Stable Cycling of Room-Temperature Sodium-Sulfur Batteries Based on an In Situ Crosslinked Gel Polymer Electrolyte

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High-temperature sodium-sulfur battery (HT Na–S) technology has attracted substantial interest in the stationary energy storage sector due to its low cost and high energy density. However, the currently used solid electrolyte (β-alumina) is expensive and can only be operated at high temperatures, which compromises safety. On the other hand, liquid electrolytes in room temperature sodium-sulfur batteries (RT Na–S) are susceptible to dendrite formation and polysulfide shuttle. Consequently, an electrolyte with both solid (shuttle blocking) and liquid (ionic conductivity) properties to overcome the above-mentioned issues is highly desired. Herein, a high-performance quasi-solid state crosslinked gel polymer electrolyte (GPE) prepared in situ using pentaerythritol triacrylate (PETA) exhibiting high ionic conductivity of 2.33 mS cm$^{-1}$ at 25 °C is presented. The GPE-based electrolyte shows high stability resulting in a high discharge capacity of >600 mAh g$^{-1}$ after 2500 cycles with an average Coulombic efficiency of 99.91%. Density functional theory calculations reveal a weak interaction between the Na$^+$ ions and the oxygen molecules of the PETA moiety, which leads to a facile cation movement. The crosslinked polymer network is tightly connected to the cathode and can confine sulfides, thereby facilitating the conversion process.

1. Introduction

The electrochemical energy storage sector has seen significant development.[1,2] Lithium-ion batteries (LIBs) are becoming indispensable in a wide range of energy storage applications such as portable electronic devices, electric vehicles, and stationary grid applications, to name just a few.[3–5] Peak power performance, gravimetric energy density, cycle life, and safety are the most important parameters for cells used in large-scale energy storage devices. LIBs for grid storage applications are increasingly used in recent years due to their high energy density (NMC–200 Wh kg$^{-1}$), long cycle life (3000 cycles at a depth-of-discharge [DOD] of 80%), and high energy efficiency (95%).[6,7] However, price fluctuations of the raw materials, capital costs, and rapid material degradation demand alternative technologies. High-temperature sodium-sulfur (HT Na–S) batteries with high gravimetric energy density (760 Wh kg$^{-1}$) have been in use for grid energy storage applications due to their ultra-long cycle life (up to 5000 cycles or 15 years). Sodium appears to be a better option for energy storage for large-scale applications since it is naturally abundant, and cheaper than lithium. The use of sulfur as a cathode material in batteries has its advantages such as low costs, natural abundance, environmental benignity, and a high theoretical energy density of 1672 mAh g$^{-1}$. Additionally, HT Na–S batteries use β-alumina operated at 300–350 °C as a solid electrolyte.[8] At this temperature, however, both sodium and sulfur exist in the molten state, which entails serious safety issues including explosion.[9]

Consequently, many attempts have been made to reduce the operating temperature and develop room-temperature sodium-sulfur (RT Na–S) batteries.[10] As a result of the formation of Na$_2$S during discharge as a final product instead of intermediate polysulfides in HT Na–S, the gravimetric energy density reaches up to 1274 Wh kg$^{-1}$ in RT Na–S batteries.[11–13] However, RT Na–S batteries experience issues similar to those observed in their lithium counterparts such as dissolution of polysulfides in ether-based electrolyte solvents, shuttling of polysulfides, electrolyte incompatibility with the anode, self-discharge, and huge volume changes (ca. 260% vs 80% for Li) on the cathode.[14] Moreover, polysulfide anions react with carbonate solvents due
to their nucleophilic nature, which significantly affects cell capacity. To overcome the reaction between the active species and carbonate solvents, substantial research efforts have been dedicated to cathode modifications, separator architecture, binder modifications, and artificial (SEI) layer formation. Sulfurized poly(acrylonitrile) (SPAN) cathodes can completely avoid soluble intermediates \( (M_2S_x, 2 \leq \alpha \leq 4, M = Li \text{ or } Na) \) in carbonate solvents by using short sulfur chains covalently bound to the polymeric matrix.\(^{[15–17]}\) SPAN-based cathodes were first proposed for lithium-sulfur (Li–S) batteries due to their low cost, ease of synthesis, high specific capacity, high energy density, and suppression of the polysulfide shuttle.\(^{[18,19]}\)

Another approach to eliminating the dissolution of polysulfides in metal-sulfur batteries entails the use of gel polymer electrolytes (GPEs). The high viscosity of GPEs compared to liquid electrolytes (LEs) suppress the dissolution of polysulfides. Since a GPE comprises an LE trapped inside the polymer matrix, it can avoid electrolyte leakage, dendrite formation, and internal short-circuiting.\(^{[20,21]}\) Moreover, GPEs also provide a synergistic effect on both liquid and solid electrolytes such as high ionic conductivity \( (>10^{-3} \text{ S cm}^{-1}) \) and high safety.\(^{[22]}\) Commonly, ex situ polymerized GPEs are prepared by solvent casting (heterogeneous) and phase inversion (homogeneous) techniques. During solvent casting, both the electrolyte salt and the polymer are dissolved in a suitable solvent and cast on a Teflon medium to evaporate the solvent subsequently obtaining a thin polymer electrolyte. However, casting and evaporation of the solvent should be controlled under inert conditions to avoid soluble intermediates (MS\(_x\), \( 2 \leq \alpha \leq 4 \)).

