An acrylate-based quasi-solid polymer electrolyte incorporating a novel dinitrile poly(ethylene glycol) plasticizer for lithium-ion batteries

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ABSTRACT

The performance of solid polymer electrolytes is characterized by lower ionic conductivity than conventional liquid electrolytes but provides advantages in terms of operational safety. A quasi-solid polymer electrolyte (QSPE) based on a new plasticizer 4,7,10,13-tetraoxahexadecane-1,16-dinitrile (bCN-PEG4) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) incorporated into a polyacrylates matrix was successfully prepared via UV-induced copolymerization. The matrix consists of units of trimethylolpropane ethoxylate triacrylate (ETPTA), poly(ethylene glycol) diacrylate (PEGDA), and the monoacrylate poly(ethylene glycol) methyl ether acrylate (mPEGa). The QSPE containing 55 wt% bCN-PEG4 exhibits highly uniform morphology, thermal stability > 200 °C, ionic conductivity of $1.8 \times 10^{-4}$ S cm$^{-1}$ at 30 °C, and $1.3 \times 10^{-3}$ S cm$^{-1}$ at 80 °C, coupled with very high electrochemical stability (> 5 V vs. Li/Li$^+$) and a low glass transition temperature (−55.7 °C). A cycling experiment in a Li/QPSE/Li cell setup demonstrated the compatibility toward lithium metal additionally. The bCN-PEG4 offers an overall satisfying performance as a plasticizer in a poly(ethylene oxide)-based solid polymer electrolyte. The new QSPE is an alternative to dinitrile-based (e.g., succinonitrile) or glycol ether-based (e.g., tetruglyme) plasticizers with application potential in high-voltage lithium-ion batteries.
Introduction

The lithium-ion battery (LIB) is an essential part of consumer electronics and devices nowadays while expanding in the fields of transportation (e.g., cars, buses, autobicycles) as well as grid energy and industry (e.g., renewable energy, portable, and stationary energy storage) [1]. Particularly, the progress of the LIB in the automotive sector is at a fast pace due to its advantageous properties over other battery technologies such as higher energy/power densities, lower costs, flexibility, and more practical cell designs [2]. Nevertheless, the cell chemistry of commercial LIBs based on liquid electrolytes has its drawbacks related to the flammable and volatile nature of the utilized non-aqueous organic solvents. Main issues emerge from safety deficiency, degradation process, and dendrite growth [3]. An important alternative to liquid electrolytes is polymer electrolytes, which can be categorized into two main groups: gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs). In general, polymer electrolytes exhibit advantages regarding safety, flexibility, density, and suppression of lithium dendrites [4, 5]. Among the most popular electrolytes for LIBs are poly(ethylene oxide) (PEO)-based solid polymer electrolytes. Their oligoether backbone (–CH$_2$–CH$_2$–O–)$_n$ is capable of dissolving lithium salts (Li$^+$X$^-$) and conducting lithium ions by transport mechanisms through flexible ethylene oxide (EO) segments [4]. Due to the exclusive ionic mobility within the amorphous phase of the PEO matrix, room temperature (RT) ionic conductivities of such binary polymer–salt complexes (semicrystalline phase) are too low for practical LIB applications and require improvement by modification. On this basis, plasticizers, inorganic fillers, or other additives can be added to the polymer matrix to enhance the amorphous state at lower temperatures [6]. Furthermore, the preparation of polymer blends or copolymers by cross-linking is another beneficial method to reduce the glass transition temperature of the matrix and improve important features such as electrochemical stability and protection against lithium dendrite growth [7–9]. The ionic conductivity of several modified SPEs at RT reached the conductivities as high as 10$^{-3}$ S cm$^{-1}$, which increased to the level of commercial organic liquid electrolytes for LIBs (about 2 × 10$^{-2}$ S cm$^{-1}$ at RT) [10] under high-temperature conditions up to 100 °C [11]. Polymer electrolytes can withstand high operating temperatures, while liquid electrolytes have relatively high flammabilities with
flashpoints around RT [12] and therefore are not suitable for such conditions.

The idea of incorporating a liquid plasticizer into a mechanically solid polymer was first introduced in 1975 by Feuillade and Perche [13]: A ternary gel was prepared by cross-linking polyvinylidene fluoride with fluoride hexafluoropropylene and subsequent impregnation of the membrane with propylene carbonate and saturated NH₄ClO₄. The ionic conductivity of GPEs can reach $10^{-3}$ S cm⁻¹ at RT, which is very close to liquid electrolytes [14, 15]. This is related to the pathway for charge transportation: In contrast to SPEs, lithium ions migrate through the liquid-like phase of the gelled polymer. The quasi-solid state of GPEs combine the ionic conductivity of liquid electrolytes with the mechanical strength of SPEs, while maintaining a freestanding membrane form [16].

Ideally, quasi-solid polymer electrolytes (QSPEs) contain plasticizers that contribute to the dissolution and solvation of lithium ions and the transport of Li⁺ ions by creating a high mobility phase. Suitable are low molecular weight organic solvents with high polarity, low volatility, and adequate miscibility with polymers. Thus, dinitrile-based plasticizers, succinonitrile (SN) being the most important one, match these requirements as additives for PEO-based polymer host materials [17–19]. The polar and electron-withdrawing nitrile group (–C≡N) ensures high oxidation resistance, strong coordination ability, and high dielectric constants [20, 21].

