

Research papers

Mitigating water effects in humid [Pyr₁₄][TFSI] at electrified surfaces via lithium-salt engineeringLeonardo B.A. Oliveira^{a,b}, Tertius L. Fonseca^a, Guilherme Colherinhas^{a,*}^a Instituto de Física, Universidade Federal de Goiás, 74690-900, Goiânia, GO, Brazil^b Departamento de Física – CEPAE, Universidade Federal de Goiás, Campus Samambaia, 74.690-900, Goiânia, Goiás, Brazil

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ABSTRACT

Ionic liquids (ILs) are attractive electrolytes for next-generation electrochemical devices; however, their hygroscopic nature leads to water uptake, which can reorganize the electrical double layer (EDL), promote interfacial water electrosorption, and contribute to the narrowing of the electrochemical stability window (ESW). In this work, we investigate lithium-salt engineering in humid 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Pyr₁₄][TFSI]) using molecular dynamics (MD) simulations at fixed electrode surface charge densities. Corrected potential differences relative to the potential of zero charge (PZC), interaction energies, and number-density profiles of ions and water were systematically analyzed for dry, humid, and Li⁺-containing ILs. The simulations show that interfacial H₂O interacts strongly with polarized electrodes and plays a central role in water-induced EDL restructuring. Upon Li⁺ addition, water molecules are increasingly coordinated by Li⁺, reducing the population of free water available for accumulation at electrified interfaces. At low surface charge densities, Li⁺ addition shifts the corrected potential differences toward those obtained for the dry IL, indicating partial mitigation of water-induced electrostatic screening. At higher polarizations and elevated Li⁺:H₂O ratios, particularly 2:1, the calculated $\Delta\delta\Phi$ values exceed those of the dry IL, suggesting an apparent overcompensation of water-screening effects within the classical MD framework. Importantly, the calculated potential differences are interpreted as electrostatic descriptors of EDL polarization and water-screening effects, rather than as direct measures of redox stability or absolute ESW. Overall, these results provide structural and electrostatic evidence that Li⁺ ions can sequester water and reduce free-water accumulation at electrified interfaces, suggesting that lithium-salt addition may help mitigate water-induced EDL perturbations in humid [Pyr₁₄][TFSI]-based electrolytes.

1. Introduction

Ionic liquids (ILs) are promising candidates for electrochemical applications owing to their low volatility, broad thermal stability, and high conductivity, but the presence of water—inevitable under ambient conditions—reorganizes the electrical double layer (EDL) [1–8], promotes interfacial adsorption/condensation, and triggers electrolysis pathways that narrow the electrochemical stability window (ESW) [9]. At the molecular level, water competes for solvation and adsorption sites, redistributes ions at the interface, and forms hydrogen-bond networks that modulate capacitance and charge dynamics [10]. Direct evidence shows potential-dependent condensation at the [Bmim][TfSA]/Au interface, confirming that positive electric fields intensify H₂O accumulation in the EDL of hydrophobic ILs [11]; atomic force

microscopy (AFM) measurements detail how water incorporation alters layering and electrostatic screening near the surface [12]. Strategies to minimize water electrosorption—through ion selection, operating potential, and electrolyte formulation—have been demonstrated experimentally and computationally, but they remain limited when ambient humidity is high [13].

Simulation and experimental studies have shown that, even at trace concentrations, water exhibits a strong propensity to accumulate at polarized electrodes—a behavior that narrows the electrochemical stability window and accelerates degradation pathways, including premature electrolysis, reduced coulombic efficiency, and increased leakage currents [13]. The anatomy of this phenomenon was detailed by Feng et al. [10], who, via MD simulations, revealed that water electrosorption is selective and preferential at positively polarized electrodes,

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where anions serve as counterions. The mechanism is governed by competition between electric-field–dipole interactions and water–ion associations, leading to local enrichment of H₂O within the EDL and heightening the interface's vulnerability to electrolysis. This behavior compromises not only the predictability of capacitive responses but also the structural integrity of the interface over extended operation.

In situ experimental evidence has corroborated these theoretical predictions: Motobayashi and Osawa showed that water condensation is highly dependent on electrode polarization at Au/[Bmim][TFSI] interfaces. They observed that interfacial structural reorganization is particularly pronounced at positive potentials, providing direct proof that water acts as a critical reorganizing agent of the EDL and a dynamic modulator of ionic density [11]. Complementarily, force-curve studies using AFM revealed that even small amounts of water—on the order of tens of ppm—are sufficient to drastically alter the cohesion and stability of the charged layers at the Au₁₁₁/BMPTFSA interface. This effect manifests as an increase in the thickness of the first interfacial layers, a reduction in their mechanical stiffness, and a shift in the point of zero charge, indicating that water destabilizes the interfacial architecture under realistic operating conditions [12].

