

Propylamine solvent co-intercalation in graphite electrodes for low temperature sodium-ion batteries[☆]

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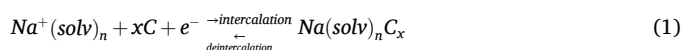
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ABSTRACT

The combined intercalation of ions and solvents in layered structures—known as *solvent co-intercalation*—opens new pathways for designing advanced electrode materials. Here, we demonstrate electrochemically driven solvent co-intercalation in graphite electrodes using propylamine (PN) as the solvent and NaPF₆ as the conductive salt, yielding an interlayer spacing of 7.09 Å. Due to its low melting point and low viscosity, PN enables excellent low-temperature performance, with effective operation down to −30 °C. The poor cycle life is shown to be significantly improved by adding diglyme (2G) as second solvent, which is well-known to also undergo co-intercalation with Na⁺. The combined intercalation of PN and 2G results in the formation of quaternary graphite intercalation compounds (q-GICs). The properties of the electrolytes and electrodes are studied by galvanostatic cycling, X-ray diffraction, electrochemical impedance spectroscopy (EIS), *operando* microscopy, *operando* dilatometry, mass measurements, and theoretical modeling. Our results show that, in PN-based electrolytes, the number of co-intercalating solvent molecules varies strongly with the state of charge. At the beginning of the sodiation, more than 90 PN solvent molecules intercalate per Na⁺. This number decreases significantly as sodiation progresses, reaching an average of 3.6 PN molecules per Na⁺ in the fully sodiated state, corresponding to a stoichiometry of [Na:(PN)_{3.6}]C₂₈ (80 mA h g^{−1}). Using PN also reduces the extent of electrode expansion and shrinkage during cycling, and it offers lower resistance and faster ion diffusion compared to pure 2G electrolytes. Overall, the combination of amines and ethers proves to be a promising strategy for tuning sodium storage properties in graphite electrodes.

1. Introduction

Reactions based on solvent co-intercalation became an emerging research field for designing new electrode reactions or materials [1]. While recently solvent co-intercalation has also been shown for layered sulfides [2,3], the most prominent example are ternary graphite intercalation compounds (t-GICs) that can be formed in sodium-ion cells through combined intercalation of Na⁺ and solvents such as diglyme into graphite electrodes at potentials below about 1 V vs. Na⁺/Na [1,4,5].



This process may enable the use of graphite as anode material for sodium-ion batteries (SIBs). The co-intercalation reaction typically provides values for the specific capacity of about 110 mA h g^{−1} and has been shown to be reversible for 1000 cycles or more without negligible capacity loss [4,6,7]. The co-intercalation reaction is also fast because the diffusion of the solvated ions in the graphite structure is easier as compared to the diffusion of bare ions [3,8,9]. Moreover, the charge transfer resistance is low as co-intercalation avoids the desolvation step, which is often the rate-limiting step at sub-zero temperatures [10,11]. Overall, this makes solvent co-intercalation an attractive approach for designing electrode reactions [4–6,12,13].

In this regard, it is important to note that recharging of conventional lithium-ion batteries (LIBs) at low temperature represents a challenge in

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general due to various factors [14]. Lowering the temperature leads to a viscosity increase and hence a conductivity decrease, especially for electrolytes containing the common ethylene carbonate (EC). Combined with the reduced ionic diffusion inside the graphite lattice, this causes polarization of the electrode and hence dendrite formation can occur which is a severe safety issue [15,16]. Several approaches have been proposed to overcome these issues such as heating [17], or the use of co-solvents to enhance the properties of the electrolyte at low temperatures [18,19]. Consequently, the combination of a process with no desolvation step and an electrolyte with a broad liquid range and low melting point can be an effective approach to overcome [13] the current limitation of LIBs at low temperatures.

Unlike for conventional intercalation reactions, in co-intercalation reactions the solvent becomes part of the electrode net reaction, meaning that the voltage profiles will depend on the electrolyte formulation (salt concentration and type of solvent(s)) [2,12,20,21]. In this sense, the voltage plateau characteristic of glyme solvents can be shifted by few hundred millivolts depending on the length of the solvent molecule employed as reported by Goktas et al. [7,13,20].

The selection of the electrolyte solvent has not only an influence on the electrochemical performance but also an effect on the structural properties of the host material. As the intercalating sodium-solvent complexes are comparably large, the reaction causes a notable expansion of the graphite lattice. For diglyme as solvent, the graphene interlayer space increases from 3.35 Å to 11.6 Å, resulting in significant electrode thickness increase ($\approx 175\%$) during the first sodiation, followed by 46–49% breathing during cycling [6,22,23].

Most studies on co-intercalation to date have focused on using ethers, particularly glymes, as solvents. To reduce the extent of volume expansion, it is crucial to explore alternative solvents that can promote a denser structure [2]. At the same time, selecting an electrolyte with superior electrochemical properties at low temperatures would be a major enhancement too. This aspect became recently more relevant as many SIBs are advertised for their better low-temperature performance compared to LIBs. Regarding the volume expansion, the addition of ethylenediamine (EN) as a co-solvent in diglyme (2G) electrolytes has been shown to be very effective [22,24]. The resulting compounds are called quaternary graphite intercalation compounds (q-GICs) as they contain Na, graphite and two different solvents. Mixing EN with 2G is necessary as EN alone reacts too violently with Na metal causing poor performance in half-cell experiments [22]. Another example is the combination of 2G with tetrahydrofuran (THF) or 1,3-dioxolane (DOL) for which also a reduced expansion was found [21]. Interestingly, neither THF nor DOL can co-intercalate on their own. In this case, 2G acts as a promoter, expanding the graphite interlayer space. Once the lattice is sufficiently expanded, both THF and DOL can co-intercalate. Recently, Gossage et al. reported that the branched diamine electrolytes e.g., 1,3-diaminopentane (13DAP), and 2-methyl-1,5-diaminopentane (2M15DAP) also show solvent co-intercalation along with Na^+ into graphite reaching a specific capacity of 130 mA h g⁻¹ [25]. The majority of studies conducted on amine-based solvent electrolytes have focused on diamines or multifunctional amines, which have been employed as co-solvents or coordinating molecules in battery electrolytes [25,26]. In contrast, primary amines containing a single amino group ($-\text{NH}_2$) are more commonly used intercalated in layered structures in applications such as adsorbents, catalysis, and photo/electro-functional materials, and chemical synthesis [27–29] as well as in CO_2 capture through nucleophilic nitrogen-electrophilic carbon bonding [30,31]. However, the use of primary amine-based solvent for the electrolyte in batteries remains largely unexplored, particularly with respect to their low-temperature electrochemical behavior.

At the same time, studies on the temperature dependent behavior of solvent co-intercalation reactions remain relatively scarce. Goktas et al. studied co-intercalation reactions between 20 °C and 80 °C and found that co-intercalation reactions (including crown ethers) can be activated at elevated temperature [20]. At negative temperatures, the mobility of

the solvated ions in the graphite lattice decreases as evidenced by Escher et al. [9] and Gotoh et al. [8] through ss-NMR measurements at -30 °C and -40 °C. Chen et al. showed that at -70 °C, sodium-ion cells with a co-intercalation anode still delivered 61% of their room temperature capacity [32]. All these studies utilized glymes as solvents for the co-intercalation reaction. Improvement may be achieved by other solvents and the use of solvent co-intercalation for low-temperature applications has gained momentum [1,33].

Here, we address for the first time the use of 1-propylamine (PN) as solvent for co-intercalation reactions in SIBs with graphite as electrode and at low temperatures of -30 °C. By structure, PN is derived from EN by the substitution of one $-\text{NH}_2$ group with a methyl group ($-\text{CH}_3$). Compared to 2G, PN is approximately 70% cheaper [34] but shows similar battery relevant properties with respect to the dielectric constant (ϵ), density (ρ), and dipole moment (μ) [35–37]. Improvement in conductivity can be expected from the lower viscosity (η) of PN compared to 2G [37,38]. Moreover, even though PN has a narrower liquid range (melting temperature – T_m to boiling temperature – T_b) than 2G, its lower T_m could enhance performance in low temperature conditions (see Table S1) [37,38].