In 2004, Armand et al. [22] found that the high mobility of Li⁺ within the plastic phase of SN (5 mol% lithium bis(trifluoromethanesulfonyl)limide (LiTFSI) in SN) resulted in ionic conductivity of $1.47 \times 10^{-3}$ S cm⁻¹ at RT. In addition, the composition showed electrochemical stability up to 6 V vs. Li/Li⁺ (Li₄Ti₅O₁₂ as the anode). Because SN cannot form a self-standing film, it is often applied as an additive into a mechanical reinforcing network [7]. In this regard, an ultraviolet (UV)-cured polymer network based on trimethylolpropane ethoxylate triacrylate (ETPTA) and a plastic crystal electrolyte (1 M LiTFSI in SN) was developed by Ha et al. [18], which provided high ionic conductivity of more than $10^{-3}$ S cm⁻¹ at RT and robust mechanical strength (tensile strength of ~ 0.13 MPa) at high plastic crystal electrolyte concentration of 85 wt%. Yang et al. [23] prepared a polymer electrolyte by cross-linking ETPTA and poly(ethylene glycol) methyl ether (mPEGa) to form a three-dimensional network in which SN was dispersed. The ionic conductivity and the Li⁺-ion transference number of the membrane were $4.6 \times 10^{-4}$ S cm⁻¹ at 25 °C and 0.45, respectively. The cathode–electrolyte-integrated all-solid-state lithium battery (LiFePO₄//Li₄Ti₅O₁₂) delivered 155.88 mAh g⁻¹ at 0.2 C (30 °C) and showed an excellent safety performance. Feng and Kyu [11] investigated the influence of the chain length of aliphatic dinitriles (NC–(CH₂)ₙ–CN, $n = 2–4$) as plasticizers in a ternary network with poly(ethylene glycol) diacrylate (PEGDA) and LiTFSI. Glutaronitrile ($n = 3$) revealed the best performance with a higher ionic conductivity, thermal stability, and wider operation temperature for low-temperature battery applications. Wang et al. [24] proposed a composite SPE, which improved the ionic conductivity and the mechanical property of the PEO-based matrix by synergistic effects between the plasticizer (SN) and a 3D framework glass fiber. An ionic conductivity of $2.85 \times 10^{-4}$ S cm⁻¹ at RT, a high electrochemical window up to 5.5 V, and a tensile strength of over 8 MPa were achieved.

Ma et al. [25] reported a multiple nitrile group-terminated oligoether, which served as a plasticizer in a PEO-based SPE. The oligoether moiety improved the compatibility with the PEO matrix, while the polar nitrile groups enhanced the ionic conductivity due to the increased lithium salt dissociation. Xie et al. [26] synthesized a dinitrile compound with a short ethylene oxide moiety (4,7-dioxa-1,10-decanedinitrile) with a similar intention, which acted as an electrolyte solvent for LIBs. The aim was to overcome the incompatibility of aliphatic dinitriles with the graphite anode and the poor dissolving capability of certain lithium salts, e.g., lithium hexafluorophosphate (LiPF₆). The introduction of the EO units led to an increase in dielectric constant and thus to an easy dissolution of the LiPF₆ conducting salt. As far as we are aware, there are no publications of EO moiety-bearing dinitriles as plasticizers in SPEs. In general, both distinct groups of such molecules, the EO chain and the nitrile end-groups contribute to lithium salt dissociation and ion solvation in polymer electrolytes.

In this paper, we firstly report applying the synthesized compound 4,7,10,13-tetraoxahexadecane-1,16-dinitrile (bCN-PEG4) as a plasticizer incorporated into a PEO-based matrix (Fig. 1) to overcome limitations primarily in the ionic conductivities of SPEs and their related electrochemical properties. The QSPE was prepared by one-step UV-irradiated
copolymers of the acrylates ETPTA, PEGDA, and mPEGa to form a robust three-dimensional polymer network with LiTFSI salt and encapsulated bCN-PEG4 as a crucial performance enhancer. Here, bCN-PEG4 is a linear oligoether with four EO repeat units (NC–(CH2–CH2O)4–CN) and nitrile-terminated groups synthesized by cyanoethylation of ethylene glycol with acrylonitrile. The synthesis procedure was inspired by a report of Arbuzov and Pozhiltsova [27], which was furthermore tweaked to our preferences. Different polymer electrolytes were prepared by adjusting the amount of the plasticizer, while the ratios of the polymer components were kept equal. The influences on the ionic conductivity as well as thermal and electrochemical properties were investigated by electrochemical impedance spectroscopy (EIS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), linear sweep voltammetry (LSV), cyclic voltammetry (CV), chronoamperometry (lithium-ion transference number), and galvanostatic cycling (lithium plating/stripping). Scanning electron microscopy (SEM) and attenuated total reflection-infrared spectroscopy (ATR-IR) were performed to study the morphological and chemical structure. In addition, stress–strain curves were recorded to determine the mechanical properties of the polymer electrolyte.

The temperature-dependent conductivity measurements showed a severe increase in ionic conductivity with increasing plasticizer content. Additionally, the polymer membranes exhibit good thermal and electrochemical stability. Therefore, the prepared and investigated polymer electrolyte based on bCN-PEG4 plasticizer shows functioning properties for application in all-solid-state LIBs and offers a new improvement possibility of PEO-based solid polymer electrolytes.