Different strategies have been explored to mitigate the adverse effects of humidity in ILs. Traditional methods—rigorous drying, controlled atmospheres, and the design of hydrophobic ionic liquids—are effective in the laboratory but face limitations in cost, scalability, and performance in practical applications. In this context, a promising approach was proposed by Chen et al., who showed that adding inorganic salts, particularly lithium salts, can sequester water molecules in the bulk of the ionic liquid, lowering their thermodynamic activity and limiting their participation in interfacial electrolysis processes. This sequestration occurs via the formation of stable hydration complexes, shifting the interfacial equilibrium and expanding the electrochemical stability window. In practical terms, this strategy yields gains such as higher energy density, greater robustness to ambient humidity, and more predictable performance in advanced electrochemical devices [14]. Complementarily, electrolyte and interface design tactics (e.g., increasing medium hydrophobicity or incorporating polymer matrices) can act synergistically with Li⁺ salting to suppress water-dependent electrolysis pathways [13,15,16].

In this manuscript, we investigate lithium-salt engineering as a molecular strategy to reduce free-water accumulation in humid [Pyr₁₄][TFSI] confined between charged graphene electrodes. The formation of Li⁺–(H₂O)_n coordination complexes is expected to decrease the availability of free water near electrified interfaces, thereby mitigating water-induced electrostatic screening within the EDL. This interfacial reorganization is consistent with reduced water availability at the electrode surface and may help mitigate ESW narrowing associated with free-water accumulation [9,13,14,18–20]. From a formulation perspective, we tested the hypothesis that Li⁺ addition can be tuned to (i) modulate water activity and number-density profiles at electrified interfaces, (ii) reduce the population of free interfacial water associated with ESW narrowing, and (iii) qualitatively assess possible transport- and localization-related tradeoffs. In this framework, water is treated not only as a limiting impurity but also as a molecular component whose interfacial activity can be controlled through electrolyte formulation. These questions were addressed via MD simulations at fixed electrode surface charge densities to reveal how water, ions, and lithium compete and reorganize near charged graphene surfaces. We emphasize that the present classical MD simulations do not explicitly describe electron transfer, bond breaking, or water redox reactions. Therefore, the electrostatic potential differences reported here are used as descriptors of EDL polarization and water screening, not as direct measurements of the electrochemical stability window.

2. Methodology

The effect of adding lithium bis(trifluoromethylsulfonyl)imide ([Li]

[TFSI]) to humid [Pyr₁₄][TFSI] in supercapacitors (SCs) with graphene electrodes was evaluated by atomistic MD simulations. We considered [Pyr₁₄][TFSI] with $\rho = 1.44 \text{ g/cm}^3$ [21]. Three compositions were studied: (i) dry IL – Model-1; (ii) humid IL with addition of 34 H₂O molecules – Model-2; (iii) humid IL + [Li][TFSI] with 1:1 salt-to-water ratio – Model-3; and (iv) humid IL + [Li][TFSI] with 2:1 salt-to-water ratio – Model-4. The numbers of species (cations, anions, H₂O, and Li⁺) and the electrode separation (L) for each model are given in Table 1.

The initial configurations were constructed using PACKMOL software [22], ensuring a random spatial distribution of the electrolyte species confined between two parallel graphene electrodes. The simulation boxes had fixed lateral dimensions of $x = 3.708 \text{ nm}$ and $y = 3.853 \text{ nm}$, corresponding to an electrode area of 14.287 nm^2 . Fig. 1 shows the initial configurations (with graphene electrodes) of four simulated models, as well as the molecular structure of the components of the ionic liquid, water and lithium ion. The intersheet separation along z was set to $z = 12 \text{ nm}$ (Model-1), $z = 12.03 \text{ nm}$ (Model-2), $z = 12.88 \text{ nm}$ (Model-3), and $z = 13.24 \text{ nm}$ (Model-4), yielding internal volumes of 171.396, 171.824, 183.965 and 189.107 nm³, respectively. To avoid interactions with periodic images, a 48 nm vacuum region was included along z (24 nm before the positive electrode and 24 nm after the negative electrode).