Signals at 1470 and 1407 cm\(^{-1}\) inside Swagelok cells, polymerization was carried out for 6 h at 70 °C in a vacuum to completely evaporate the solvent. This dried GPE was then characterized by scanning electron microscopy (SEM) to visualize the surface texture. SEM pictures at different magnifications (Figure S2, Supporting Information) revealed a smooth surface where the polymer network acts as an ion-conductive matrix while the LE inside allows for ion motion (Figure 1c). For the in situ polymerization inside Swagelok cells, polymerization was carried out for 6 h at 70 °C to ensure maximum monomer conversion. To confirm polymerization, both PETA and the final GPE were subjected to Fourier-transform infrared spectroscopy (FTIR, Figure 1d). Signals at 1470 and 1407 cm\(^{-1}\) (C–H bending, 1263 cm\(^{-1}\) (C–O, antisymmetric stretching), and 1174 cm\(^{-1}\) (C–O, symmetrical stretching) appeared for all three samples.\(^{[29,30]}\) The signal at 1722 cm\(^{-1}\) (C=O, stretching) of PETA shifts to higher energy (1739 cm\(^{-1}\) and is weaker than in the monomer. Additionally, the bands at 1633 and 1618 cm\(^{-1}\) represent stretching vibrations of the C=O double bond, which almost disappeared in the final GPE. Quantification of the FTIR signals revealed a high degree of double bond conversion \( (>99.7 \pm 5\%\)\(^{[31,32]}\) Figure S3 and Equation S4, Supporting Information). The thermal stability of the GPE and LE were compared using thermogravimetric analysis (TGA, Figure 1e). At the beginning of heating, both the GPE and the LE behave similarly, yet at 220 °C a weight loss of up to 85 wt.% was observed for the LE compared to 64 wt.% for the GPE. This weight loss begins at 212 °C by evaporation of volatile compounds at a faster rate for the LE compared to the GPE. Above this temperature, the GPE shows a reduced weight loss of at least up to 400 °C. Complementary, the weight loss at constant temperature (23 °C) and atmospheric pressure was measured as a function of time for both the GPE and the LE. Figure S4, Supporting Information shows that the GPE and LE exhibit weight losses of up to \( \approx 6 \) and \( \approx 14 \) wt.% after 24 h, respectively, which indicates that the solvents (PC and FEC) in the LE are more volatile compared to those encapsulated in the polymeric matrix.

2. Results and Discussion

2.1. Synthesis and Characterization of the GPE

The GPE was synthesized by free radical polymerization of a precursor solution containing PETA and the LE using AIBN as a thermal initiator at 70 °C (Figure 1a). This way, a crosslinked, viscous, translucent polymeric network with encapsulated LE was obtained (Figure 1b).\(^{[27]}\) To verify the confinement capability of the GPE for the LE, a swelling method was used to calculate the crosslinking density of the PETA-derived polymer (Equations S1–S3, Supporting Information).\(^{[28]}\) According to these measurements, poly-PETA shows high crosslinking density with low molecular weight polymer chains between the individual crosslinks (Table S1, Supporting Information). Importantly, poly-PETA can form a high gel content even at low concentrations in the LE. When combining an LE and PETA, the highly cross-linked poly-PETA network can effectively confine the LE and prevent leaking (Figure S1, Supporting Information).

The GPE was polymerized under inert conditions on a glass plate and subjected to a vacuum to completely evaporate the solvent. This dried GPE was then characterized by scanning electron microscopy (SEM) to visualize the surface texture. SEM pictures at different magnifications (Figure S2, Supporting Information) revealed a smooth surface where the polymer network acts as an ion-conductive matrix while the LE inside allows for ion motion (Figure 1c). For the in situ polymerization inside Swagelok cells, polymerization was carried out for 6 h at 70 °C to ensure maximum monomer conversion. To confirm polymerization, both PETA and the final GPE were subjected to Fourier-transform infrared spectroscopy (FTIR, Figure 1d). Signals at 1470 and 1407 cm\(^{-1}\) (C–H bending, 1263 cm\(^{-1}\) (C–O, antisymmetric stretching), and 1174 cm\(^{-1}\) (C–O, symmetrical stretching) appeared for all three samples.\(^{[29,30]}\) The signal at 1722 cm\(^{-1}\) (C=O, stretching) of PETA shifts to higher energy (1739 cm\(^{-1}\) and is weaker than in the monomer. Additionally, the bands at 1633 and 1618 cm\(^{-1}\) represent stretching vibrations of the C=O double bond, which almost disappeared in the final GPE. Quantification of the FTIR signals revealed a high degree of double bond conversion \( (>99.7 \pm 5\%\)\(^{[31,32]}\) Figure S3 and Equation S4, Supporting Information). The thermal stability of the GPE and LE were compared using thermogravimetric analysis (TGA, Figure 1e). At the beginning of heating, both the GPE and the LE behave similarly, yet at 220 °C a weight loss of up to 85 wt.% was observed for the LE compared to 64 wt.% for the GPE. This weight loss begins at 212 °C by evaporation of volatile compounds at a faster rate for the LE compared to the GPE. Above this temperature, the GPE shows a reduced weight loss of at least up to 400 °C. Complementary, the weight loss at constant temperature (23 °C) and atmospheric pressure was measured as a function of time for both the GPE and the LE. Figure S4, Supporting Information shows that the GPE and LE exhibit weight losses of up to \( \approx 6 \) and \( \approx 14 \) wt.% after 24 h, respectively, which indicates that the solvents (PC and FEC) in the LE are more volatile compared to those encapsulated in the polymeric matrix.