**Experimental**

**Materials**

For the synthesis of 4,7,10,13-tetraoxahexadecane-1,16-dinitrile, triethylene glycol (99%), t-butanol (≥ 99.5%), acrylonitrile (≥ 99%), and calcium hydride (≥ 97%) were purchased from Sigma-Aldrich.
The polymer electrolytes consist of the precursors ETPTA ($M_n \approx 692 \text{ g mol}^{-1}$), PEGDA ($M_n = 700 \text{ g mol}^{-1}$), mPEGa ($M_n = 428 \text{ g mol}^{-1}$), LiTFSI ($\geq 99\%$), and 2,2-dimethoxy-2-phenyl acetophenone (DMPAP, 99%), which were purchased from Sigma-Aldrich and used as received. All materials were stored and processed in an argon-filled glove box.

**Synthesis of 4,7,10,13-tetraoxahexadecane-1,16-dinitrile (bCN-PEG4)**

Triethylene glycol (300 g, 2 mol) was added to a mixture of dissolved calcium hydride (1.68 g, 0.04 mol) in 100 mL $t$-butanol at RT under argon atmosphere, followed by dropwise addition of acrylonitrile (212.2 g, 4 mol). The drop rate was adjusted to the temperature of the reaction mixture, which should not exceed 30 $^\circ\text{C}$ by cooling with a laboratory water bath to prevent polymerization. Afterward, the crude product was filtered through silica gel to remove unreacted calcium hydride, while $t$-butanol was removed under vacuum on a rotary evaporator. The product was then dried over calcium hydride while stirred for 2 days. After filtration through silica gel, the product was obtained as a yellowish liquid.

$^1\text{H} \text{ NMR (CDCl}_3, 250 \text{ MHz)}, \delta (\text{ppm}): 3.69 (t, 4\text{H}, J = 6.4 \text{ Hz}), 3.62 (s, 12\text{H}), 2.59 (t, 4\text{H}, J = 6.3 \text{ Hz}).$

$^{13}\text{C} \text{ NMR (CDCl}_3, 63 \text{ MHz}), \delta (\text{ppm}): 117.85, 70.57, 70.49, 65.75, 18.72 (\text{Fig. 2}).$

**Preparation of polymer electrolyte membranes**

A series of polymer electrolyte membranes (named as bCN-SPEX%, where “X%” defines the weight percentage of the bCN-PEG4 plasticizer) with different plasticizer content of bCN-PEG4 (0–55 wt%) were prepared by stirring ETPTA, PEGDA, mPEGa, LiTFSI, and bCN-PEG4 in a glass vial overnight. The ratio of ETPTA/PEGDA/mPEGa was fixed at 1:1.25:3.75, respectively, with a LiTFSI content of 10 wt%. DMPAP (2 wt% of the acrylate monomer proportion) was added to the homogeneous solution and stirred until dissolved. The precursor solution was cast onto a glass plate, which was provided with poly(1,1,2,2-tetrafluoroethylene) (PTFE) thread seal tape (12 mm × 0.1 mm × 12 m, 60 g m$^{-2}$) on the sides as a spacer. Another glass plate was placed carefully to ensure no trapping of air bubbles. The glass plates with the uniformly spread electrolyte precursor in between were placed under a UV lamp (8 W, 365 nm, model MLR-58, UVP Ultra-Violet Products Ltd.), and the polymerization was carried out via UV irradiation for 5 min. The freestanding and flexible polymer electrolyte membranes were obtained with a thickness range of 135–225 $\mu\text{m}$ (Fig. 3).

**Characterization**

**Material characterization**

ATR-IR was used to characterize the chemical composition and the conversion characteristics of the samples before and after polymerization. The spectra were recorded with a Bruker Alpha spectrometer (platinum-ATR module) equipped with a diamond crystal. The morphology of the polymer electrolyte membranes was analyzed by scanning electron microscopy (SEM). The images of the sputtered (Pt/Pd, approx. 3 nm) polymer membranes were obtained with an FEI Helios NanoLab 600. TGA (TG 209 F1 Libra®, NETZSCH) of the SPE membranes was performed to determine the thermal stability through weight loss. The samples were heated in a temperature range of 28–600 $^\circ\text{C}$ at a rate of 5 $^\circ\text{C min}^{-1}$ under an argon atmosphere. DSC was conducted on a DSC 3500 Sirius (NETZSCH) at a heating/cooling rate of 5 $^\circ\text{C min}^{-1}$ for two cycles between −70 and 150 $^\circ\text{C}$. The standard tensile test was performed using stress–strain curves on a Zwick BZ2.5/TN1S. Dumbbell-shaped tensile specimens with gauge length dimensions of 25 mm (length) × 4 mm (width) × 2 mm (thickness) were prepared and analyzed at RT with an elongation speed of 5 mm min$^{-1}$. Young’s modulus was determined from the slope of the linear course of the stress–strain curve by the following equation, where $E$ is the modulus of elasticity, $\sigma$ is the tensile stress, and $\varepsilon$ is the tensile strain:

$$E = \frac{\sigma}{\varepsilon}.$$
Electrochemical characterization

Temperature-dependent ionic conductivity of the different polymer electrolyte compositions was determined by EIS on a potentiostat (Autolab PGSTAT302N, Metrohm) in combination with a temperature oven (UM100, Memmert). The samples were prepared as discs by using a hollow punch (Forum®/C210, 10 mm), and the thickness was measured by a micrometer screw gauge (Helios, 0–25 mm, 0.01 mm). Symmetric cell setup was used for the measurement, in which the sample was placed between two blocking stainless steel (SS) electrodes (SS/SPE/SS). The ionic conductivity was calculated by the following equation, where \( r \) is the ionic conductivity, \( l \) is the thickness of the sample, \( R_b \) is the measured bulk resistance, and \( A \) is the area of the sample:

\[
r = \frac{l}{R_b A}
\]

