cooled using an IKA RC 2 basic circulation cooler, with a liquid coolant (silicon-based oil) and a cooling medium temperature of -15°C. The velocity of the two mixing screws was expressed as follows: a horizontal screw operated at a speed of 32 rpm, while the vertical screws functioned at a rate of 36 rpm. The extruder's operational speed was 40 rpm. Feeder 2 supplied Al₂O₃-PCL to a mixing barrel at a rate of 108 g h⁻¹, Feeder 3 supplied the benzophenone in a mixture with Al₂O₃ nanoparticle at a rate of 1.45 g h⁻¹:9.63 g h⁻¹, while Feeder 4

supplied LiTFSI at flow rate of 42 g h^{-1} . The melt was extruded through a slit die with dimensions (H: 0.2 mm, W: 50 mm). The extrudate was subsequently compressed between two release films in the heated calender rolls, resulting in a thickness of 35 μm and a width of 70 mm. The temperature of the calender rolls was set to 145°C , and the speed was set at 700 mm min^{-1} . Subsequently, the membrane underwent rolling or cutting into strips with an approximate length of 80 cm, that were then stored for further processing. The membrane was sectioned into 15 cm long segments, subsequently undergoing cross linking in an UVACUBE 100 from Dr. Hönle AG for a duration of 7.5 minutes on each side, employing UV radiation.

Cathode preparation

Cathodes with a higher areal capacity of 1 mAh cm^{-2} were commercially available and purchased from CustomCells. Cathodes with a moderate areal capacity of approximately 0.4 mAh cm^{-2} were fabricated in house using the following procedure: NMC₆₂₂ electrodes consisting of 90 wt.% (3.42 g) NMC₆₂₂-Powder (BASF TODA Battery Materials LLC), 7 wt.% (0.266 g) Carbon Black (Super C65, Imerys Graphite & Carbon) and 3 wt.% (0.1140 g) PVdF (Solef® 5130, Solvay) were prepared by first dissolving PVdF in 3.77 ml (3.88 g) NMP (99.5%, Sigma Aldrich) using an ARM-310 ThinkyMixer (THINKY) for 20 minutes at 2000 RPM. Subsequently, carbon black and NMC₆₂₂ were added and the mixture was homogenized using a ThinkyMixer for 20 min at 2000 RPM followed by 10 minutes at 300 RPM to remove entrapped air bubbles. The resulting slurry was cast onto a previously cleaned aluminum foil (20 μm , Evonik Industries) using a doctor blade (ZUA 2000 Universal Applicator, Zehnter GmbH) with a wet film thickness of 40–50 μm , employing an automatic film applicator (1133 N, Sheen Instruments) at a coating speed of 50 mm s^{-1} . The coated electrodes were dried in an oven (Binder GmbH) at 80°C for 2 h, followed by drying under reduced pressure ($1 \times 10^{-3} \text{ mbar}$) over night at 110°C . After drying, the electrodes were calendered to a final thickness of approximately 35–40 μm . The cathodes were prepared and cut in the laboratory under ambient air and subsequently dried for 48 hours at a temperature of 120°C and a pressure of $1 \times 10^{-3} \text{ mbar}$. The cathodes and the Bt-PCL catholyte membranes were combined and subsequently processed in a dry room with a dew point of -50°C . The cathode sheets were cut with a fiber laser (Taumark 100 W MOPA) applying a power of 50 W, a frequency of 50 kHz, and a cutting speed of 600 mm s^{-1} . The pulse length was 200 ns at a spot delay time of 0.1 ms. The single-side coated sheets were cut with the bare aluminum side facing the laser source.

Infiltration of Bt PCL catholyte membrane

To execute this procedure, it is necessary to affix the cut-out cathodes to a copper foil. Subsequently, (3 * 4.5 cm Bt-PCL, for pouch cells) and (14 mm in diameter, for coin cells) membranes that were appropriate for the given application were positioned on the cathodes. Initially, the release film is removed, and the membrane was subsequently pressed onto the cathode. The Bt-PCL membrane exhibits a size that was marginally larger than the area of the active material. The adhesive properties of the Bt-PCL enable the removal of the second release film, thereby ensuring the uniform adherence of the Bt-PCL film to the cathode. Subsequently, the cathodes on the copper foil were positioned within a vacuum chamber (see Figure S 7). The vacuum chamber was then placed on a heating plate and set under vacuum. Subsequent to the attainment of a vacuum of $<10 \text{ mbar}$, the heating plate was activated, thereby elevating the cathode stacks to a temperature of 100°C . The cathodes are subjected to these conditions for a duration of one hour. Subsequent to a cooling period, the cathodes were compressed between two mylar foils within a hot press (Polystat 200T) at 100°C and 15 bar for a duration of two minutes, constituting a post-treatment step. Subsequently, the cooled cathodes were installed in coin or pouch cells.

Cell fabrication

The cells were built in a dry room with a dew point of -50°C .

Coin full cells: Model CR2032 coin cells were utilized in this study. The cathode had a diameter of 12 mm and the SPE, with a diameter of 16 mm, was placed on top of it. The lithium anode (20 μm Li on copper),

with a diameter of 14 mm, was then placed on top of the SPE.