Overall, PN shows properties that make it a promising solvent for designing low-temperature batteries. The use of PN in co-intercalation reactions is also motivated by findings from Maluangnont et al. on the chemical synthesis of Li^+ and Na^+ t-GICs with PN molecules with a composition of $\text{Na(PN)}_{0.7}\text{C}_{16}$ [39,40]. The electrochemical and reversible formation of these compounds, however, has not been demonstrated to date yet. In this work, we investigate the electrochemical reaction of graphite in half cells with Na as counter electrode and 2G and PN as electrolyte solvents. The behavior was studied at various temperatures in the range of -30 and $+20$ °C. The reaction mechanism was studied by X-ray diffraction (XRD) and by *operando* electrochemical dilatometry (ECD). The latter method probes the thickness variation of the electrode during charging/discharging [22]. Finally, the stoichiometry of the resulting GICs was determined by support of mass measurements and theoretical calculations were carried out to support these findings.

2. Results and discussions

Fig. 1 shows some key properties of the solvents used in this study. While the viscosity has an impact on the ion mobility, the dielectric constant reflects the ability of the solvent to dissociate salts. In theory, high dielectric constant and low viscosity improve ion transport. As can be observed in Fig. 1c), 1-propylamine (PN) has a similar dielectric constant value as 2G, and a lower viscosity. Beyond individual physicochemical properties, the electrostatic potential (ESP) is another descriptor also a factor worth considering for selecting solvents in electrolyte design. The ESP reflects the unbalanced distribution of charge of solvent molecules, with the values $\text{ESP}_{\min}$ and $\text{ESP}_{\max}$ indicating the most negative and positive electrostatic potential [44]. Zhao et al. classified solvents with $\text{ESP}_{\min}$ below -35 kcal mol⁻¹ as strong coordinating towards cations i.e. lower $\text{ESP}_{\min}$ values correspond to stronger cation-solvent interactions [45]. As can be observed in Fig. 1b), PN has the lowest $\text{ESP}_{\min}$ among the compared solvents [41–43], indicating a strong interaction with cations such as Na^+ . The liquid range of the solvents is shown in Fig. 1d). Among them, 2G has the second highest boiling point and has low melting temperature at sub-zero. Two solvents with lower melting temperatures than 2G are THF and PN. However, THF has been shown to be unable to co-intercalate into graphite layers without support from 2G and had a sluggish ion mobility from THF solvent molecule [21]. Therefore, PN can be considered a promising substitute solvent, especially for low temperature applications. Nevertheless, the toxicity of the PN solvent, comparable to that of EN, represents a drawback and therefore careful handling during cell preparation is necessary (a comparative analysis of the solvent hazards is summarized in Table S3). Consequently, the balance between electrochemical performance and safety must be carefully evaluated in cell

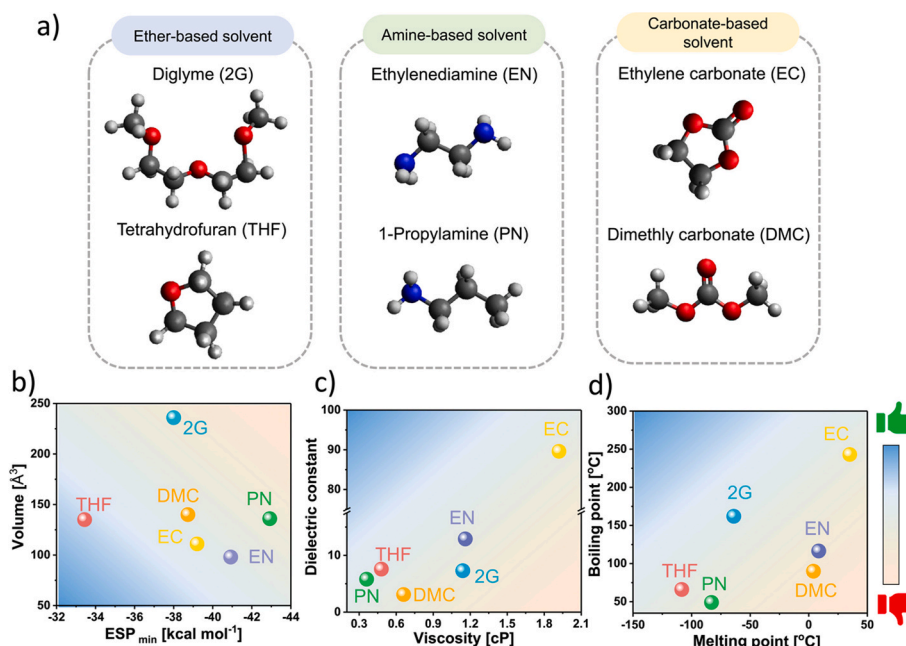


Fig. 1. Summary of solvent properties. a) 3D molecular structures with abbreviations. b) Molecular size and electrostatic potential (ESP_{min}) minimum (summarized in Table S2) [41–43] of the solvent molecules. c) Dielectric constant and viscosity of solvent molecules. d) Melting point and boiling point of solvent molecules. Details are summarized in Table S1.

design.

Given the favorable physicochemical properties of PN, such as low viscosity and strong coordinating ability, we further examined its compatibility with sodium metal since, as it has been reported before, the use of amines can have a detrimental effect on the electrochemical measurements on half cells due to the reaction of the sodium metal with the solvent [22].

Prior any electrochemical experiments, the chemical stability of Na against various electrolyte formulations was tested. The electrolytes contained NaPF₆ as conductive salt and PN or mixtures of PN and 2G as solvent(s) with volume fractions of PN of 10%, 50% and 90%. The use of pure PN or PN-rich electrolyte solutions causes an immediate reaction with the Na metal, seen by gas formation and darkening of the surface, see Fig. S1. The addition of 2G mitigates these side reactions. Interestingly, however, the dark surface layer disappears over a few days indicating that the Na metal is passivated and a stable condition is obtained that allows the assembly of electrochemical cells. Such a behavior was previously observed with longer branched diamines based electrolytes [25]. Next, the electrochemical stability was then tested in Na//Na symmetrical cells. For the pure PN electrolyte, a sufficient stability is observed over 170 h (~ one week) with values for the polarization that are even smaller compared to 2G (up to about 1.5 mV at 0.1 mA cm⁻²), see Fig. S1). Thus, even though the PN solvent initially reacts with the sodium metal, it does not impede the electrochemical study in a half cell configuration.

2.1. Electrochemical properties in different electrolytes

Fig. 2 shows the results from the voltage profiles of graphite//Na metal half cells between 2.0 and 0.001 V versus Na⁺/Na and their differential capacity plots. As can be seen in Fig. 2a), the voltage profile for the pure PN electrolyte exhibits a less defined shape compared to the pure 2G electrolyte and the capacity of $\approx 80 \text{ mA h g}^{-1}$ at 0.05 V is lower too. For the PN electrolyte, however, additional capacity is obtained by an additional low voltage plateau at 1 mV. While the origin of that plateau remains unclear, it might be caused by underpotential metal plating which can occur in case of uneven interface formation and hence

local changes in the potential (the measured value is always an average value). Similar findings have been observed for hard carbons, for example [46]. Smoother voltage profiles with less polarization were obtained when adding 2G to the electrolyte. Fig. 2a) shows the voltage profiles for a series of PN/2G mixtures – PN10, PN30, PN50, PN70 and PN90 electrolytes (the number corresponds to the volume fraction of the PN solvent in %). With the addition of 2G, the onset voltage for sodiation shifts slightly to higher values which can be well understood as 2G can act as promoter to other solvents for solvent co-intercalation, i.e., 2G molecules preferentially intercalate first and this way enable other solvents to co-intercalate [21].