EIS was performed from 30 to 80 °C (temperature interval of 10 °C) at a frequency range of 10^6–10 Hz with an alternating current (AC) amplitude of 20 mV. The spectra were fitted using NOVA 2 software (Metrohm Autolab). The value of the cell capacitance with sample \( (C_p) \) was calculated from the EIS spectra of the polymer electrolytes using the correlation of capacitance with angular frequency \( \omega \) (\( \omega = 2\pi f \)) and the imaginary part of the impedance \( Z'' \) [28]:

\[
C_p = -\frac{1}{\omega Z''}
\]

On this basis, the dielectric constant \( \varepsilon' \) of the polymer membranes was calculated with Eq. (5) [29], where \( C_p \) is the cell capacitance with the sample, \( d \) is the thickness of the sample, \( \varepsilon_0 \) is the vacuum permittivity, and \( A \) is the area of the sample:

\[
\varepsilon' = \frac{C_p d}{\varepsilon_0 A}
\]

Cyclic voltammograms of the bCN-SPE55% polymer membrane were recorded in a two-electrode setup (SS/bCN-SPE55%/SS) at 30 °C. Six cycles were performed between – 0.8 and 0.8 V at different scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, and 500 mV s\(^{-1}\)), from which the fifth cycle is displayed as CV profile. Capacitance values were calculated from the CV curves using Eq. (6) [30].

\[
C = \int \frac{IdV}{\nu \Delta V}
\]

where \( C \) is the capacitance, \( I \) is the measured current, \( \Delta V \) is the potential window, and \( \nu \) is the potential scan rate of the measurement. The integral in the numerator is the total area of the CV curve.

The electrochemical stability window of the bCN-SPE55% electrolyte membrane was measured using LSV with SS as working electrode and lithium metal as counter/reference electrode (SS/bCN-SPE55%/Li) at a scan rate of 1 mV s\(^{-1}\) (vs. Li/Li\(^+\)) at 25 °C.

The lithium transference number \( (t_{Li^+}) \) was determined in a Li/bCN-SPE55%/Li electrode setup using the Bruce–Vincent–Evans method [31] according to the following equation:

\[
t_{Li^+} = \frac{I_{SS}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{SS} R_{SS})}
\]

The initial \( (I_0) \) and steady-state \( (I_{SS}) \) polarization currents were recorded at a direct current (DC)
polarization voltage of 20 mV (ΔV), whereas the interfacial resistances were recorded before (R₀) and after (Rₜₐₚ) the polarization using AC impedance in a frequency range of 10⁻⁶–0.1 Hz at 25 °C.

A lithium plating/stripping experiment was performed to analyze the electrochemical interfacial stability and reversibility of the bCN-SPE55% electrolyte membrane. In a symmetric electrode setup (Li/bCN-SPE55%/Li), a constant current density of 0.05 mA cm⁻² at RT was applied while changing the direction of the current every 60 min. Pause times after every charge/discharge step allowed the cell to equilibrate. A voltage response in the negative direction is related to lithium plating and voltage response in the positive direction is related to lithium stripping.

Results and discussion

Chemical structure and morphology

ATR-IR analysis was performed to verify the cross-linking reaction of the bCN-SPE55% precursor mixture before and after UV irradiation. For comparison, the synthesized bCN-PEG4 was examined in its pure form to detect the characteristic functional groups in the polymer matrix. Figure 4 shows the relevant IR spectrums. The peak at 1635 cm⁻¹, which is only visible in the curve of the precursor mixture, can be assigned to the acrylic C = C bonds of the ETPTA, PEGDA, and mPEGa monomers. This peak disappears after photopolymerization of the acrylate groups, which indicates a successful cross-linking reaction [32]. The nitrile (–C≡N) absorption band at 2251 cm⁻¹ of the plasticizer is present in the polymer membrane, confirming the incorporation of the liquid domain within the polymer matrix. The absorption band at 2874 cm⁻¹ can be assigned to the stretching vibration of the methylene group (–CH₂) within the PEO backbone, while the bands at 1459 cm⁻¹ and 1352 cm⁻¹ represents the scissoring and wagging vibration of –CH₂, respectively. The band at 1249 cm⁻¹ is characteristic of the –CH₂ twisting mode, which indicates an amorphous state [33]. Furthermore, the –C–O–C– stretching vibration of the EO chains can be observed at 1101 cm⁻¹, whereas the absorption peak at 1722 cm⁻¹ belongs to the vibration mode of the carbonyl groups (C=O) [34].