2.2. Electrochemical Characterization

The anodic stability of the GPE was evaluated by linear sweep voltammetry (LSV) against various metal electrodes. As shown in Figure 2a, the GPE possesses high oxidative stability against an aluminum (Al, \( \approx 6 \) V), carbon paper (3.3 V), graphite
(3.45 V), platinum (Pt, 3.55 V), and stainless steel (SS, 4.2 V) current collector. Notably, the anodic stability of the GPE electrolyte against Al reported here is the highest for Na batteries published so far.\textsuperscript{[34–36]} Since the ion movement in the electrolyte is crucial for the kinetics during the redox reaction,\textsuperscript{[37]} the ionic conductivity of both the LE and the GPE was measured with the help of blocking SS electrodes at various temperatures (Figure 2b). The bulk resistance of both the GPE and LE was extracted from the impedance spectroscopy data in the high-frequency region (Table S2, Supporting Information). Usually, the ionic conductivity of a GPE is lower than the one of the LE due to the increased viscosity, which impedes ion movement. However, a PETA-based GPE showed an ionic conductivity ($\sigma$) of $2.33 \times 10^{-3}$ S cm$^{-1}$ at 25 °C, virtually identical (within experimental error) to the one of the LE ($2.32 \times 10^{-3}$ S cm$^{-1}$). This can well be expected in view of the low polymer content (1.5 wt.%). At elevated temperature (40 °C), the ionic conductivity of the GPE was $3.77 \times 10^{-3}$ S cm$^{-1}$, thereby significantly exceeding the one of the LE ($3.39 \times 10^{-3}$ S cm$^{-1}$). These findings suggest that the polymer segmental motion at high-temperature influences ionic conductivity. A plot of log $\sigma$ versus $T^{-1}$ was non-linear, indicating a strong coupling between polymer segmental relaxation and ionic motion.\textsuperscript{[38]} This behavior can be well described by the Vogel–Tamman–Fulcher (VTF) type equation (Equation S5, Supporting Information).\textsuperscript{[39,40]} By employing the VTF equation for non-linear curve fitting, the pseudo-activation energy ($E_a$) can be obtained. The $E_a$ value obtained for the GPE (73.5 meV) is virtually identical to the one for the LE (73.9 meV), implying that ion transport across the polymer chains is as fast as in an LE.

The low activation energy of the GPE suggests that the polymeric matrix promotes ion motion in the electrolyte. Generally, cations are stabilized by the coordination of solvent molecules, which then transport the cations across the electrodes. The coordination number of the cation affects its mobility.\textsuperscript{[41,42]} To elucidate the coordination of the cation by the solvent and PETA, respectively, molecular electrostatic potential (MEP) and binding energy calculations were carried out. MEP calculations revealed the favorable binding sites for Na$^+$ by mapping the charge distribution in PC and PETA, respectively. Figure 2c,d
shows the electrostatic potential response of the PC solvent molecule (in the LE) and of the ester groups of PETA (also present in the GPE) towards Na$^+$. The Van der Waals surface is colored red for a negative electrostatic potential, which attracts Na$^+$, and blue for positive electrostatic potential. Clearly, the MEP on the Van der Waals surface of the carbonyl oxygen atom in PC interacts with Na$^+$ stronger than the ester groups in PETA. Moreover, PC shows strong single-site coordination, whereas multiple coordination occurs in PETA, indicating an overall weaker interaction of Na$^+$ with PETA. Notably, Na$^+$ does not prefer coordination with the carboxylate and hydroxyl groups. Thus, when placed close to the C–O–C or -OH groups in density functional theory (DFT) simulation, Na$^+$ spontaneously moves to the nearest -C=O group as the preferred coordination site. The different coordination possibilities and their respective binding energies are summarized in Figure S5a–d and Table S3, Supporting Information. DFT calculations based on the same coordination numbers always reveal stronger binding energy between Na$^+$ and PC of $-427.4$ kJ mol$^{-1}$ compared to the binding of Na$^+$ to PETA ($-316.9$ kJ mol$^{-1}$). It is, therefore, reasonable to assume that, despite the higher viscosity of GPEs compared to LEs (Figure S6, Supporting Information), the weaker coordination of Na$^+$ to the PETA-derived polymer is responsible for the high Na$^+$ mobility in the GPE. Ultimately, DFT calculations also suggest that weak coordination of Na$^+$ to the ester groups in PETA promotes ion hopping.

Generally, both the cation and anion contribute to the current transport across electrodes. An ionic current preferentially carried by the cation significantly reduces the concentration polarization caused by the accumulation of anions near the electrode, which in turn affects the rate at which the battery operates.$^{[44,45]}$ A combination of chronoamperometric and alternating current (AC) impedance spectroscopy was used to obtain the Na$^+$ transfer number ($T_{\text{Na}^+}$) of the GPE and the LE (Equation S6 and Figure S7, Supporting Information). The $T_{\text{Na}^+}$ of the GPE was 0.44 and thus higher than the $T_{\text{Na}^+}$ of the LE (0.33). This high $T_{\text{Na}^+}$ value of the GPE indicates that the movement of the anion is restricted by the polymer network due to the interaction between the bulky anion with delocalized charges and the polymer chains. This reduces the cell’s polarization and leads to dendrite-free, stable Na deposition.$^{[46–48]}$

To identify the redox potentials of Na-SPAN cells, cyclic voltammetry (CV, Figure S8a,b, Supporting Information) was performed at a scan rate of 0.1 mV s$^{-1}$. Both the GPE and the LE show similar redox potentials and current densities, indicating that the performance of the GPE-containing cell is not hampered by the high viscosity of the polymeric matrix. Reduction of sulfur to Na$_2$S$_x$ ($x = 3–4$) occurs at 1.77 V and an additional broad reduction peak around 1.20 V indicates the conversion of Na$_2$S$_x$ into Na$_2$S. Likewise, during oxidation Na$_2$S is converted into Na$_2$S$_x$ at 2.0 V and then reattaches to the SPAN composite in the fully charged state above 2.3 V.$^{[50]}$ To determine reaction kinetics at the sulfur cathode, CV measurements were carried out by increasing the scan rate stepwise from 0.2 to 1.2 mV s$^{-1}$. The resulting graph (Figure 3a,b) shows an increase in peak current density and potential shift (polarization) with an increasing