Electrodes and electrolytes, [Pyr₁₄][TFSI] and [Li][TFSI], were described with the OPLS-AA force field [23,24], using the TIP3P model for water [24]. These parameter sets have been widely used to capture electrolyte–electrode interactions and electrostatic properties in supercapacitors. A constant surface charge density (σ) was applied to each electrode to reproduce the imposed potential; the atomic partial charge results from distributing σ uniformly over the carbon atoms. Five charge densities were simulated ($\sigma = 0.00, 1.60, 3.20, 4.81, 7.20$ and $9.62 \text{ } \mu\text{C/cm}^2$). This procedure, widely employed in graphene-based SCs [25–30], is accurate for low charge densities—that is, when the potential difference does not exceed $\sim 2 \text{ V}$. Therefore, the results obtained at $\sigma = \pm 7.20$ and $\pm 9.62 \text{ } \mu\text{C/cm}^2$ should be interpreted with caution. These higher charge densities are retained as qualitative high-polarization stress tests to reveal limiting trends in water redistribution, Li⁺ localization, and EDL screening. Quantitative conclusions regarding electrochemical stability are based primarily on the low-to-moderate polarization regime, whereas the highest-polarization cases are not intended to represent directly accessible non-reactive electrochemical operation.

We note that OPLS-AA/TIP3P is a non-polarizable force-field combination. Although this approach has been widely used for comparative simulations of ionic liquids, aqueous mixtures, and supercapacitor interfaces [28,31–35], it does not explicitly account for electronic polarization. This limitation may affect the quantitative strength of Li⁺ coordination, ion pairing, and interfacial interactions, particularly at high electrode polarization. Accordingly, the present results are interpreted mainly in terms of relative structural and electrostatic trends among the four models, rather than as absolute electrochemical energetics.

All simulations were carried out in the NVT ensemble, keeping the number of particles, volume, and temperature constants (at 450 K), using a v-rescale thermostat (coupling constant $\tau = 0.1 \text{ ps}$) [36]. A temperature of 450 K was chosen to increase molecular mobility and improve sampling in the highly viscous ionic liquid environment, within

Table 1

Configuration parameters of the molecular dynamics simulation systems, including the number of cations, anions, water molecules, and Li⁺ ions, as well as the salt–water molar ratio and the electrode separation distance (L, in nm).

	MD system	cation	anion	water	Li ⁺	salt: water	L
Dry IL	Model 1	336	336	0	0	0	12.00
Humid IL	Model 2	336	336	34	0	0	12.03
Salt-in-humid IL	Model 3	336	370	34	34	1:1	12.88
	Model 4	336	404	34	68	2:1	13.24