The voltage profiles in the mixed PN/2G-based electrolytes can be divided into three regions: i) Region I: sloping behavior; ii) Region II: main plateau and iii) Region III: additional region characterized by a pseudo-plateau. An exception for region III is found for the pure 2G and PN10 electrolyte, which also shows an almost linear behavior similar to a pseudocapacitive mechanism [47]. It is seen that the voltage profiles depend on the PN/2G ratio clearly showing that both solvents participate in the co-intercalation reaction. An important observation is that only small amounts of 2G are sufficient to improve cycle life and Coulomb efficiency which can be ascribed to the better interaction between 2G solvent and the sodium metal leading to less side reactions in the half-cell configuration. In this sense and as shown in Fig. S2, pure PN demonstrates unstable capacity fading, while PN90 already exhibits improved cycling stability. Moreover, the addition of 2G also avoids the appearance of the low voltage plateau that is evident for pure PN. For PN30, PN50, and PN70, the voltage profiles are similar to pure 2G in Region I and II but deviate in Region III. This indicates again that 2G is preferentially co-intercalated at the beginning (Regions I and II) while at the end of sodiation, also PN impacts the storage behavior. This is in line with the findings by Son et al. for the combination of 2G with either DOL or THF, which also caused changes in the low voltage region [21].

The specific capacities achieved for the PN/2G-based electrolytes are similar to that observed for the pure 2G electrolyte. Fig. S3 displays the rate capability of graphite for cells with mixed electrolytes, with pure 2G electrolyte and with THF/2G-based electrolyte [21], reported before. Differing from the THF/2G-based electrolyte, the PN/2G-based

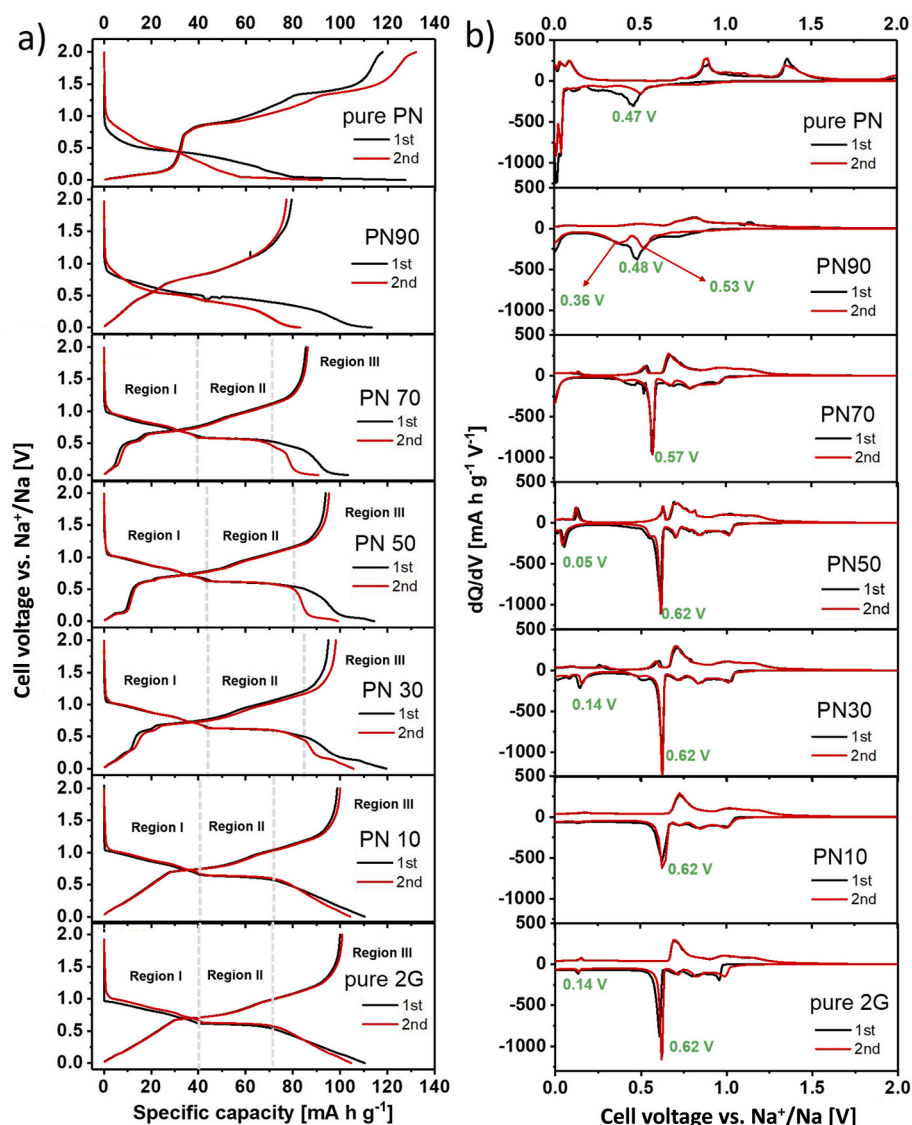


Fig. 2. a) Voltage profiles (first and second cycle) and b) differential capacity dQ/dV plots for graphite//Na metal half cells for electrolytes (1 M NaPF₆) containing different volume fractions of PN and 2G. Galvanostatic cycling was done at $C/10 = 11 \text{ mA g}^{-1}$ (1C corresponds to 110 mA g^{-1}) in a voltage range of 2.0–0.001 V versus Na^+/Na .

electrolyte demonstrates an excellent and better stability at high current densities, with nearly no capacity loss at 2C, comparable to pure 2G electrolyte confirming the good kinetics when PN/2G-based electrolytes are used.

Derivative plots show distinct differences across the various ratios of PN/2G-based electrolytes (Fig. 2b)). For the pure 2G electrolyte, a strong reductive peak at 0.62 V is observed, corresponding to the main plateau at high voltage, as well as a small peak at 0.14 V. In contrast, the derivative plot of pure PN electrolyte displays a broad reductive peak at 0.47 V and a sharp peak at 1 mV resulting from the low voltage process. The addition of PN to the 2G-based electrolyte resulted in a shift of the reductive peak from 0.62 V to a lower potential, as confirmed by the corresponding downward shift in the voltage plateau. This behavior is consistent with previously reported trends in THF/2G-based electrolytes [21], indicating a modified reduction process induced by PN.

2.2. Temperature-dependent measurements

In rechargeable batteries with graphite as the anode material, the desolvation process is considered the rate-determining step for thin electrodes and/or at low temperatures [10,48]. Therefore, suppressing

this step and enhancing charge transfer kinetics is important to improve battery performance, especially at very low temperatures. In particular, it has been shown that the co-intercalation mechanism enables a rapid charge transfer compared to the conventional intercalation reaction [49,50]. As discussed before, the physicochemical properties of different electrolytes are shown in Fig. 1 and Table S1. PN shows lower values for the melting temperature (T_m) and the viscosity (η) compared to 2G, indicating that the addition of PN can improve the low temperature performance. First, we investigated the ionic conductivities (σ) of the electrolytes at different temperatures (–30 to 80 °C), as electrolyte conductivity is a key metric for the electrochemical properties [36,51]. The ionic conductivities across different temperature ranges were evaluated and the activation energy was calculated separately for sub-zero and above-zero temperature. As can be seen in Fig. 3a), at above-zero temperatures, the conductivities of all electrolytes are relatively similar and in the same range. With decreasing temperature, PN-based electrolytes exhibit consistently higher ionic conductivity compared to the pure 2G electrolyte, and this difference becomes more noticeable as the temperature approaches –30 °C. According to the Arrhenius equation, the slope of the $\ln \sigma$ vs. $1000/T$ plot is proportional to the activation energy (E_a) for ion conduction. Therefore, the steeper the slope observed