Figure 2. Characterization of the GPE. a) Oxidative stability of the GPE determined by linear sweep voltammetry (LSV) at a scan rate of 1 mV s$^{-1}$ against carbon paper, graphite, Pt, SS, and Al; b) ionic conductivities of the GPE (black dots) and the LE (red dots) measured with a blocking SS electrode at various temperatures. Molecular electrostatic potential (MEP) mapping of possible binding sites (colored in red) of Na$^+$ with, c) PC; and d) PETA.
scan rate. The GPE displayed enhanced peak current density and sharper peak shapes compared to the LE at similar scan rates, indicating fast electrode kinetics at the cathode. A diminished reduction peak current (peaks A and B) was observed for the LE in contrast to the sharp peak in the GPE, specifying sluggish reaction kinetics during the reduction in the LE.\textsuperscript{[51,52]} The \( \text{Na}^+ \) diffusion coefficient (\( D_{\text{Na}^+} \)) was determined by using the Randles–Sevcik equation based on the relation between peak current (\( i \)) versus square root of the scan rate (\( \sqrt{v} \)) (Figure S8c,d, Supporting Information).\textsuperscript{[53,54]} Since peak B is broad for the LE, only peaks A and C were taken into consideration to maintain the accuracy of the \( D_{\text{Na}^+} \) value. The apparent diffusion

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**Figure 3.** Cyclic voltammogram of a Na-SPAN cell at different scan rates. a) GPE and b) LE; c) calculated values of the \( \text{Na}^+ \) ion diffusion coefficient (\( D_{\text{Na}^+} \)) for the main anodic and cathodic peaks (peak A and peak C) for a GPE and an LE; d) calculated slope (\( K \)) values for the peaks A and C based on the double logarithmic plot of peak current versus scan rate; e) overpotential voltage profile at 1 mA cm\(^{-2}\) (0.5 mAh cm\(^{-2}\)); f) expanded view of overpotential at various intervals.
coefficients (Figure 3c) in peaks A and C for the GPE ($65 \times 10^{-10}$ and $212 \times 10^{-10} \text{ cm}^2 \text{s}^{-1}$) were slightly higher than those for the LE ($37 \times 10^{-10}$ and $138 \times 10^{-10} \text{ cm}^2 \text{s}^{-1}$), suggesting facile ion movement in the GPE network. A double logarithmic plot (Figure 3d) shows a higher k value (slope) for both the cathodic peak (A) and the anodic peak (C) for the GPE, corroborating the results from CV and suggesting faster reaction kinetics at the electrodes in GPE-based cells. This enhanced reaction kinetics for the GPE can be explained as follows. In the case of the LE, the final discharge products, Na$_2$S$_2$/Na$_2$S, can deposit throughout the cathode, thereby blocking the pores, which leads to an increase in overpotential during long-term cycling (Figure S9a,b, Supporting Information). In contrast, in the GPE, the cathode pores are (partially) blocked or even filled with polymer but the polymer itself can confine Na$_2$S$_2$/Na$_2$S locally, resulting in an efficient conversion of the active material. To support this theory, SEM pictures together with energy-dispersive X-ray (EDX) spectra of a pristine cathode, a discharged SPAN cathode with an LE, and a discharged SPAN cathode with a GPE after 600 cycles were recorded (Figure S10a–c, Supporting Information). EDX images show several agglomerated sulfur spots with the LE (Figure S10b, Supporting Information) whereas the GPE (Figure S10c, Supporting Information) shows no clustered sulfur spots, indicating that sulfur reduction results in a homogeneous distribution of Na$_2$S$_2$/Na$_2$S throughout the polymer.

The overpotential for deposition and dissolution of Na$^+$ during cycling was analyzed using a symmetric Na||Na cell (Figure 3e,f). The GPE showed an increased overpotential during the first 60 cycles, attributable to the formation of a stable SEI layer leads to the reduction in resistivity between the electrodes. Both GPE- and LE-based cells maintain a good reversible capability (Figure 4a,b). Two voltage plateaus during discharge at 1.7 and 1.0 V and one major plateau during the charge at 2.0 V were observed, corroborating the CV results obtained (Figure S7a, Supporting Information). Figure 4c compares the rate capabilities of a GPE and an LE in Na|electrolyte/SPAN cells at C-rates between 1 and 4 C. The GPE-based cell exhibited a stable capacity of 962, 850, 725, and 590 mAh g$^{-1}$ at 1, 2, 3, and 4 C, respectively, whereas LE-based cells delivered a capacity of only 922, 805, 692, and 564 mAh g$^{-1}$ at these C-rates. This enhanced performance of GPE-based cells points towards improved electrode kinetics resulting from the rapid movement of Na$^+$ ions between the electrodes. Both GPE- and LE-based cells maintain a good reversible capability when the C-rate returns to 1 C. A comparison of the long-term galvanostatic cycling performance of GPE- and LE-based cells is shown in Figure 4d. Cells were cycled at 2 C (3.35 mA g$^{-1}$) in a potential window between 0.5–3 V at room temperature (23 °C). An initial discharge capacity of 1577 mAh g$^{-1}$ for GPE-based cells at 0.3 C versus 1556 mA g$^{-1}$ for LE-based cells was observed. Both values point towards irreversible side reactions, which lead to CEIs >100% (Figure 4e).[56] This initial increase in CE is accompanied by an irreversible discharge capacity that likely arises from the reduction of SPAN, SEI formation, and irreversible sodium ion insertion.[57] For the first 200 cycles, GPE-based cells showed a steady increase in discharge capacity, which we hypothesize to be related to the formation of ion channels (slow activation process) in the GPE. The Na$^+$ movement between the electrodes is greatly affected by the viscosity of the electrolyte. Since GPEs have higher viscosities than LEs (Figure S6, Supporting Information), we surmise that this increase in discharge capacity during the activation process is due to the slow movement of Na$^+$ between the GPE and the cathode and vice versa.[58]