The relatively high content of the plasticizer ensures complete dissociation of lithium salt, which is clarified by SEM images of the surface and the cross section of the bCN-SPE55% polymer film. Figure 5a shows the highly homogenous and smooth surface without any salt particles, even at high magnification (see inset of Fig. 5a). No wrinkles or pores are present, emphasizing the uniform morphology without phase separation [32]. The cross section images in Fig. 5b, c show a compact and dense polymer membrane structure, which is important to prevent lithium dendrite growth as a cause of interfacial electrode/electrolyte irregularities (uneven local current density during battery cycling) [35].

The tensile measurements determined the mechanical strength of the freestanding polymer electrolyte without and with 55 wt% plasticizers. As shown in Fig. 6, a distinct effect of incorporating plasticizer on the tensile stress–strain behavior can be seen. The polymer matrix without plasticizer (bCN-SPE0%) possesses a tensile strength of 425 kPa with an elongation of 3.2%. At a plasticizer content of 55 wt%, the polymer electrolyte bCN-SPE55% shows reduced strength (105 kPa) but an increased strain at break (5.2%). A decrease in Young’s modulus from 136 to 20 kPa can also be observed by increasing the plasticizer content, which relates to the greater chain mobility and, therefore, less resistance to deformation [36]. While mechanical blocking implies a strategy for dendrite suppression, a high shear modulus is not essential for cross-linked systems [37].
introduction of high plasticizer content reduces the effective cross-linking density so that the cross-linked network of ETPTA and PEGDA amounts to only 13.1 wt%, in contrast to 33.8 wt% of bCN-SPE0%. Furthermore, the monoacrylate mPEGa reduces the cross-linking points by forming unlinked sidechains. Overall, the rigid polymer matrix becomes more deformable with the incorporation of 55 wt% bCN-PEG4, but exhibits reduced mechanical strength.

**Thermal properties**

TGA and DSC examined the thermal stability of the bCN-SPE electrolyte membranes with different plasticizer content. Figure 7 depicts the TGA thermograms of the pure bCN-PEG4 plasticizer and the polymer electrolytes, which contain increasing bCN-PEG4 proportions in 10 wt% steps up to 55 wt%. The polymer electrolyte bCN-SPE55% (55 wt% bCN-PEG4) marks the electrolyte with the highest plasticizer content, which provides enough robustness to form a flexible and freestanding membrane. As observable from the thermogram, the weight loss of the neat polymer electrolyte without additive starts largely at 341 °C (onset temperature; i.e., the intersection of two tangent lines) and indicates decomposition of the polymer matrix (cross-linked network of ETPTA, PEGDA, and mPEGa). The second weight loss step at around 400 °C is affiliated with the decomposition of the conductive salt LiTFSI. The pure compound bCN-PEG4 has a liquid state at RT so that the evaporation can be mainly observed at an onset temperature of 259 °C. When incorporated into the PEO-based polymer matrix, the plasticizer starts to evaporate first until its complete evaporation, followed by the decomposition of the polymer matrix and LiTFSI, respectively. Therefore, a higher percentage of bCN-PEG4 leads to a faster decrease in weight overall.

In conclusion, the bCN-SPE55% membrane has a relatively high thermal stability up to 263 °C (onset temperature) with a weight loss of 5% at 244 °C and 10% at 259.4 °C. This is sufficient for general applications of the polymer electrolyte in LIBs, which have a practical operating temperature between 0 and
45 °C [38]. The recent progress of solid electrolyte applications (ceramic–polymer electrolytes, polymer electrolytes, ionogels, and hydrogels) shows the possibility of bCN-SPE55% functioning as a high-temperature electrolyte in the range of 80–200 °C [39].

Figure 8a shows the second cycle DSC curves in the temperature range from −70 to −20 °C of the UV-cured polymer matrix without bCN-PEG4 and with increasing plasticizer content up to 55 wt%. The aim was to analyze the glass transition temperature ($T_g$), an important factor for polymer electrolytes. The requirement is a low $T_g$ that can suppress the crystallization of PEO and increase the ion motion for higher ionic conductivity [16]. A $T_g$ of −42.2 °C was obtained for the polymer matrix bCN-SPE0% without plasticizer. The value is already relatively low for a PEO matrix, considering such systems’ high degree of crystallinity. In this case, the relatively high content of the monoacrylate mPEGa ensures Li$^+$ mobility by flexible, non-cross-linked sidechains and leads to an increase in amorphous regions. The $T_g$ can be lowered continually by adding the dinitrile bCN-PEG4 to the polymer electrolyte to −55.7 °C at 55 wt% plasticizer content. Figure 8b shows the corresponding DSC profile of all polymer electrolyte samples with varying plasticizer content for the second heating/cooling cycle in the temperature range from −70 to 150 °C. No phase transitions from melting or crystallization processes are detectable, which leads to the conclusion that there is no presence of crystalline phases [29]. The plasticization of the polymer host by bCN-PEG4 is mainly related to its chemical structure, which positively effects salt dissociation and lithium-ion transport employing EO moieties [26].

**Electrochemical properties**

The electrochemical performance of the different polymer electrolyte compositions was examined in terms of ionic conductivity by EIS. The electrochemical stability versus lithium metal and the lithium-ion transference number experiment were also performed for the membrane bCN-SPE55%, which had the highest ionic conductivity.