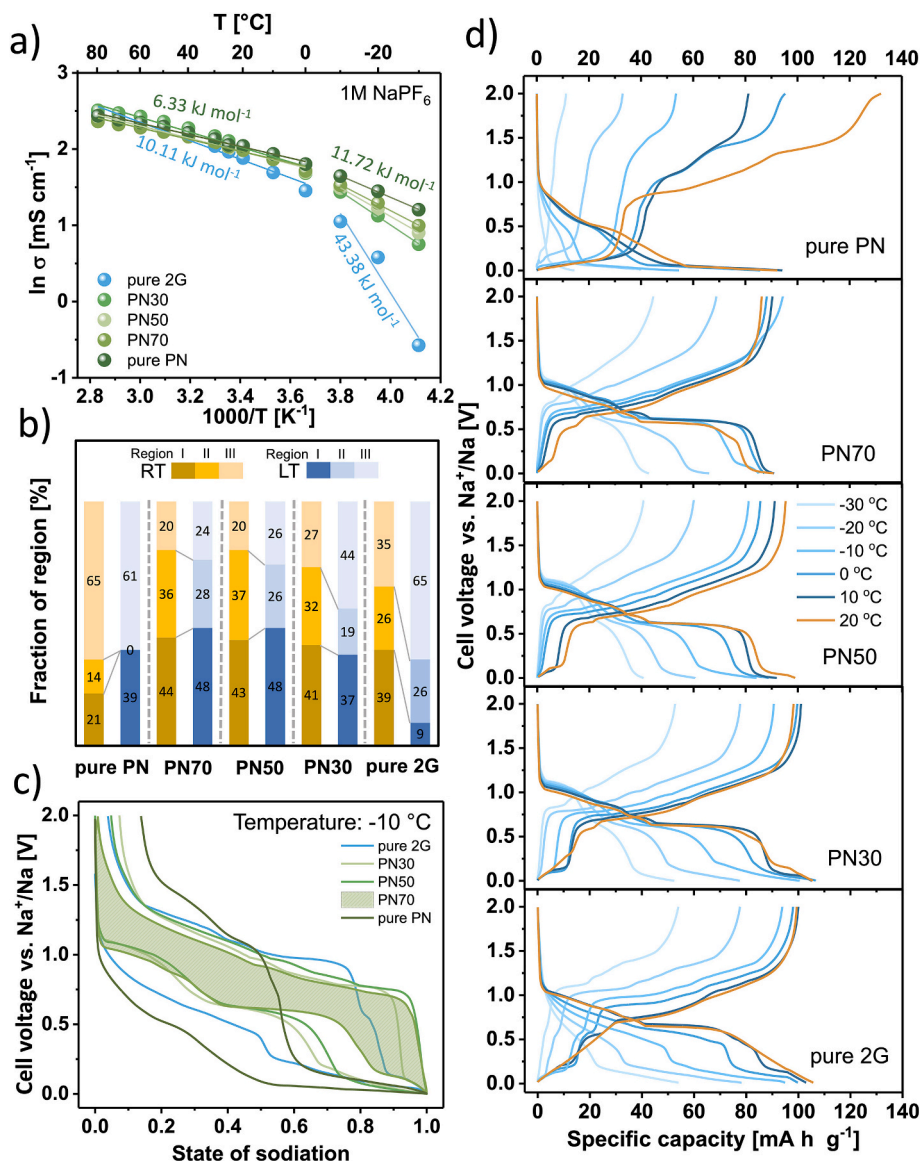


Fig. 3. a) Arrhenius plots of ionic conductivities vs. temperature for electrolytes containing different volume fractions of PN and 2G between -30 $^{\circ}\text{C}$ to $+80$ $^{\circ}\text{C}$, b) Voltage profiles of the graphite electrode for electrolytes containing different volume fractions of PN and 2G between -30 and $+20$ $^{\circ}\text{C}$ for the second cycle, c) schematic illustration depicting the fraction of each region (region I, II, III) at the different temperatures – room temperature (RT: 20 $^{\circ}\text{C}$) and low temperature (LT: -30 $^{\circ}\text{C}$) extracted from b) and d) Hysteresis plots of graphite//Na metal half cells for the various electrolytes at -10 $^{\circ}\text{C}$. All measurements were done at 11 mA g^{-1} with NaPF_6 (1 M) as conductive salt.

for the pure 2G electrolyte indicates a higher activation energy in the sub-zero temperature region compared to the PN/2G-based electrolytes. In particular, the conductivity of pure PN electrolytes (σ_{PN}) exhibits the least variation with temperature with the lowest activation energy, and values of 11.72 kJ mol^{-1} at temperatures below zero and 6.33 kJ mol^{-1} at temperatures above zero, as determined from the Arrhenius plot. Both values are lower than those observed for the pure 2G electrolyte. The activation energy values of pure 2G and PN/2G-based electrolytes in sub-zero and above-zero are summarized in Table S4.

Fig. 3b) displays the voltage profile changes of graphite in the examined electrolytes across a temperature range of -30 to $+20$ $^{\circ}\text{C}$. Notably, the pure 2G electrolyte manifests the most significant change in voltage profile with a substantial decrease of the main voltage plateau, and the appearance of an additional plateau region at low potentials (Region III) and an increased in overpotential. However, when PN was added to the 2G electrolyte, the voltage profiles retain relatively well their curves at different temperatures (see Fig. 3b)).

Fig. 3c) shows the voltage profile fraction of each region for all the

electrolytes at room and at low temperatures. As can be observed, with increasing content of PN, the fraction of each region remains more stable and less affected by the temperature drop, as seen in PN70. The second cycle of hysteresis plots of graphite electrodes at -10 $^{\circ}\text{C}$ for different electrolytes is displayed in Fig. 3d). Among all the samples, PN70 exhibits the smallest voltage gap of 220 mV, indicating the lowest polarization, unlike the 2G electrolyte with a much larger gap of 750 mV.

2.3. Electrochemical impedance measurements (EIS)

Temperature-dependent electrochemical impedance spectroscopy (EIS) was carried out to study activation energy trends in different electrolyte solutions (1 M NaPF_6 in pure PN, pure 2G, and PN70) in the range of -30 $^{\circ}\text{C}$ to $+35$ $^{\circ}\text{C}$ with respect to R_{bulk} and R_{pore} . R_{bulk} represents the resistance of the electrolyte solution while R_{pore} is the diffusion resistance of the solvated ions inside the pores. To eliminate contributions from a sodium metal counter electrode in the EIS measurements, temperature-dependent impedance measurements were performed

using a symmetrical cell setup (see Fig. 4d)), as described by Ogiwara et al. [52]. Therefore, two graphite electrodes with similar mass loadings were cycled to the same state of charge (SOC = 50%), harvested and reassembled in a new cell prior to the EIS measurements.

To obtain the respective values for R_{bulk} and the R_{pore} , the impedance results have been fitted to the equivalent circuit model (ECM) displayed in Fig. 4e), and Fig. S4. The ECM includes a TLM (transmission line model) to model the ion diffusion. The TLM, incorporating a CPE element as described by Bisquert et al. [53], is used to represent the nature of the co-intercalation process, especially the ion transport through the electrolyte-filled porous graphite electrode. In the TLM (see Fig. S4), generally R_{pore} describes the resistance encountered by solvated ions during the diffusion through a porous system – in the case of solvent co-intercalation, the porous system is formed through the expansion of the interlayer space [47]. The ion transport is indicated in the Nyquist plot by the slope in the mid-frequency region and the blocking-condition is indicated by the capacitive behavior in the low frequency region. As shown in Fig. 4 a-c), PN-based electrolytes exhibit lower resistance compared to that of pure 2G electrolyte. Particularly, the R_{bulk} of 2G increases substantially under sub-zero temperature conditions as can be observed in Fig. 4c).

The activation energies were determined from the obtained values of R_{bulk} and R_{pore} by performing Arrhenius fits and are shown in Fig. 4 f-g). It can be seen from Fig. 4f) that R_{bulk} and the respective activation energy (see inset table) of the PN containing electrolyte solutions are lower than those obtained with 2G as solvent. R_{pore} shows a similar trend (see Fig. 4g)), indicating that the ion transport mechanism proceeds to a high

degree through ion transport within the electrolyte solution filled pore, and that electrolyte conductivity highly affects the diffusion properties in the porous electrode. While 2G as a solvent exhibits a severe decrease in activation energy for the respective conductivities below 0 °C, the activation energy for PN-based electrolytes remains relatively stable.