2.3. Cycling Performance of Na-SPAN Full Cells

To demonstrate the advantages of GPEs, we further investigated their application in RT Na-SPAN batteries. Full cells containing metallic Na as an anode, SPAN as cathode, and an in situ polymerized GPE were cycled at 0.2 C to identify the reduction steps involved (Figure 4a,b). Two voltage plateaus during discharge at 1.7 and 1.0 V and one major plateau during the charge at 2.0 V were observed, corroborating the CV results obtained (Figure S7a, Supporting Information). Figure 4c compares the rate capabilities of a GPE and an LE in Na|electrolyte/SPAN cells at C-rates between 1 and 4 C. The GPE-based cell exhibited a stable capacity of 962, 850, 725, and 590 mAh g$^{-1}$ at 1, 2, 3, and 4 C, respectively, whereas LE-based cells delivered a capacity of only 922, 805, 692, and 564 mAh g$^{-1}$ at these C-rates. This enhanced performance of GPE-based cells points towards improved electrode kinetics resulting from the rapid movement of Na$^+$ ions between the electrodes. Both GPE- and LE-based cells maintain a good reversible capability when the C-rate returns to 1 C. A comparison of the long-term galvanostatic cycling performance of GPE- and LE-based cells is shown in Figure 4d. Cells were cycled at 2 C (3.35 mA g$^{-1}$) in a potential window between 0.5–3 V at room temperature (23 °C). An initial discharge capacity of 1577 mAh g$^{-1}$ for GPE-based cells at 0.3 C versus 1556 mA g$^{-1}$ for LE-based cells was observed. Both values point towards irreversible side reactions, which lead to CEIs >100% (Figure 4e).[56] This initial increase in CE is accompanied by an irreversible discharge capacity that likely arises from the reduction of SPAN, SEI formation, and irreversible sodium ion insertion.[57] For the first 200 cycles, GPE-based cells showed a steady increase in discharge capacity, which we hypothesize to be related to the formation of ion channels (slow activation process) in the GPE. The Na$^+$ movement between the electrodes is greatly affected by the viscosity of the electrolyte. Since GPEs have higher viscosities than LEs (Figure S6, Supporting Information), we surmise that this increase in discharge capacity during the activation process is due to the slow movement of Na$^+$ between the GPE and the cathode and vice versa.[58] Figure S14a,b and Table S4, Supporting Information shows that an increase in the PETA content (1.5, 5, and 10 wt.%) in the electrolyte adversely affects the activation process and subsequent cycling. Increasing the salt concentration to 2 M in the GPE resulted in a gradual increase in discharge capacity up to 250 cycles, indicating an extended activation period (Figure S14c, Supporting Information). Similarly, a Na–S cell containing 1.5 wt.% PETA showed a decrease in overpotential from the 45th to the 200th cycle (Figure S15a,b, Supporting Information). GPE-based Na-SPAN cells showed excellent cycling performance with a high discharge capacity of 1013 mAh g$^{-1}$ at the 250th cycle maintaining > 600 mAh g$^{-1}$ for up to 2500 cycles (Figure 4d). From the initial discharge (2 C, 787 mAh g$^{-1}$), the cell exhibited
a capacity decay of only 0.0091% per cycle resulting in a discharge capacity of 644 mAh g\(^{-1}\) at the 2500\(^{th}\) cycle. The cell also showed a stable CE over 2500 cycles with an average CE\(_{avg}\) of 99.91%. In contrast, LE-based cells showed a gradual decrease in discharge capacity accompanied by unstable cycling after 1000 cycles (Figure 4e). X-ray photoelectron spectroscopy (XPS) was employed to monitor the product formation at the end of the charge/discharge cycles. Cells were stopped at 0.5 V (after discharge) and 3 V (after charge) and transferred to the XPS chamber. Figure S16 (Supporting Information) shows the sulfur species formed during charging and discharging. The pristine SPAN shows two signals for the S–S/C–S x and C–S bonds at 164.0 and 162.3 eV, respectively. Sulfate species are observed at 167–172 eV. During discharge, the formation of Na\(_2\)S at 159.6 eV was observed.\[^{[30,50]}\] The signal observed at 161.5 eV overlaps with the signal for the C–S bonds (162.3 eV) and is assigned to Na\(_2\)S\(_2\) and unreacted C–S bonds in the SPAN cathode. After charging, the C–S, Na\(_2\)S, and Na\(_2\)S\(_2\) signals disappear but the signal for the C–S/S–S bond at 164.0 eV reappears, indicating successful reoxidation during charging.\[^{[17]}\]

High sulfur loading in the cell is one of the most vital parameters that govern the feasibility of SPAN batteries in practical applications. Figure S17a,b, Supporting Information shows the cycling and rate performance of GPE-based cells with a sulfur loading of 0.88 mg per cathode. The cell showed an increased capacity of 968 mAh g\(^{-1}\) at the 2nd cycle at 0.5 C and a discharge capacity of 913, 439, 157, and 87 mAh g\(^{-1}\) at 0.5, 1, 1.5, and 2 C, respectively. Increasing the sulfur loading to 3.5 mg per cathode by increasing the sulfur content in the cathode to 90 wt.% delivered a discharge capacity of 986 mAh g\(^{-1}\) in the 2nd cycle at 0.1 C (Figure 4f). As cycling proceeded, a reversible discharge capacity of 680 mAh g\(^{-1}\) was retained at the end of the 63\(^{rd}\) cycle with a capacity retention of 68.9%. Throughout cycling, the areal capacity of the cathode stayed above 2 mAh cm\(^{-2}\).
The impact of temperature on the electrochemical performance of GPE-based cells was examined by cycling a full cell close to 0 °C at 0.2 C and then reversing the temperature to room temperature (23 °C). Figure 4g shows the increase in discharge capacity from 669 to 951 mAh g⁻¹ up to 100 cycles, indicating a strong activation process due to the restricted movement of Na⁺ ions at low temperatures. Upon reversing to room temperature, the cell showed a stable capacity of 1190 mAh g⁻¹.