Pouch full cells: The cathode active area was measured at $25 \times 20 \text{ mm}$, the SPE was measured at $35 \times 30 \text{ mm}$ and the anode (20 μm Li on copper) was measured at $30 \times 25 \text{ mm}$. Furthermore, aluminum strips served as conductive elements, capable of being connected externally to the pouch cell. Subsequent to the assembly of the electrodes and the SPE, the pouch cell was sealed under vacuum.

Li||Li cells: Model CR2032 coin cells were used. 20 μm lithium on copper with a diameter of 10 mm was placed on either side of the SPE, which had a diameter of 12 mm.

Electrochemical characterization

Cycling: The NMC₆₂₂|Al₂O₃-PCL|Li and the NMC₆₂₂|Bt-PCL/Al₂O₃-PCL|Li cells were cycled at 60°C in a Memmert oven, using a Maccor (series 4000 Battery Tester). The coin cells were cycled at a cell pressure of approximately 2 bar. No additional pressure was applied to the pouch cells. All cells underwent a 0.1 C formation step for two cycles. Subsequently, the cells were cycled at 0.1 or 0.25 C for long-term cycling. All cells were cycled at a cell voltage of 3 to 4.3 V (constant current CC).

Li stripping and plating experiments were done using a VMP-3e Multichannel potentiostat (BioLogic) in a Memmert oven at 60°C . Subsequent to a 12 h rest period, the cells impedance was measured and labeled as "Initial". Afterward, the Li||Li cells were cycled at a current density of 0.1 mA cm^{-2} for 10 cycles. The duration of each half cycle was 1 h. After completing 10 cycles, the impedance of the cells was measured, this procedure was repeated four times.

EIS measurements of Li||Li cells were performed prior to and after the stripping and plating experiments. All the measurements were carried out with a Multi Autolab M204 in a temperature range of 20 to 80°C (Binder MK 053). Impedance was measured at 10°C intervals, with a temperature accuracy of $\pm 0.02 \text{ K}$. To determine the cell impedances, logarithmic frequency scans of 50 steps were performed in a frequency range of $1\text{--}10^6 \text{ Hz}$, applying an alternating voltage of 10 mV.

Linear sweep voltammetry tests were measured in a three electrode Swagelok cell setup. Lithium served as the counter and reference electrode. Nickel was used for the reductive scan as working electrode and Platinum was used as working electrode for the oxidative scan. Measurements were performed by an Autolab PGSTAT302 N (Metrohm). The reductive scan was done between OCV and $-0.4 \text{ V vs. Li|Li}^+$ or until lithium plating, the oxidative scan was done between OCV and 7 V vs. Li|Li⁺ or up to a potential where the current reached the threshold of 10^{-5} A .

Further characterization

Size exclusion chromatography (SEC) measurements were performed using a 1260 Infinity GPC/SEC System (Agilent). The separation was achieved with one SDV 10 μm pre-column (8 mm * 5 mm) and three SDV 10 μm columns (8 mm * 300 mm) at a temperature of 35°C , employing tetrahydrofuran (THF) as the eluent at a flow rate of 1 ml min^{-1} . Detection was carried out using a refractive index detector, and the system was calibrated with an Agilent ReadyCal Kit for poly(styrene) standards (high molecular weight range).

Differential scanning calorimetry (DSC) measurements were carried out using a DSC 2500 heat flux calorimeter (TA Instruments) equipped with a liquid nitrogen cooling system (LN2P) and Tzero technology. Approximately 10 mg of sample was placed in an aluminum pan and hermetically sealed. Measurements were performed in two heating cycles from -150°C to 150°C at a heating rate of 10 K min^{-1} under nitrogen atmosphere (50 ml min^{-1}). The peak maxima were used to determine the melting point, while the inflection points of the curves used to determine the glass transition temperature (T_g).

Thermogravimetric analyses (TGA) were conducted on a Discovery TGA 5500 device (TA Instruments). The sample was heated to 900°C with a temperature ramp rate of 10 K min^{-1} (Helium flow rate: 25 ml min^{-1}).

Laser plasma focused ion beam scanning electron microscope (PFIB-SEM) used for data collection was done with a Thermo Fisher Scientific Helios 5 device. Area preparation was executed by a

femtosecond laser (515 nm second harmonic wavelength, pulse duration < 300 fs). For cathode cross sections, a Pt/C layer was *in-situ* sputtered on-top of the sample surfaces using the PFIB (12 kV, 20 nA). The layer was required to protect the polymer surface against the PFIB beam as well as evening out the cathode surfaces to avoid any PFIB artifacts. Samples containing polymers were cooled to -50°C before PFIB polishing (30 kV Xe⁺ ions at current of 15 nA) and imaging was performed. Here, an ETD detector (2 kV, 0.4 nA) in SE mode and a CBS detector (3 kV, 1.6 nA) in BSE mode were applied. For elemental mapping, an Oxford instruments EDS detector (5 – 10 kV, 1.6 nA) was invoked. To analyze cathode porosity, all the images were processed by Thermo Fisher Scientific Avizo 3D (software version 2024.2).

CRediT authorship contribution statement

Felix Scharf: Writing – original draft, Investigation, Conceptualization. **Phil Brockmeyer:** Investigation. **Nadine Tänzer:** Writing – original draft, Investigation. **Peter Lennartz:** Investigation. **Martin Winter:** Writing – review & editing. **Gunther Brunklaus:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

All authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ensm.2026.105363](https://doi.org/10.1016/j.ensm.2026.105363).

Data availability

Data will be made available on request.

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