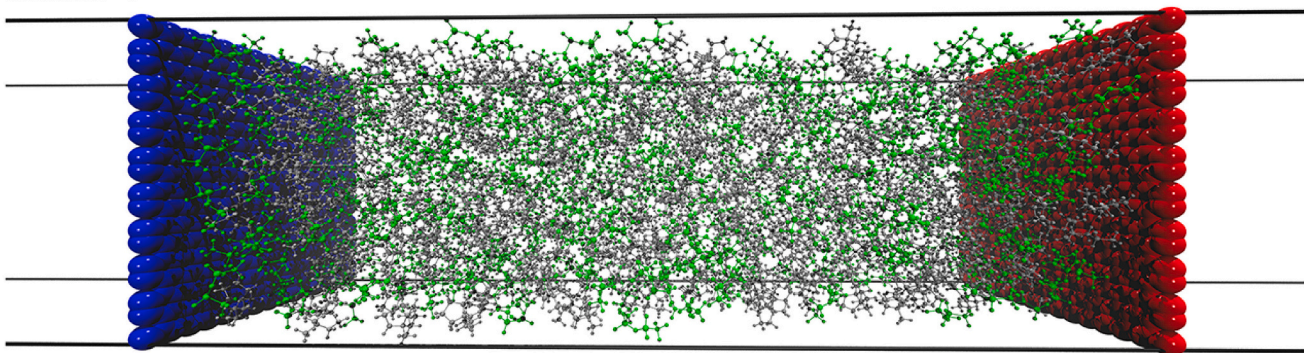
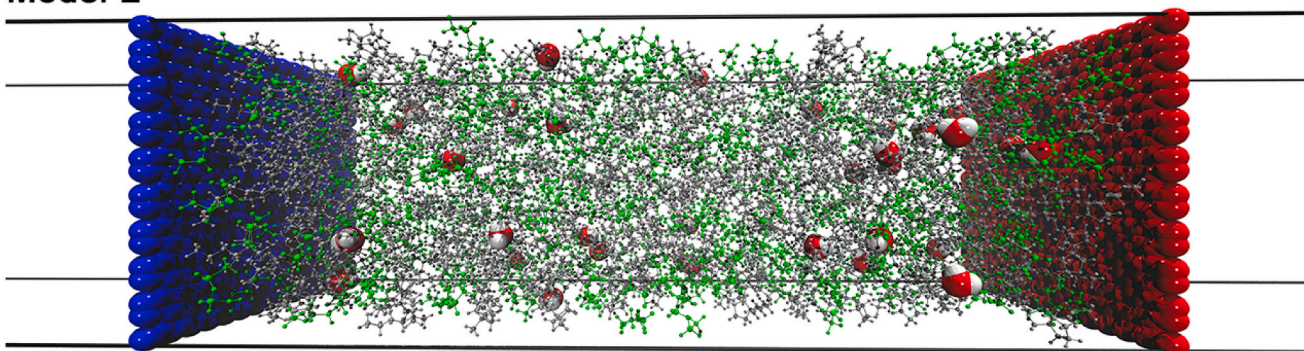
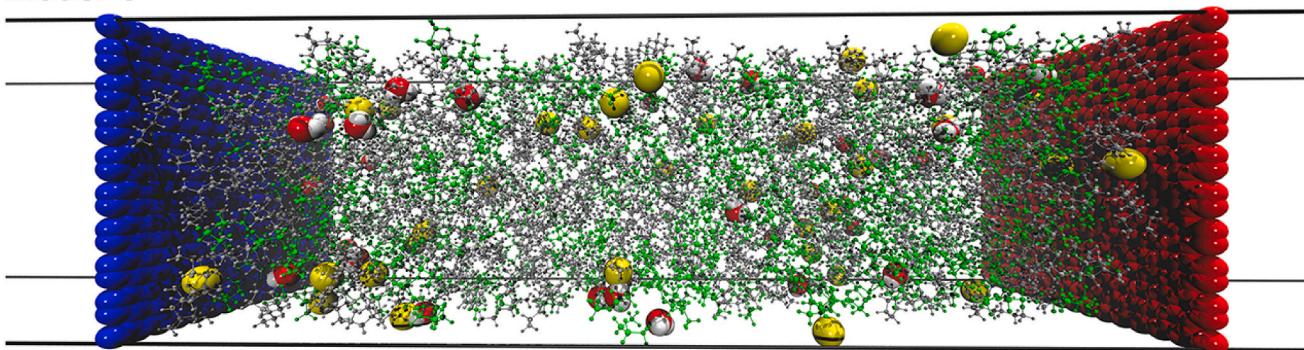
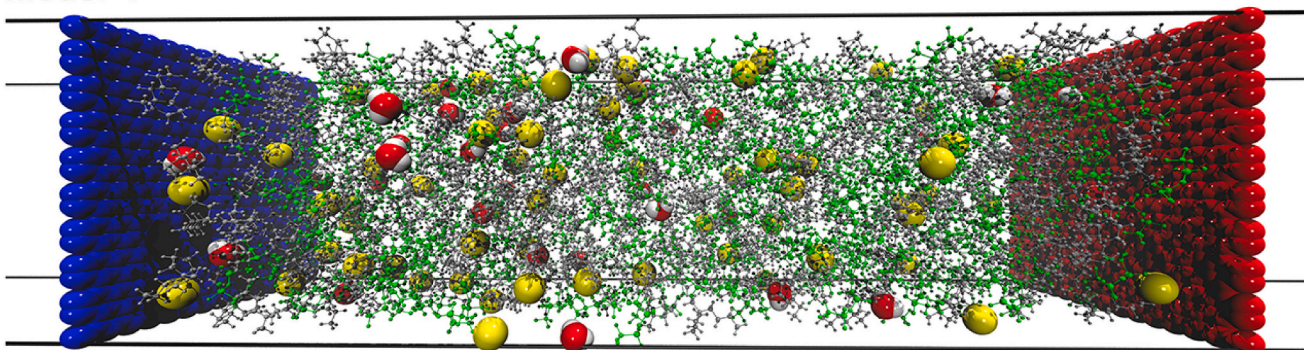
(a) Model-1**(b) Model-2****(c) Model-3****(d) Model-4**