Figure 9a shows the Nyquist plots of the polymer membranes with 0–55 wt% plasticizer content at 30 °C. The bulk resistance is characterized by the high-frequency semicircle of the impedance spectrum. A circle fit simulation was carried out to determine the bulk resistance and thus calculate the ionic conductivities. The experimental EIS data were fitted using the electrochemical equivalent circuit $[R_s(R_bQ_1)Q_2]$. $R_s$ is the solution resistance, $R_b$ is the bulk resistance and $Q_1$ and $Q_2$ are the constant phase elements (CPEs). The strong influence of the plasticizer bCN-PEG4 on the conductivity of the polymer matrix is visible because of the decreasing $R_b$ with higher bCN-PEG4 content. This concludes that more plasticizer within the polymer matrix favors ionic dissociation and ionic mobility accordingly [40]. The correlation with the $T_g$ is also a factor that proves the effectiveness of bCN-PEG4 to lower the $T_g$ of the host matrix, increase the polymer chain mobility, and decrease the polymer crystallinity [41].
The temperature-dependent ionic conductivity is depicted in Fig. 10 as Arrhenius plots within a temperature range from 30 to 80 °C. An ionic conductivity of $1.8 \times 10^{-4}$ S cm$^{-1}$ at 30 °C was measured for bCN-SPE55%, almost 14 times higher than the neat polymer matrix without the plasticizer (bCN-SPE0%, $\sigma = 1.3 \times 10^{-5}$ S cm$^{-1}$). At 80 °C, the ionic conductivity of the bCN-SPE55% membrane reaches the superconductor level of $1.3 \times 10^{-3}$ S cm$^{-1}$, which exceeds the Li$^+$ conductivity criteria of $10^{-4}$ S cm$^{-1}$ for SPEs at battery operating temperature [42]. For practical applications, polymer electrolytes should achieve ionic conductivities from $10^{-3}$ to $10^{-2}$ S cm$^{-1}$ to minimize ohmic drops [17]. Various effects regarding the plasticizers’ properties can positively influence ionic conductivity with increasing temperature, e.g., the viscosity, the ion–plasticizer coordination, the dielectric constant, or the polymer–plasticizer interaction [43]. In general, nitrile or cyano-based polymer electrolytes have high dielectric constants and strong coordination ability [17]. bCN-PEG4 has two crucial molecule properties that contribute to the ionic conductivity enhancement: an oligoether moiety to prevent phase segregation and crystalline regions and polar nitrile end-groups, which increase the dielectric constant by ion dissociation [25]. Typical temperature dependence for polymer electrolytes can be observed as the ionic conductivity increases with higher temperatures. The increase in the ionic conductivity follows linear behavior and highlights the low degree of crystallinity of the material since a phase transition upon heating, i.e., melting, is usually expressed by a nonlinear Arrhenius plot with a concave trend [44]. The Arrhenius equation can describe the Arrhenius plots in Fig. 10 to calculate the activation energy for lithium-ion conduction, which is accomplished by linear fitting of the data points. The activation energy decreases continually from 0.162 eV (bCN-SPE0%) to 0.142 eV (bCN-SPE55%) with the incorporation of increasing plasticizer content. Thus, the lowest value of 13.73 kJ mol$^{-1}$ is achieved for the highest conducting polymer electrolyte. This means that the lithium ions require lower energy for migration through the conducting phase [45].

The investigation on the conductivity enhancement by plasticizer content was continued by means of dielectric analysis, which explains ion conduction in...
electrolyte films. An interpretation of the polarization effect of the electrode–electrolyte interface is possible with this technique. The dielectric constant describes the capability of a material to retain an electric charge [46]. The dielectric constant versus the frequency of the polymer electrolytes at 30 °C is depicted in Fig. 11a. High dielectric constants of the polymer electrolytes at low frequency result from polarization effects near the blocking electrode where ion species accumulate [47]. With the increase in plasticizers content, the number of free charge carriers increases, related to an increase in dielectric constant and an indication of complete salt dissociation within the polymer matrix [29]. Accordingly, the highest dielectric constant was found for the highest ion-conducting material bCN-SPE55%, which contains the highest plasticizer content. All plots show the tendency to decrease its dielectric constant with increasing frequency up to a certain constant point close to zero. Such behavior is related to the reversal of the applied electric field, which occurs too fast for the rotation and reorientation of dipoles and charge carriers along the applied electric field. The consequence is a reduced diffusion of ions that decreases the dielectric constant [46]. The temperature dependence of the dielectric constant for the sample bCN-SPE55% is shown in Fig. 11b. The step-wise temperature increase benefits the dipole orientation, which leads to a continuous increase in the dielectric constant. Overall, the temperature increase facilitates the salt dissociation and re-dissociation of ion aggregates, which increases free ions or charge carrier density [48]. Summarizing, the dielectric spectra analysis shows that the polymer electrolyte with the highest plasticizer content exhibits the highest temperature-dependent dielectric constant. This confirms the ionic conductivity enhancement of the polymer electrolyte network by bCN-PEG4 incorporation, which increases the charge carrier concentration due to increased ion dissociation.