Overall, the EIS measurements suggest that the enhanced properties for the PN-based electrolyte are mainly caused by the higher electrolyte conductivity in the electrolyte filled pores. Activation energies for the PN-based electrolytes are lower compared to 2G-based electrolytes with a stable trend even at low temperatures. Two important conclusions can be drawn when taking results from EIS, galvanostatic cycling and plating/stripping experiments together. First, PN-based electrolytes exhibit lower resistance and faster ion mobility, which can lead to reduced polarization during sodium plating/stripping measurements compared to 2G. Second, the beneficial properties of PN could explain why it delivers better electrochemical performance than the pure 2G electrolyte at low temperatures.

2.4. Structural analysis: X-ray diffraction

To further investigate the reaction mechanism of the PN/2G-based electrolyte system, XRD measurements were performed at different de/sodiated states (see Fig. 5). Previous studies on Na^+ -2G-GICs have shown peaks related to co-intercalated graphite appear at 15.5° (002), 23.3° (003), 31° (004) [4,6,50,54]. For the pure PN electrolyte, multiple peaks appear in the XRD pattern with a high-intensity peak at $\approx 7.3^\circ$, in the fully sodiated samples (see Fig. 5a)). We have conducted

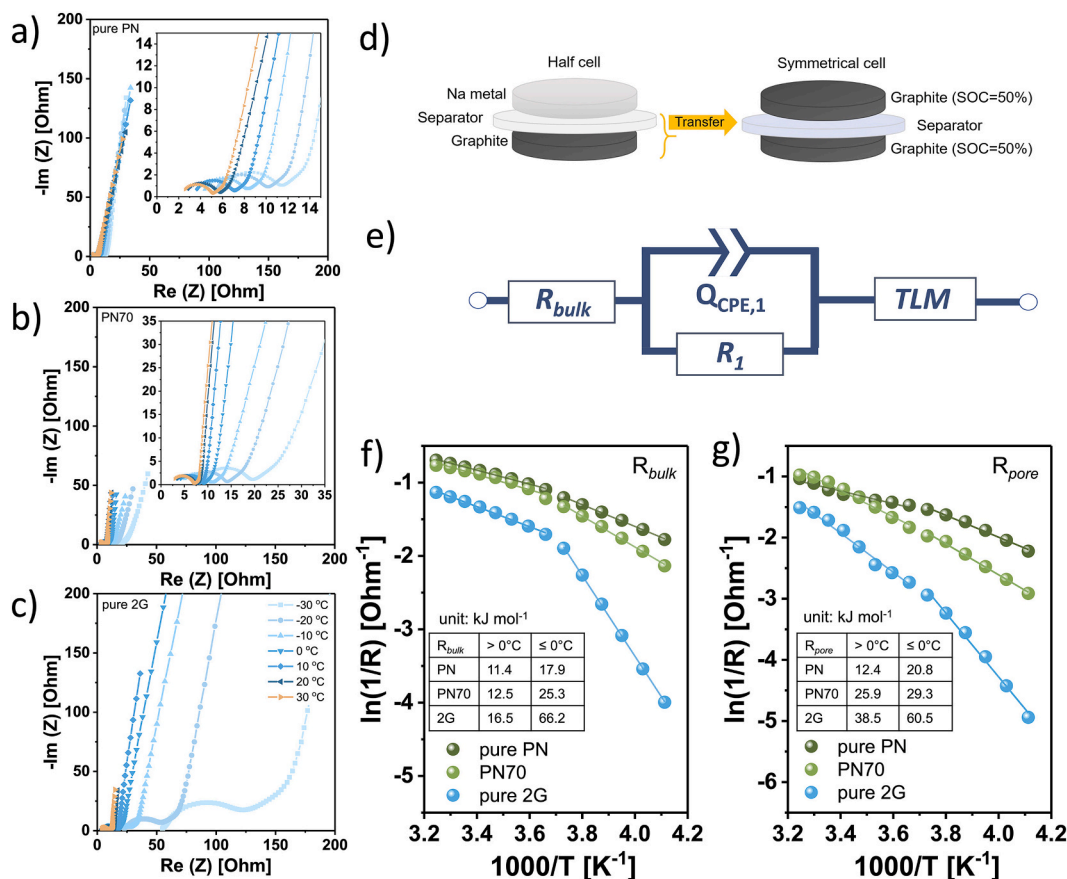


Fig. 4. Nyquist plots of graphite//graphite (SOC = 50%) symmetrical cells with of NaPF_6 (1 M) in a) pure PN, b) PN70 and c) pure 2G as electrolyte solution at various temperatures. d) Illustration of the preparation of the symmetrical cell setup and e) applied equivalent circuit model (ECM) with R_{bulk} indicative of the resistance of the electrolyte solution, R_1 and $Q_{\text{CPE},1}$ for the semi-circle in the high-frequency region are indicative of setup and/or surficial transport processes. Arrhenius plot of f) the bulk conductivity of the electrolyte solution and g) the ionic conductivity of the ions within the pores retrieved by applying the transmission line model (TLM).

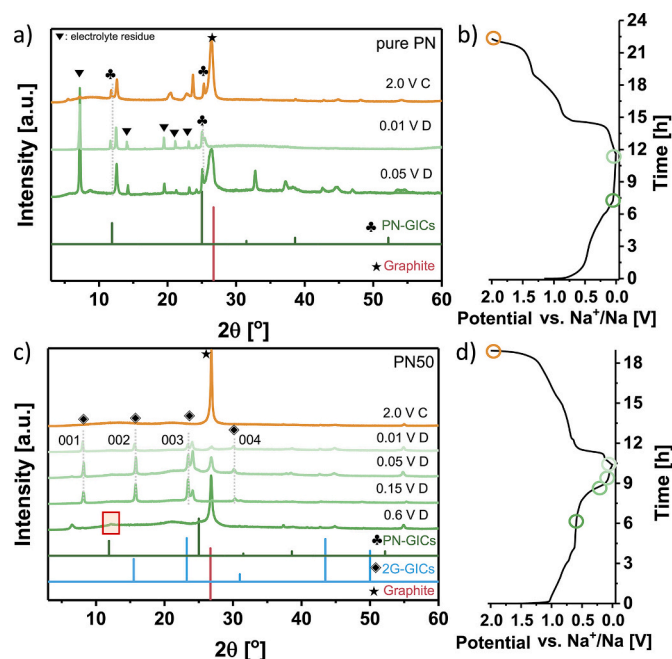


Fig. 5. X-ray diffraction patterns of the graphite electrodes at different voltages in a) pure PN and c) PN50 based-electrolytes and b) and d) their corresponding voltage profiles. (XRD pattern of Na⁺-2G-GICs at fully sodiated state is taken from reference [5], and chemically synthesized Na⁺-PN-GICs is taken from reference [39].)

supplementary XRD experiments on the uncycled graphite electrode immersed in the electrolyte and observed the aforementioned peak in conjunction with additional signals at approximately 14°, 21°, and 23° (refer to Fig. S5). After drying, only the peaks located at 21° and 23° remain, attributed to residual electrolyte salt [47]. Thus, this peak likely results from solvent uptake, which disappears during drying process. Maluangnont et al. already correlated the existence of the peaks at 12° and 25° to the formation of t-GICs of sodium with PN, with an interlayer distance of 7.01 Å [39,40]. In the present study, the peaks at 12° and 25° are observed at both 0.05 V and 0.01 V, accompanied by a decrease in the (002) graphite peak when using the pure PN electrolyte with an interlayer distance of 7.09 Å, which is comparable to the reference. Upon desodiation, the graphite peak at 26.5° reappears, along with some electrolyte impurities. In addition, there is still the presence of co-intercalation peaks that can be explained by the incomplete reversibility of the process. The XRD pattern showed no sign for sodium metal plating. This could be attributed to the small amount, amorphous nature or nanoscopic size of the plated sodium.

When the electrodes are cycled with the mixed electrolyte (PN50), no residual electrolyte is observed compared to pure PN electrolyte which can be attributed to the lower boiling point of the PN solvent that affects the ex-situ results and to the proximity of the 2G co-intercalated peaks that can obscure the regions where residual electrolyte peaks would otherwise appear. Notably, only the solvent co-intercalation signal of pure 2G electrolyte is observed, which can be correlated to the larger expansion compared to the pure PN electrolyte, making it dominant. Besides, Fig. S6 shows the results of XRD measurement in different PN/2G-based electrolytes at fully sodiated state. Interestingly, when PN is the dominant solvent (PN70), a small co-intercalation peak that corresponds to that observed previously for pure PN (12° and 25°) is observed. Overall, at an equal volume ratio of 2G and PN, 2G dominates the co-intercalation reaction at the fully sodiated state.