To further demonstrate their capability to work at near 0 °C temperature, the rate performance of a GPE-based Na-SPAN cell was investigated at discharge rates of 0.5, 1, 1.5, and 2 C at which the cells delivered a discharge capacity of 408, 154, 77, and 46 mAh g⁻¹ at 0 °C (Figure 4h). When the C-rate was reversed to 0.5 C, the cell retained its initial capacity of 408 mAh g⁻¹.

Next, the self-discharge propensity of GPE- and LE-based full cells was addressed (Figure 5a). Na-SPAN cells were stored for 200 h and then cycled at 2 C for 100 cycles. Subsequently, the cells were stopped in the charged state (3 V) with a resting period of 100 h, followed by a cycling process over 1000 cycles. GPE- and LE-based cells showed a similar trend in discharge capacity over the first 100 cycles. However, from the 101st cycle, LE-based cells displayed an accelerated degradation in discharge capacity due to loss of active material. Accordingly, the capacity retention between the 101st and the 1000th cycle of GPE-based cells was 90%, whereas LE-based cells exhibited only 73%. Clearly, the polymeric matrix of GPEs restricts the diffusion of intermediates or Na₂S towards the anode, thereby providing robust protection against the self-discharge of the cell.

Poly-PETA not only inhibits the diffusion of intermediate polysulfides via a physical barrier but also by preferred interaction. Na₂S₃/Na₂S₄ are the intermediates formed in the SPAN cathode. To validate the favorable interaction between Na₂S₃/Na₂S₄ and PETA, DFT calculations were carried out (Figure 5b). Na₂S₃ and Na₂S₄ show stronger interaction towards PETA with binding energies of −84.91 and −83.58 kJ mol⁻¹ than with PC and FEC. When comparing PC and FEC alone, the interaction with the intermediate polysulfides is stronger for FEC. Thus, the binding energy values of PC-Na₂S₃ (−63.25 kJ mol⁻¹) and PC-Na₂S₄ (−61.90 kJ mol⁻¹) are lower than that of FEC-Na₂S₃ (−68.94 kJ mol⁻¹) and FEC-Na₂S₄ (−67.76 kJ mol⁻¹). The GPE contains PC, FEC, and PETA in decreasing order (wt.%); the strong binding energy of Na₂S₃/Na₂S₄ with PETA indicates that the polysulfides are immobilized by the crosslinked polymer network, thereby suppressing diffusion in the electrolyte. A static adsorption test was carried out to support the DFT calculations on the preferable interactions between PETA and Na₂S₃. 0.005 M of Na₂S₃ solution was prepared in DME by adding the required amount of Na₂S and S₈. Poly-PETA was added and the mixture was allowed to stand for more than 6 h. After this time, the color of the solution changed from green to light yellow (Figure S18a, Supporting Information). The solution was filtered and UV–vis absorption spectra were measured at various time intervals. The resulting solution showed two broad peaks around 265–295 nm, indicating a mixture of S₂⁻/S₄⁻ while the peak at 418 nm corresponds to a mixture of S₄⁻/S₆⁻. The graph depicting absorption intensity versus time (Figure S18b, Supporting Information) shows that absorption intensity first decreases gradually but stabilizes after 6 h compared to the parent Na₂S₃ solution. This indicates that the polysulfide species are adsorbed by poly-PETA via preferred interaction, corroborating the DFT calculations.
2.4. Confinement Properties of GPEs

Binders are an indispensable part of cathodes. They help in the physical retainment of the cathode components, thereby preventing volume expansion and polysulfide dissolution.\cite{61} The ratio of active material to binder obviously affects the electrochemical performance of a cell. While the use of large amounts of binder prevents the diffusion of the electrolyte into the porous structure of a cathode, ultimately leading to poor cycling performance, low amounts of binder result in active material dissolution and poor adhesion of the active material during volume expansion.\cite{62,63} Therefore, it is essential to optimize the binder content in a way that does not compromise the cathode’s electrical and ionic conductivity. To realize the GPEs confinement abilities, SPAN cathodes were fabricated with varying amounts of the binder.

SEM and EDX images of cathodes with different binder (Na-CMC) content shown in Figure S19a–d, Supporting Information reveal that a reduction in the binder content resulted in high porosity of the cathode. This way, a low amount of binder in the cathode facilitates the penetration of the GPE into the cathode’s pores. Figure 6a shows the rate performance of GPE-based Na-SPAN cells with SPAN cathodes containing different amounts of the binder at C-rates between 1 and 4 C. Cathodes containing 2 wt.% binder showed the highest discharge capacity (625 mAh g\(^{-1}\)) compared to cathode containing 15 wt.% binder (140 mAh g\(^{-1}\)). Similarly, galvanostatic long-term cycling (Figure 6b) revealed high discharge capacities for cathodes containing 2 wt.% binder, whereas cathodes with high binder content showed fast degradation. Figure S20a–d, Supporting Information shows plots of current density versus potential at different scan rates for cathodes containing different amounts of the binder. A reduction in binder significantly enhances the current density and leads to sharp peaks, pointing towards improved reaction kinetics at the cathode.

**Figure 6.** Electrochemical influence of the binder quantity (B – 2, 5, 10, 15 wt.%) on a GPE-containing Na-SPAN cell. a) Rate capability; b) galvanostatic cycle stability; c) GITT analysis of SPAN cathodes with varying binder content; apparent diffusion coefficient \(D_{\text{Na}^+}\) versus cell potential during, d) discharge; and e) charge.
The difference in potential (ΔV) from the CV curve (peak C – peak A, Table S5, Supporting Information) and during cycling (1st, 100th, and 300th cycle at 2 C, Figure S21a–c, Supporting Information) signifies that cathodes containing 2 wt.% binder experience reduced polarization, which in turn promotes high-capacity utilization. The excellent electrochemical performance of cathodes with a low amount of binder (2 wt.%) is not only influenced by the increased carbon content (electronic conductivity) but also by higher ionic conductivity due to the larger amounts of the GPE that are in contact with the active material.