CV measurements further examined the electrochemical performance of the bCN-SPE55% polymer electrolyte in a dielectric capacitor setup concerning the dielectric analysis. The experiment was focused on the capacitive behavior, which polymer electrolytes show at high scan rates [49]. CV of the bCN-SPE55% membrane was evaluated within a wide potential range. It was found that the material exhibits capacitive behavior in the potential range from −0.8 to 0.8 V. Figure 12a depicts the CV curves of the bCN-SPE55% polymer electrolyte at different scan rates. The almost rectangular shapes of the CV profiles at low scan rates indicate that a capacitive behavior is the dominating factor of the electrode/electrolyte kinetics, which is caused by charge accumulation (double layer charging current) in the absence of an electrode reaction (Faradaic current) [50]. Dependence of the capacitance on the scan rate is noticeable: The rectangular shapes of the CV profiles become more distorted at higher scan rates, which is a factor of the resistive nature of the material and the polarization influence [51]. Figure 12b shows the calculated capacitance as a function of the scan rate. The initial capacitance value of 18.8 μF at a scan rate of 10 mV s⁻¹ decreases continually with increasing scan rate. The capacitance at a scan rate of 500 mV s⁻¹ amounts to 7.4 μF. Because of controlled charge carrier movement, ion accumulation occurs at
low scan rates at the electrode/electrolyte interface. The capacitance loss at increasing scan rates is related to increased internal resistance, which arises from slow charge carrier reorganization at the switching potential. [52]

This polarization effect shows similarity to the results from the dielectric analysis, in which the dielectric constant decreased with increasing frequency. For the EIS measurement, CPEs were used as circuit elements to describe the non-ideal capacitive behavior of the electrode, which depends on frequency dispersion or time constant dispersion [53]. Thus, the capacitance value from the EIS measurements was compared to the results from the CV experiment. Figure 12c shows the frequency-dependent capacitance values calculated from EIS data as part of the dielectric constants. The polymer electrolyte exhibits a capacitance value of 15.7 μF at the lowest measured frequency of 10 Hz. The capacitance is 7.8 μF at 1 kHz, comparable to the value at 500 mV s⁻¹ from the CV measurement. Increasing the frequency reduces capacitance due to the limitation of polarization response time by ion mobilities [54]. In conclusion, the evaluation of the capacitance of CV and EIS measurement showed similar values. It highlighted the capacitive behavior of the polymer electrolyte bCN-SPE55%, which is an important criterion for energy storage capacitors, i.e., electrical double-layer capacitors [55]. Regarding the ionic conductivity, the capacitive and the dielectric behavior, an application of bCN-SPE55% in such systems could be possible.

The electrochemical stability window of the polymer electrolyte bCN-SPE55% and the polymer matrix
without plasticizer (bCN-SPE0%) was investigated by LSV at 25 °C. Similar PEO-based SPEs with polymerized acrylate networks and nitrile-bearing compounds as plasticizers show electrochemical stability windows in the range of 4.5–4.8 V vs. Li/Li⁺ [19, 23, 56, 57]. Their high electrochemical stability and more comprehensive electrochemical window result from the strong electron withdrawing nitrile group, which reduces the lowest unoccupied molecular orbital (LUMO) energy [17]. Figure 13 shows the oxidative stability of bCN-SPE0% and bCN-SPE55% vs. Li/Li⁺. The polymer matrix bCN-SPE0% without bCN-PEG4 plasticizer showed excellent stability over the measuring range. A degradation process at 5 V of bCN-SPE55% was observed. The onset potential at 5.6 V marks the point of critical oxidation current that leads to material failure. The polymer electrolyte bCN-SPE55% is safely applicable in high-voltage LIBs up to 5 V.

The lithium transference number \( t_{\text{Li}^+} \) gives information about the performance of the electrolyte regarding lithium-ion motion. A value closer to unity is preferable since ion correlations (e.g., with anions) reduce the transference number and thus hinder the cycling performance of LIBs [58]. \( t_{\text{Li}^+} \) for the polymer membrane without plasticizer (bCN-SPE0%) as a control group, and bCN-SPE55% was obtained by combining chronoamperometry and EIS. Figure 14 shows the chronoamperometry curve of the symmetric Li/polymer/Li cell setup with a DC polarization of 20 mV (a, c)) and the corresponding impedance spectra before and after polarization (b, d)). bCN-SPE0% exhibits a \( t_{\text{Li}^+} \) of 0.29, which is expected for a PEO-based polymer electrolyte. Usually, PEO–salt mixtures have values lower than 0.5 because of the interaction of dissociated Li⁺ ions with dipoles of ether oxygens within the polymer backbone and the relatively weak solvation of the TFSI⁻ anion [59, 60]. The \( t_{\text{Li}^+} \) for aliphatic dinitriles-plasticized polymer electrolyte membranes with LiTFSI can reach 0.7 with high salt concentrations since the cationic transference number depends on the bulk molar concentration in the salt-rich region [11, 61]. A value of 0.28 was calculated for the lithium-ion transference number of bCN-SPE55%, the same as for the commercially available polypropylene separator [37]. The plasticizer bCN-PEG4 has EO units, which facilitate the lithium-ion dissociation but hinder the mobility of lithium ions regarding the transference number. Furthermore, it can be summarized that the ion transport at a lithium transference number of 0.28 is dominated by the organic anions, which promotes local polarization and uneven Li⁺ deposition. The cycle life and power density are consequently reduced [42].