Fig. 1. An initial configuration of the supercapacitors for molecular dynamics simulation. Snapshots of (a) Model-1: dry IL; (b) Model-2: humid IL; (c) Model-3: humid IL + 1:1 added salt-water ratio; (d) Model-4: humid IL + 2:1 added salt-water ratio; confined between two planar graphenes electrodes. $[\text{Pyr}_{14}]^+$ = Gray molecules; $[\text{TFSI}]^-$ = Green molecules; water = red and white molecules; $[\text{Li}]^+$ = yellow sphere; Positive Electrode = red sphere; Negative Electrode = blue sphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the available simulation time, thus creating more statistically uncorrelated configurations. Previous work [25] has shown the low dependence of the device's electrical properties on the simulation temperature at various densities of the confined liquid using the same methodology. Lennard-Jones (LJ) interactions were truncated at 1.2 nm with the Potential-shift-Verlet modifier. Long-range electrostatics were treated with Particle Mesh Ewald (PME) [37], employing 1.2 nm as the real-space cutoff. Periodic boundary conditions were applied in all directions. The simulations were conducted in two stages: (i) equilibration (~15 ns), until thermodynamic quantities stabilized; and (ii) production (100 ns), for sampling. All simulations were performed considering a time step of 0.001 ps for each classical MD step. During production, 50000 configurations were collected, corresponding to a 1 ps sampling interval per frame. The monitored thermodynamic quantities reached stationary behavior over the sampled window, supporting the use of these trajectories for comparative, rather than absolute, analyses of EDL structure, as illustrated in Fig. S1. These configurations were used for statistical analysis. Electrostatic potential profiles were obtained by integration of the charge density using GROMACS 'gmx potential' utility [38,39]. All simulations were performed with the GROMACS 2023 software package [38,39], with bond lengths constrained using the LINCS algorithm [40]. System visualization was carried out with VMD [41].

3. Results and discussion

3.1. Effects of initially random Li^+ distribution on water redistribution, interaction energies, and electrostatic potential differences

We begin our analysis of EDL structure at the electrolyte/electrode interface by comparing four systems (Models 1–4). Fig. 2 illustrates the number density profiles of ions $[\text{Pyr}_{14}]^+$ and $[\text{TFSI}]^-$ along the z-axis — perpendicular to the electrode planes — highlighting how the distribution of electrolyte components varies across the supercapacitor at a surface charge density of $\sigma = 4.81 \mu\text{C}/\text{cm}^2$. Upon electrode polarization, the counterions— $[\text{Pyr}_{14}]^+$ at the negative electrode and $[\text{TFSI}]^-$ at the positive—migrate toward the charged surfaces, in agreement with previous study [14]. This behavior reflects the expected Coulombic interactions between electrolyte species and the polarized interfaces. Prominent number density peaks for $[\text{Pyr}_{14}]^+$ and $[\text{TFSI}]^-$ are observed near the negative and positive electrodes, indicating layered ion organization within the EDL. A comparison between humid ionic liquids with Li^+ and without Li^+ shows that cations and anions largely retain the structural characteristics of the dry IL at the electrode. The salt-to-water ratio exerts little influence on the IL number-density profiles, particularly within the interfacial contact-adsorption region (0.0–0.60 nm). Bi et al. [13] have shown that the hydrophobicity of ionic liquids (ILs) plays a decisive role in determining the behavior of water at electrified interfaces. In hydrophobic ILs, exemplified by $[\text{Pyr}_{14}][\text{TFSI}]$, water exhibits a strong tendency to accumulate near the electrode surfaces, regardless of whether the polarization is positive or negative. This interfacial accumulation of H_2O is stronger near positively charged electrodes than near negatively charged electrodes under a wide range of the electrode potential.

Fig. S2 (see Support Information) shows the H_2O and Li^+ number-density profiles as a function of electrode polarization at the humid $[\text{Pyr}_{14}][\text{TFSI}]$ /electrode interface and the salt-in-humid $[\text{Pyr}_{14}][\text{TFSI}]$ /electrode interface (Model-3, salt:water = 1:1), respectively. The results show that water molecules preferentially accumulate at the charged electrode surface, consistent with prior reports on IL–water mixtures [10,13]. Even with the addition of $[\text{Li}][\text{TFSI}]$, in this case, a certain fraction of free water is still maintained at the interfaces. Our results contrast with Chen's results [14], which revealed that most water molecules are pushed away from the cathode and anode by the addition of salt in a 1:1 salt to water ratio (Model-3). Here, Li^+ addition at a 1:1 salt-to-water ratio (Model-3) appears insufficient to fully suppress free-water

accumulation at the electrified interface. Within the classical MD framework, this suggests only partial mitigation of water-induced EDL perturbations and electrostatic screening, rather than complete protection against water-related interfacial effects. Importantly, complementary studies show that Li^+ ions generally have difficulty penetrating the first layer of ions directly adsorbed on the electrode, tending instead to remain confined to the second molecular layer; this behavior arises from strong complexation with anions ($[\text{TFSI}]^-$), which creates significant energetic barriers to direct approach. Free energy profiles confirm the formation of stable solvation wells in regions away from the electrode, whose depth increases with polarization, reinforcing the unfavorable nature of Li^+ migration to the innermost interfacial layer [42].