To support the findings obtained from XRD diffraction, *operando* optical microscopy was employed. The results of pure PN indicate a color change in the graphite particles during cycling (see Fig. S7). During discharge, graphite progressively darkens, appearing blue in the

fully sodiated state. Upon desodiation, the graphite recovers its original dark gray coloration, demonstrating the reversible process. This color change is characteristic of GICs and also in line with our previous findings on co-intercalation reactions [47,55,56] suggesting that PN is reversibly co-intercalating into the graphite structure (See Fig. S7).

2.5. Mass and volume changes of graphite electrode

Mass measurements were conducted based on the methodology outlined by Åvall et al. [47] to investigate the mechanism of solvent co-intercalation into graphite with pure PN and PN/2G-based electrolytes. At high voltages (i.e., low state of sodiation, SOS), a mass increase of approximately 20–30% was observed in all electrolytes, with a slightly higher increase for the PN-based electrolytes. This result suggests that a large amount of solvent, in addition to [Na_x:PN_y]⁺ complexes (similarly to those observed with the pure 2G electrolyte), initially co-intercalate into the graphite layers. Thus, this process likely creates space for additional free solvent molecules to flood into the graphite structure. Compared to 2G, there is mass increase trend in the PN50 electrolyte similar with 2G until the main plateau is reached. During the last stage of sodiation, a decrease in mass is observed in the PN50 during the slope region which can be ascribed to the ejection of the solvents on the last stages of sodiation (see Fig. 6a).

Based on the weight change, the calculation of PN solvent molecule per Na⁺ into the graphite galleries was conducted. Åvall et al. have already provided two different approaches to analyze the number of PN solvent per Na⁺; i) difference method: determining the mass difference directly between the sodiated and desodiated samples, without accounting for the drying time and ii) extrapolation method: Applying an extrapolation to fit the data, accounting for the degradation of the sodiated samples over drying time and the mass of initial time point [47]. Here, we applied extrapolation method for the calculation of the solvent molecules. The mass change of the sodiated and desodiated samples as well as the total weight change calculated from extrapolation method are displayed in Fig. S8. As same as the previous report [47], the results from the PN50 electrolyte exhibit trends similar to those observed with the 2G-based electrolyte. In the case of the pure PN electrolyte, the sodiated sample exhibits a dynamic increase in mass change throughout the SOS, while the desodiated sample maintains relatively stable mass until the end of the plateau region. The plateau region refers to the SOS point at 0.4. After this point, both the sodiated and desodiated samples show a sharp increase in mass, which may be relate to the sodium plating (as previously discussed).

From the mass variation, the number of PN per Na⁺ in graphite can be calculated and the results are displayed in Fig. 6b). The pure PN electrolyte displays a similar trend, compared to the pure 2G electrolyte, of solvent flooding and presenting a high number of PN solvent molecules per Na⁺ at low SOS. When the sodiation continues, a drastic decrease in the number of PN molecules per Na⁺ in graphite is observed, indicating the replacement of free solvent molecules in the graphite galleries with sodium solvated ions. Ultimately, at 0.8 SOS, just before entering the low voltage plateau, 3.6 PN molecules co-intercalate with each Na⁺, yielding an approximate stoichiometry of [Na:(PN)_{3.6}]C₂₈. This calculated stoichiometry differed to that previously reported for the chemically synthesized Na⁺-PN-GICs with the monolayer arrangement of solvent molecules with a ratio of PN molecules per sodium ion of 0.7, forming [Na:(PN)_{0.7}]⁺C₁₆[40]. The low voltage plateau followed a final mass increase between that might correspond to sodium metal plating in Fig. 6b).

In summary, the results of mass measurements show that more PN molecules are coordinated with sodium ions compared to chemically synthesized Na⁺-PN-GICs. At the beginning of sodiation the number of co-intercalated solvent molecules per Na⁺ is even higher than that of Na⁺-2G-GICs. This finding indicates the PN solvent can be also an attractive candidate for (electro)catalysis under nanoconfinements due to the fast diffusion kinetics [57].