Therefore, a lithium plating/stripping experiment was performed to analyze the compatibility between the polymer electrolyte bCN-SPE55% and the lithium electrode, crucial for interfacial stability and cell performance. The galvanostatic cycling profile is depicted in Fig. 15a, which shows the performance of the polymer electrolyte over 50 cycles at a constant current density of 0.05 mA cm⁻² at RT. The overpotential rises in the initial cycles up to 600 mV but decreases subsequently, whereas the polarization potential fluctuates slightly during cycling. Contact area differences can explain this behavior at the electrode/electrolyte interface. The interface resistance enhances cell polarization, which ultimately increases the voltage. Non-uniform voltage hysteresis of the respective stripping and plating cycle, i.e., the cell voltage in the ninth cycle (around 21 h of cycling) is much higher for lithium plating (664 mV) than stripping (582 mV). This supports the fact of interphase delamination of the polymer electrolyte, which results in augmenting overpotential from increasing interfacial resistance [62, 63]. Higher overpotentials promote lithium plating, which can be identified by the wedge-shaped voltage plateaus (Fig. 15b). These result from increasing lithium ion transport resistance [64]. Therefore, the risk of cell failure due to

Figure 13 Linear sweep voltammograms of the polymer membranes bCN-SPE0% and bCN-SPE55% at 25 °C with a scan rate of 1 mV s⁻¹.
short circuit is still present. Nevertheless, the polymer electrolyte prevented lithium dendrite penetration of the polymer membrane during the measurement, which would otherwise result in a voltage drop due to an internal cell short circuit. Figure 15c shows the voltage hysteresis of each measurement cycle. A reduction in voltage hysteresis over time was monitored after forming the artificial solid electrolyte interphase (SEI). The voltage hysteresis decreased even to 15 mV in the 50th cycle, which is important for stable cell performance. It can be assumed that the high plasticizer content ensures uniform current distribution after an interface activation [64]. Crucial parameters of polymer electrolytes that contribute to the interfacial stability and compatibility with lithium electrodes are the transference number, the mechanical strength, and the ability to form a protective SEI [9, 65, 66]. Particularly, the relatively low mechanical strength and transference number of the bCN-SPE55% polymer electrolyte should be improved by modifying the polymer matrix to increase the lithium plating/stripping performance. One approach could involve the enhancement of cross-linking density for higher mechanical strength. The growth of lithium dendrites can be reduced by improvement in the mechanical strength and dimensional stability of the polymer membrane [67]. A higher lithium salt content could also contribute to a higher transference number and better lithium plating/stripping due to higher Li$^+$ concentration [66]. However, the plasticizer bCN-PEG4 can contribute to reversible plating and stripping process by creating a pathway for Li$^+$ transport. Figure 15d shows the voltage profiles of the symmetric Li/bCN-SPE55%/Li cell. The cell achieved a capacity of 140 μAh g$^{-1}$ at a constant current density of 0.05 mAh cm$^{-2}$. The charging and discharging behavior shows that lithium’s deposited amount (plating) is recovered to a high degree during the experiment. The voltage curves exhibit overall stable plateau, which can be attributed to lower lithium ion transport resistance due to the liquid phase of the plasticizer. In the first cycle, the voltage plateau of the stripping process is irregularly shaped,
which arises from changes in the electrode surface and shape [68]. This could be a characteristic of the resistive SEI formation during the first cycles and thus the corresponding overvoltage increases.

**Conclusions**

QSPEs were prepared by incorporating bCN-PEG4 as a plasticizer through in situ UV polymerization, synthesized beforehand by cyanoethylation. The new application of this dinitrile poly(ethylene glycol) plasticizer in an acrylate-based polymer matrix enabled the preparation of a freestanding membrane up to 55 wt% plasticizer content (bCN-SPE55%). The functionality of the plasticizer with its oligoether backbone and nitrile-terminated end-groups can prevent crystalline regions and increase ion dissociation, which was confirmed by thermal and electrochemical experiments. Dielectric analysis showed the highest dielectric constant for the polymer electrolyte with the highest plasticizer content. This study was accompanied by various results, which confirmed bCN-SPE55% as the best ion-conducting material. An ionic conductivity of $1.8 \times 10^{-4}$ S cm$^{-1}$ at 30 °C and $1.3 \times 10^{-3}$ S cm$^{-1}$ at 80 °C was achieved. At the same time, the activation energy of $13.73$ kJ mol$^{-1}$ (0.142 eV) facilitated the lithium-conducting mechanism through the liquid-like phase of the plasticizer. Thermal analysis revealed high stability with an extrapolated onset temperature of 263 °C (weight loss as the cause of evaporation of bCN-PEG4) and a decreased $T_g$ of $-55.7$ °C. bCN-SPE55% is electrochemically stable up to 5 V vs. Li/Li$^+$, which allows the application as a polymer electrolyte in high-voltage electrochemical storage systems. The $t_{Li^+}$ of 0.28 confirms strong lithium-ion coordination through the ethylene oxide-dominated polymer backbone of the polymer matrix and the plasticizer. Furthermore, the application in symmetric Li/bCN-
SPE55%/Li cell showed the compatibility of the polymer electrolyte toward lithium metal in short-term experiment over 50 cycles. Hence, this QSPE based on a new dinitrile poly(ethylene glycol) plasticizer meets the requirements for an application in all-solid-state LIBs. Apart from that, bCN-PEG4 offers the opportunity to enhance important properties of PEO-based polymer electrolytes, making it an attractive plasticizer for researching new material compositions.

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Declarations

Conflict of interest The authors declare that they have no known competing for financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors certify that they have no affiliations with or involvement in any organization or entity with any financial or non-financial interest in the subject matter or materials discussed in this manuscript. The authors have no financial or proprietary interests in any material discussed in this article.

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