Finally, GITT measurements (Figure 6c) were carried out to determine the diffusion coefficient of Na\(^+\) in the cathode as well as the charge and discharge kinetics.\(^{[52,64,65]}\) During discharge, the initial discharge potential of cathodes containing 2 wt.% binder was 2.7 V versus Na/Na\(^+\), whereas, those containing 15 wt.% binder started at a lower potential of 2.4 V, suggesting that larger overpotentials are required to reduce the sulfur with increasing amounts of binder. A similar trend was observed during charging. At 50–100% state of charge, the potential curve of cathodes containing 15 wt.% binder displayed an increased potential loss at each relaxation cycle compared to cathodes containing 2 wt.% binder. This is likely a result of an impeded Na\(^+\) ion movement in the insulating binder environment. To prove this hypothesis, the diffusion coefficient of Na\(^+\) (Figure 6d,e) was calculated by the transient voltage method developed by Weppner and Huggins.\(^{[66,67]}\) During sodiation, the Na\(^+\) ions tend to diffuse faster at low binder content (2 wt.%); good contact between the GPE and the active material promotes ion mobility. Thus, at a discharge potential of 1.2 V, at which intermediate polysulfides are formed, the sodium diffusion coefficient (\(D_{Na^+}\)) of a cathode containing 2 wt.% binder was \(3.87 \times 10^{-12}\) versus \(2.53 \times 10^{-12}\) for a cathode containing 15 wt.% binder. At the end of sodiation and desodiation, cathodes with 15 wt.% binder display sluggish Na\(^+\) ion diffusion, indicating poor conversion at the cut-off potentials. These data suggest that a lower binder amount in the cathode provides a higher degree of conversion, which helps in achieving high-rate capability with Na-SPAN full cells.

A comparison of the present system with other, existing liquid and gel polymer electrolytes in terms of ionic conductivity, capacity, cycling stability, and cathode materials used is given in Table S6, Supporting Information.

### 2.5. Application of GPEs in Flexible Batteries

Finally, to assess the potential application of a GPE-based flexible Na-SPAN battery, as proof of concept, a laboratory-scale pouch cell measuring 4 × 4 cm\(^2\) (Figure 7a) was fabricated. The glass fiber separator was placed on a thin sodium anode, which was rolled onto the stainless-steel current collector. The soft packaged pouch cell was sealed and subjected to galvanostatic cycling at a rate of 1 C. First, the cell was cycled in its original flat state, later, cycling was continued by folding the pouch cell to 180°. Due to the good contact between the GPE and the electrodes, the cell was able to deliver a first discharge capacity of 807 mAh g\(^{-1}\) and 668 mAh g\(^{-1}\) in the flat and bent states, respectively. Even after bending, the cell was still able to maintain its capacity for the rest of the cycles. Moreover, the GPE-containing glass fiber membrane showed good mechanical stability and flexibility even after multiple bending cycles. Equally important, the pouch cell was able to light a light-emitting diode (LED) when tested under intentional flattening, bending (180°), and folding (Figure 7b). This mechanically robust pouch cell was further able to deliver current to the LED even after cutting it into three separate pieces. As outlined above, both the GPE-filled pores of the cathode and the initially formed polymer layer on the Na anode enhance the adhesion.
between the electrolyte and the electrodes. This improved interfacial contact obviously allows to withstanding extreme deformations without affecting performance.

3. Conclusion

In summary, we developed a novel crosslinked GPE based on PETA for use in room temperature sodium-sulfur batteries. The as-prepared gel polymer electrolyte shows high ionic conductivity of 2.33 mS cm$^{-1}$ at 25 °C in a Na-SPAN battery. DFT studies revealed strong one-site coordination of Na$^+$ to the propylene carbonate-based solvent, which restricts the free ion movement in the liquid electrolyte. By contrast, the interaction of Na$^+$ with the PETA-based polymer in the GPE is weak, which facilitates ion hopping, leading to high ionic conductivity. The GPE maintains ultra-stable cycling of 2500 charge-discharge cycles with discharge capacities >600 mAh g$^{-1}$ at 2 C, ultimately achieving an average CE of 99.91%. In contrast, the liquid electrolyte exhibits degrading capacity accompanied by unstable CE after 1000 cycles. The confinement properties of the crosslinked GPE were studied by varying the amount of binder in the cathode between 2 and 15 wt.%. Cathodes containing 2 wt.% of binder showed improved rate capability, discharge capacity, and a higher diffusion coefficient compared to cathodes with higher binder contents. Results suggest that the reduction in the amount of binder leads to better contact between the GPE and the active material, which in turn favors rapid ion movement in the interfaces with the active material. The advantages of GPEs outlined here are expected to pave the way to the successful use of Na–S batteries in flexible energy storage devices.

4. Experimental Section

Preparation and Characterization of GPEs: NaTbP (≥99.5% purity, Sigma-Aldrich) was dried under vacuum at 120 °C overnight. PC (C$_6$H$_{12}$O$_6$, 99.7% purity) and FEC (C$_4$H$_6$O$_3$, ≥99% purity) battery grade solvents were purchased from Sigma-Aldrich. The preparation of PETA-based GPEs was carried out in an inert sealed glass vial for characterization of the GPE. The precursor solution containing 1.5 wt.% of PETA (abcr) and 0.5 wt.% of azobisisobutyronitrile (AIBN, Sigma-Aldrich) was mixed with liquid electrolyte (1 M NaTbP in PC and 7 wt.% FEC) under constant stirring for 1 h. Then the precursor solution was filtered through a syringe filter to remove any impurities and kept in an oven at 70 °C for 3 h to obtain a translucent GPE block.