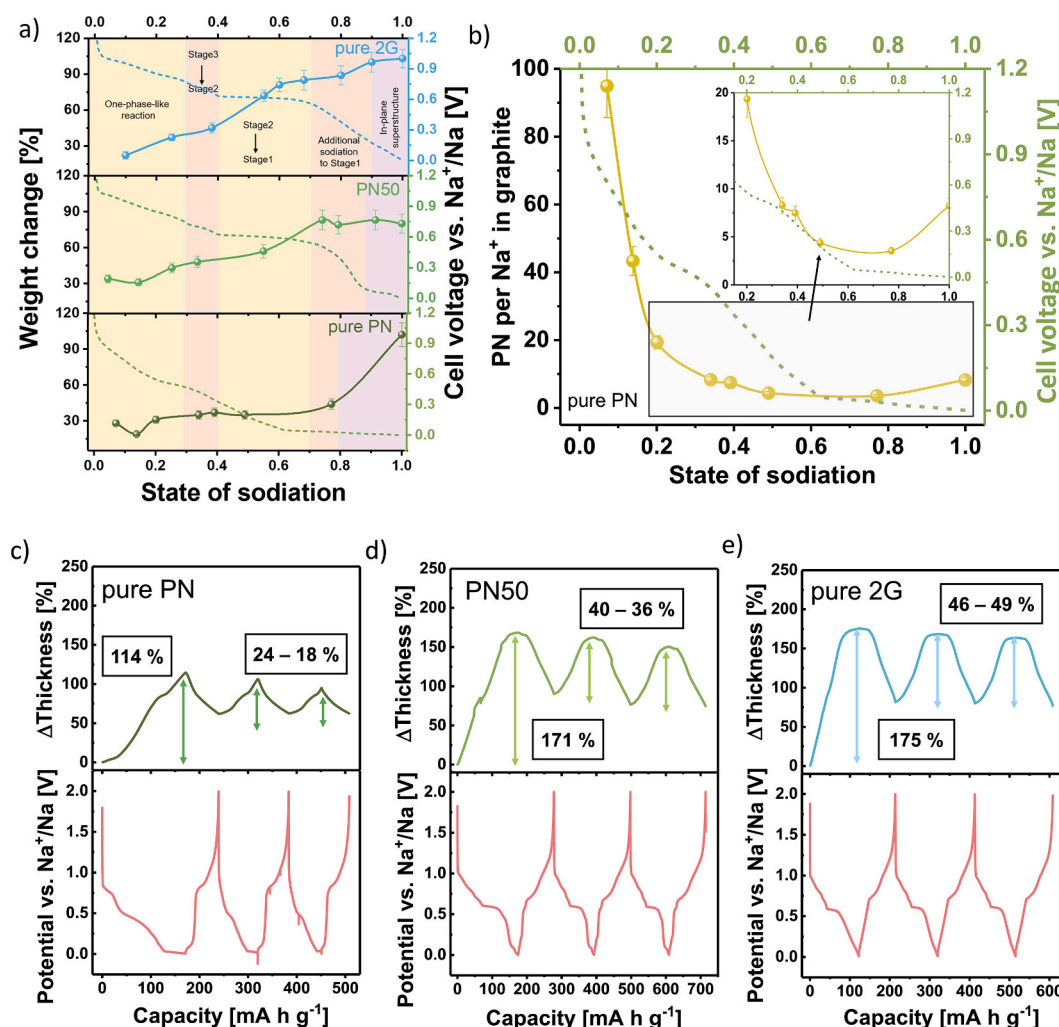


Fig. 6. a) Weight change of graphite electrodes in 1 M NaPF₆ with pure 2G (blue), PN50 (green), and pure PN (olive) electrolyte after sodiation. The dashed line corresponds to the voltage profile of the first sodiation, while the solid line represents the mass change due to the intercalant (solvent and cation), calculated using the mass extrapolation method (see the reference [47]). b) The number of PN per Na^+ in graphite, calculated by the mass extrapolation method (olive line) and voltage profile of the second sodiation (olive dashed line). Error bars were calculated with the standard formula for the propagation of error from the mass measurements. *Operando* electrochemical dilatometry measurement (three-electrode set-up) of graphite electrodes over 3 cycles with NaPF₆ (1 M) in c) pure PN, d) PN50 and e) pure 2G. The cells were equilibrated for six hours at open circuit potential. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Operando electrochemical dilatometry is a valuable tool for observing the macroscopic volume expansion of electrodes during cycling. Compared to pure 2G electrolyte, pure PN electrolyte exhibits a lower volume expansion and breathing of the graphite electrode, with values of 114% and 24–18%, respectively. A similar behavior has been reported for the co-intercalation of ethylenediamine [22]. This result shows that the use of amines can mitigate the electrode expansion/shrinkage during cycling compared to pure 2G electrolytes. When comparing the dilatometry profiles, one can easily see a different behavior for the PN-based electrolyte compared to the others. The curve becomes steeper at potentials below 0.05 V versus Na^+/Na , which, as discussed before, hints on sodium plating, unlike the pure 2G electrolyte, which exhibited a constant thickness below the plateau [58]. This behavior has been discussed by Escher et al. for the case of hard carbon [46]. In the case of the PN50 electrolyte, which contains 50 vol% 2G, the volume expansion and breathing are fairly reduced relative to pure 2G electrolyte which indicates that the PN solvent can suppress volume expansion similarly to other diamine additives [22], as a result of the lower interlayer distance increase (see XRD discussion).

2.6. Theoretical considerations

It has been previously established that the solvation Gibbs free energy and the size of the solvation shell are essential parameters that determine the ability of reversible solvent co-intercalation [21,47,59]. Fig. 7 provides the calculated standards solvation Gibbs free energies of $[\text{Na}:(2\text{G})_n]^+$ ($n = 1-3$) and $[\text{Na}:(\text{PN})_m]^+$ ($m = 1-6$), calculated via $\Delta G^\circ = G([\text{Na}:(\text{solv})_n]^+) - G(\text{Na}^+) - nG(\text{solv})$, together with the optimized geometric structures of the most exergonic solvation shells. The molecular structures of the other solvation shells are provided in Fig. S9 in the Supporting Information. The calculated free energies per coordinating oxygen atom for $[\text{Na}:(2\text{G})_n]^+$ are in good agreement the literature for the solvation of sodium ions with other ether-based electrolyte solvents [60]. In line with previous studies, the most exergonic solvation Gibbs free energy, which corresponds to the thermodynamic equilibrium structure, is achieved for two 2G molecules that are six-fold coordinating the sodium ion [2,21,61].

The solvation free Gibbs energies of $[\text{Na}:(\text{PN})_m]^+$ are lower than that of $[\text{Na}:(2\text{G})_n]^+$ and other non-chelating oxygen-coordinating solvents [60]. This is due to the weaker donor-acceptor interaction between the

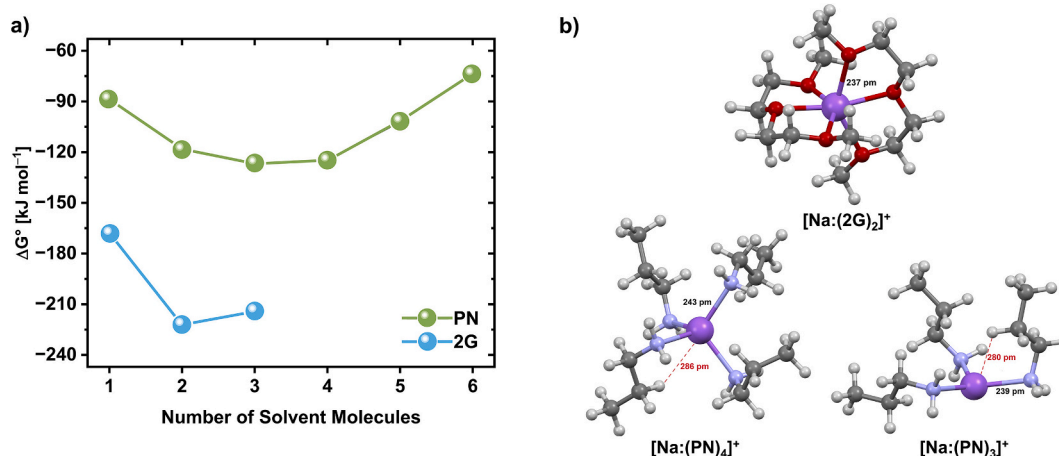


Fig. 7. a) Calculated solvation free energies of $[\text{Na}:(2\text{G})_n]^+$ ($n = 1\text{--}3$) and $[\text{Na}:(\text{PN})_m]^+$ ($m = 1\text{--}6$) together with b) the optimized geometric structures of the most exergonic solvation shells.

sodium ion and the nitrogen atom of PN. However, the Gibbs free energies remain reasonably exergonic, which rationalizes the observed reversible solvent co-intercalation. Interestingly, there is a near degeneracy between the Gibbs free energies for three and four PN molecules in the solvation shell, with -127 kJ mol^{-1} and -125 kJ mol^{-1} , respectively. This agrees with the experimental observation that sodium ions with three to four solvent molecules enter the graphite lattice. In addition to the donor-acceptor interaction of the nitrogen atom, a secondary dispersion interaction is present between the sodium ion and the β -hydrogen atom of PN, resulting in a quasi-chelating coordination. Consequently, while the molecular volume of PN solvent of PN is smaller than that of 2G solvent (Table S2), the volume of the solvation shell influenced the outcome. The volume of the $[\text{Na}:(\text{PN})_{3,4}]^+$ solvation shell (including the van der Waals radii of the hydrogen atoms) for three and four PN molecules are 268 and $340 \text{ \AA}^3$, respectively, which is very similar to that of $[\text{Na}:(2\text{G})_2]^+$ with $311 \text{ \AA}^3$. The radii of both $[\text{Na}:(\text{PN})_{3,4}]^+$ are with $6.8 \text{ \AA}$ found to be larger than for $[\text{Na}:(2\text{G})_2]^+$ with $5.46 \text{ \AA}$.

Overall, the calculated properties of $[\text{Na}:(\text{PN})_m]^+$ support the claim that PN, when used as an electrolyte solvent by itself, enables reversible solvent co-intercalation. Similar to our previous study [21], the calculated properties also indicate that when a mixture of 2G and PN is used as the electrolyte solvent, $[\text{Na}:(2\text{G})_n]^+$ initially co-intercalates within the graphite lattice, followed by $[\text{Na}:(\text{PN})_{3,4}]^+$ and potentially sodium ions with mixed solvation shell. This is well in line with the stoichiometry of $[\text{Na}:(\text{PN})_{3,6}]\text{C}_{28}$ as determined by the mass measurements.

3. Conclusion

This study presents the electrochemical demonstration of PN co-intercalation reaction in SIBs and its advantages at low temperatures for the first time. It also further highlights the rich chemical landscape of solvent co-intercalation processes, as multiple solvents can be involved in the reaction process, forming higher order graphite intercalation compounds beyond t-GICs. During galvanostatic cycling in Na//Na symmetrical cells, the pure PN electrolyte provided enhanced stability with lower polarization compared to the pure 2G electrolyte. In half cells (with Na as counter electrode), graphite exhibited a specific capacity of 130 mA h g^{-1} between 2.0 and 0.001 V, and 80 mA h g^{-1} in the voltage range of 2.0–0.05 V. The results obtained from XRD, and *operando* optical microscopy validated the co-intercalation of PN solvent molecules without the need for additional solvents or additives as promoters.

The stoichiometry of the Na^+ -PN solvation structure was determined using mass measurements and theoretical calculations. These findings corroborate the formation of stable solvation complexes, each

containing approximately three to four phosphorus-nitrogen (PN) molecules per sodium ion, resulting in an approximate stoichiometry of $[\text{Na}:(\text{PN})_{3,6}]\text{C}_{28}$. Additionally, *operando* electrochemical dilatometry (ECD) exhibited significantly lower graphite electrode expansion of 114% (breathing: 24–16%) in pure PN electrolyte compared to conventional pure 2G electrolytes. Even though cycle life was insufficient, it could be improved already significantly by adding smaller amounts of 2G.

Beyond demonstrating electrochemical solvent co-intercalation for PN, its favorable properties (low melting point, and low viscosity) combined with the low charge transfer resistance allows for an improved low-temperature performance. Notably, when using the mixed PN/2G-based electrolyte (PN70), graphite electrodes exhibited highly consistent voltage profiles over a wide temperature range from -30 to 30°C . This formulation also showed the lowest polarization among all tested electrolytes, including the pure 2G electrolyte. EIS experiments confirmed that PN-based electrolytes provide low resistance and faster ion mobility at lower temperatures in comparison to pure 2G electrolytes. This enhanced performance is attributed to the higher electrolyte conductivity in the pores of the graphite electrode.

In summary, these findings demonstrate the potential of PN as a cost-effective, high-performance electrolyte solvent for graphite electrodes in sodium-ion batteries (SIBs) for low-temperature applications.

4. Experiments

4.1. Cell preparation

Graphite electrodes were prepared by mixing graphite powder (MTI Corp.) with polyvinylidene fluoride (PVdF, from PI-KEM Ltd) at a mass ratio of 9:1 in *N*-methyl-2-pyrrolidone (NMP, from Sigma-Aldrich) as solvent. The mixed slurry was casted on carbon-coated copper current collector by doctor blade and dry at the room temperature for overnight. After punching the electrodes out in a diameter of 12 mm, the punched electrodes were dried at 110°C under vacuum. The average mass loading of the active material was $8\text{--}10 \text{ mg cm}^{-2}$.

The electrolytes were pre-dried overnight using porous molecular sieves ($3\text{--}4 \text{ \AA}$). Diglyme (2G, Sigma Aldrich) and 1-propylamine (PN, Alfa) were used with sodium hexafluorophosphate (NaPF_6 , purity $>99\%$, E-Lyte) as conductive salt.

4.2. Electrochemical measurement

Electrochemical measurements were carried out using CR2032 coin cell (MTI Corp.). The coin cells were assembled in an argon-filled glove box ($\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 0.1 \text{ ppm}$). The assembled coin cells contain

the prepared graphite electrodes as a working electrode and sodium metal (BASF) as the counter electrodes. For the separator, Whatmann glass fiber membrane (GF/A) was used with 100 μl of electrolyte. For galvanostatic cycling, the coin cells were cycled in the voltage range of 2.0 V – 0.001 V versus Na^+/Na .

Temperature-dependent galvanostatic cycling measurements were performed in the temperature chamber (Binder KB53). For the equilibrium of the OCV of the cell in particular temperature, the resting time was taken for 6 h for each temperature. After resting, the cycling measurements proceeded in the same manner as mentioned in the electrochemical measurement part.

4.3. Mass measurement

Mass measurements were carried out based on the previous publication from the Åvall et al. [47] All samples were prepared in graphite//Na metal half-cell in a coin cell set up. For each sodiated sample, a desodiated control sample was prepared. The sodiated sample implies the electrode sodiated to a specific state of sodiation while the desodiated sample was done by applying the same cycling protocol but adding a desodiation step at the up to 2.0 V versus Na^+/Na . The cells were held at the voltage for 6 h. All the cells were taken to an argon-filled glove box and were disassembled. Immediately after a cell was opened, the graphite electrode was carefully peeled from the separator and placed in a weighing boat to measure the mass on a Pioneer PX225D balance with a readability of 0.01 mg. The masses of the sodiated and desodiated samples were compared in order to exclude any time-dependent processes. A detail explanation of the method can be found here [47].

4.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were carried out using a symmetrical cell setup (graphite//graphite). Prior to the assembly of the symmetrical cell, the single electrodes were pre-cycled to 50% state of charge (SOC), defined as 50% of their previously determined specific capacity, under identical cycling conditions, in the respective electrolyte solutions (1 M NaPF_6 in pure 2G, PN70, and PN100). The symmetrical coin cells were probed via EIS using a potentiostat (BioLogic GmbH, SP-150) in the frequency range of 1 MHz – 50 mHz with a potential perturbation of ± 10 mV at different temperatures ranging from - 30 to 35 °C. Before each temperature step, the cell was left to equilibrate for at least 30 min. The results of the impedance measurements were fitted to the described ECM using an analyzing software (Relaxis 3) from rhd instruments.

4.5. Characterization

The ionic conductivities of electrolytes were induced with a conductometer (BioLogic GmbH) within the temperature range from -30 to 80 °C. The prepared electrolytes were stirred overnight and transferred to the conductometer. This process was conducted in the argon-filled glove box.

X-ray diffraction (XRD) measurements were performed by using a D2 Phaser XRD from Bruker with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm, 30 kV, 10 mA) between 3° and 60° (2 θ), with a step width of 0.02°. All electrodes for XRD measurements were prepared from the disassembled cells in an argon-filled glove box and measured in air-tight sample holders with a fixed knife edge which blocks background scattering relevant for the measurement below 5°.

Operando cell for optical microscopy was prepared in an argon-filled glove with an EL-Cell ECC Opto-10 cell holder with a face-to-face arrangement of the cut graphite electrode in rectangular shape as working electrode and 8 mm diameter of sodium metal as counter electrode with 45 μl of electrolyte. Two separators were used, one Whatman glass fiber membrane (GF/A) and one Celgard separator. The

cells were cycled at C/10. A digital optical microscope (Keyence VHX-7000) with a 500 $\times$ magnification was used and each image was taken every two minutes.

Operando electrochemical dilatometry (ECD) was assembled in an argon-filled glove box with a graphite electrode (diameter of 10 mm) using a The ECD cell (ECD-3 nano by EL-CELL GmbH) designed in a three-electrode configuration. Working electrode (graphite, 10 mm), counter electrodes (sodium metal plate, 10 mm) and reference electrode (sodium metal piece) were prepared and separated by a fixed glass ceramic separator (T-frit) with a glass fiber separator (Whatmann). Each prepared electrolyte was used with ≈ 350 μl . The thickness change of the electrodes was measured synchronously during the galvanostatic cycling experiment. The relative thickness change (%) was calculated by the following equation:

$$h_{\text{relative}}(\%) = \frac{(h_n - h_0)}{h_0} \times 100 \quad (2)$$

h_n represents the electrode thickness at each cycle, and h_0 denotes the initial thickness of the electrode after six hours of equilibrium in the OCV state, excluding both the thickness of the current collector. A detailed explanation of the method can be found here [62].

4.6. Computational details

All calculations were performed using the program package ORCA 6.0.1 [63,64] with the Becke-style GGA-hybrid functional B3LYP [65–67], which is widely used for calculating the solvation free energy and associated chemistry in lithium- and sodium-based batteries [60,68,69], together with the Grimme atom-pairwise D4 dispersion correction [70,71], the Ahlrichs triple- ζ valence doubly polarized basis set def2-TZVPP [70,71], and the implicit SMD solvation model [72,73] with the dielectric constants set to 4.99 and 7.23 for PN and 2G, respectively. Geometric structure optimizations were conducted as implemented in ORCA using the *verytightscf* and *verytightopt* convergence settings and the *defgrid3* integration grid. Thermochemistry property calculations were performed at a temperature of 298.15 K and pressure of 1 atm, with the cut-off frequency for thermal corrections of 1 cm^{-1} .

CRediT authorship contribution statement

Youhyun Son: Conceptualization, Methodology, Investigation, Writing – original draft. **Guillermo A. Ferrero:** Conceptualization, Methodology, Writing – review & editing, Supervision. **Knut Arne Janßen:** Investigation, Formal analysis. **Winni Schwedland:** Investigation, Formal analysis. **Gustav Åvall:** Methodology, Writing – review & editing. **Yanan Sun:** Writing – review & editing. **Philipp Adelhelm:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ssi.2026.117178>.

Data availability

Data will be made available on request.

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