SEM (Zeiss Gemini 500) was used to analyze the sample's surface by applying an electron acceleration voltage of 3.5 keV. EDX was carried out on a Bruker Nano using an acceleration voltage of 5 keV. Thermal degradation was measured via thermogravimetric analysis (TGA, PerkinElmer) under a constant nitrogen flow (19.8 ml min$^{-1}$) at 2 C, ultimately achieving an average CE of 99.91%. In contrast, the liquid electrolyte exhibits degrading capacity accompanied by unstable CE after 1000 cycles. The confinement properties of the crosslinked GPE were studied by varying the amount of binder in the cathode between 2 and 15 wt.%. Cathodes containing 2 wt.% of binder showed improved rate capability, discharge capacity, and a higher diffusion coefficient compared to cathodes with higher binder contents. Results suggest that the reduction in the amount of binder leads to better contact between the GPE and the active material, which in turn favors rapid ion movement in the interfaces with the active material. The advantages of GPEs outlined here are expected to pave the way to the successful use of Na–S batteries in flexible energy storage devices.

Cathode Preparation: The SPAN active material was synthesized according to the literature.$^{[10]}$ Briefly, 2.0 g of poly(acrylonitrile) (PAN, $M_w = 150,000$ g mol$^{-1}$, D = 3.6, Sigma-Aldrich) was placed in a quartz tube together with sulfur (ca. 20 g, Carl Roth) and the mixture was deoxygenized with nitrogen. The tube was heated to 150 °C to compact the sulfur and then transferred to a furnace (Nabetherm, Germany) to further increase the temperature to 550 °C for 3 h under a constant nitrogen flow (200 L h$^{-1}$). To remove excess sulfur, the SPAN was subjected to Soxhlet extraction with toluene for 48 h. Elemental analysis revealed a sulfur content of 40.24 ± 0.03 wt.%. The composite cathode was prepared by mixing 70 wt.% of SPAN, 20 wt.% of carbon (C-65 MTI corporation), and 10 wt.% of Na-CMC binder (high viscosity, Sigma-Aldrich) in water using a planetary mixer (Thinky, Japan) at 2000 rpm for 15 min. The resulting slurry was coated (wet thickness, 300 μm) on a carbon-coated aluminum foil (16 μm, MTI Corporation) with the help of a blade coater (Erichsen, Germany). After drying at 60 °C overnight, the cathode was punched into disks 12 mm in diameter. The average sulfur content per cathode was 0.7–0.8 mg. Pure metallic sodium was cut and rolled on a polyethylene surface and then pressed into 12 mm disks.

In situ Polymerization of Precursor Solution and Cell Assembly: The cell assembly was carried out in an argon-filled glovebox (O$_2$, H$_2$O < 0.1 ppm). Swagelok-type cells were used for in situ polymerization and subsequent electrochemical characterization. First, sodium metal was placed inside the cell container on a stainless-steel stem followed by a single glass fiber sheet (Ø = 13 mm, Whatman). To maintain accurate conditions, 80 μL precursor solution were injected into the glass fiber separator for all cells. The SPAN cathode was wetted with precursor solution before placing it into the cell compartment. The assembled cells were aged for 2 h before placing them inside an oven at 70 °C. To ensure steady-state temperature throughout the cell, 6 h of heating was maintained. Finally, cells were cooled to room temperature followed by resting at OCV for 2 h to maintain a constant voltage before testing.

Electrochemical Characterization: A Biologic VMP3 analyzer (France) was used for LSV, CV, potentiostatic electrochemical impedance spectroscopy (PEIS), galvanostatic intermittent titration technique (GITT), and overpotential measurements. Galvanostatic long-term cycling tests and rate performance tests were conducted using BasyTec XCTS-LAB systems (Germany). LSV was conducted applying a scan rate of 1 mV s$^{-1}$ in a three-electrode setup with platinum, copper, carbon paper, graphite, and stainless steel working electrodes (all vs Na/Na$^+$). CV measurements were conducted between 0.5–3 V using SPAN as a working electrode and sodium as a reference and counter electrode. Ionic conductivity measurements were carried out using PEIS between 0.5 Hz and 500 kHz applying an alternating current amplitude of 10 mV using SS blocking electrodes. Cells were measured between −25 to 40 °C using temperature intervals of 5 °C and rested for 4 h at each temperature to attain thermal equilibrium. The resulting impedance curve was fitted using the built-in Z-fit library. GITT of Na–S cells was performed at different cycles by cycling the cell at 0.1 C for 20 min, followed by a 2 h relaxation period until the battery was fully charged/discharged. Symmetric Na||Na cells with a GPE were measured to obtain the plating/stripping overpotential at defined current densities. Galvanostatic charge/discharge was conducted at different C-rates (1 C = 1672 mA g$^{-1}$) between 0.5–3 V versus Na/Na$^+$. Unless mentioned otherwise, all cells were subjected to one preformation cycle at 0.3 C prior to testing.

Statistical Analysis: All electrochemical tests were carried out with the help of two identical cell setups. The standard deviation was calculated for each data point and the maximum value was taken into account. The standard deviation (%) for all long-term cycling tests (at 2 C) and for cycling at 0.2 C was <6% and <4% for the rate capability tests (1–4 C).

Computational Details: Binding energies of the molecular geometries were calculated with the Gaussian 09 software package$^{[68]}$ using DFT. Geometries were optimized on the B3LYP/6-31+G(d,p) level. On these optimized geometries, single-point energies were calculated at the B3LYP/6-31+G(2d,p) level. Binding energies include zero-point vibrational energies (ZPE) and are related to the energies of the separated compounds. Molecular electrostatic potential (MEP) maps were computed on the B3LYP/6-31+G(2d,p) level.

Supporting Information

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

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

gel polymer electrolytes, in situ polymerized electrolyte, polysulfide confinements, room-temperature sodium-sulfur batteries, sulfurized poly(acrylonitrile)

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