By contrast, in salt-in-humid $[\text{Pyr}_{14}][\text{TFSI}]$ with a 2:1 salt-to-water ratio (Model-4), water is strongly excluded from the electrode interface: under certain negative polarizations the contact layer is completely depleted of H_2O , and at high polarization interfacial free water is largely removed. Fig. 3 shows the evolution of water and water and Li^+ number density profiles at the humid $[\text{Pyr}_{14}][\text{TFSI}]$ /electrode interface and at the salt-in-humid $[\text{Pyr}_{14}][\text{TFSI}]$ /electrode interface (Model-4, salt:water = 2:1) for two surface charge densities ($\sigma = 4.81$ and $9.62 \mu\text{C}/\text{cm}^2$). Driven by stronger electrostatic attraction to the negatively polarized electrode, Li^+ ions overcome the interfacial IL ion-layer barrier and subsequently adsorb at the surface (Fig. 3d). Interfacial H_2O then coordinates to Li^+ , and the fraction of Li^+ -bound water increases at 2:1 ratio, thereby depleting free water near the negative electrode. At the negative electrode, water depletion is associated with direct electrostatic attraction of Li^+ toward the negatively charged surface, followed by $\text{Li}^+-\text{H}_2\text{O}$ coordination. At the positive electrode, however, the mechanism is different: Li^+ is electrostatically disfavored near the positively charged surface and therefore does not dehydrate the interface by direct adsorption. Instead, Li^+ coordinates water in the bulk and outer EDL region, lowering the population of free water available to enter the anion-rich interfacial layer. Thus, the apparent reduction of water near the positive electrode is mainly an indirect consequence of bulk/outer-layer water sequestration rather than direct Li^+ adsorption at the positive surface. Fig. 4 presents representative snapshots of the H_2O and Li^+ distributions between two planar carbon electrodes at $\sigma = \pm 4.81 \mu\text{C}/\text{cm}^2$.

We emphasize that the term “water depletion” refers primarily to the reduction of free, uncoordinated water in the interfacial contact region. Residual water molecules may still appear near the electrode, especially when coordinated to Li^+ . Therefore, water density profiles alone do not distinguish free water from Li^+ -bound water, and this distinction is addressed below using $\text{Li}-\text{O}$ coordination analysis.

To verify whether the residual interfacial water is free or Li^+ -bound, we calculated the $\text{Li}^+-\text{O}_{\text{water}}$ radial distribution function (RDF) and the corresponding $\text{Li}^+-\text{O}_{\text{water}}$ coordination number (Fig. S3). The $\text{Li}^+-\text{O}_{\text{water}}$ RDF displays a well-defined first maximum at approximately 0.21 nm and a first minimum at approximately 0.30 nm, indicating the formation of a clear first $\text{Li}^+-\text{O}_{\text{water}}$ coordination shell. Therefore, water molecules were classified as Li^+ -bound when the $\text{Li}^+-\text{O}_{\text{water}}$ distance was shorter than 0.30 nm. Integration of $\text{Li}^+-\text{O}_{\text{water}}$ RDF up to this first minimum gives an average coordination number of approximately 1.79 water molecules per Li^+ for Model 3 and 1.72 for Model 4. This result indicates that increasing the number of Li^+ ions from 34 to 68 does not substantially change the local Li^+ hydration environment. Instead, the higher Li^+ concentration increases the number of available Li^+ coordination centers, favoring water sequestration and reducing the population of free water molecules able to accumulate at the electrified interface. This analysis suggests that a significant fraction of the residual water near the negative electrode is associated with Li^+ .

The selection of the 1:1 and 2:1 $[\text{Li}][\text{TFSI}]:\text{H}_2\text{O}$ ratios follows the experimental and computational framework established by Chen et al. [14], who investigated lithium-salt engineering in humid ionic liquids and demonstrated that these compositions are both experimentally accessible and electrochemically functional. Their results showed that

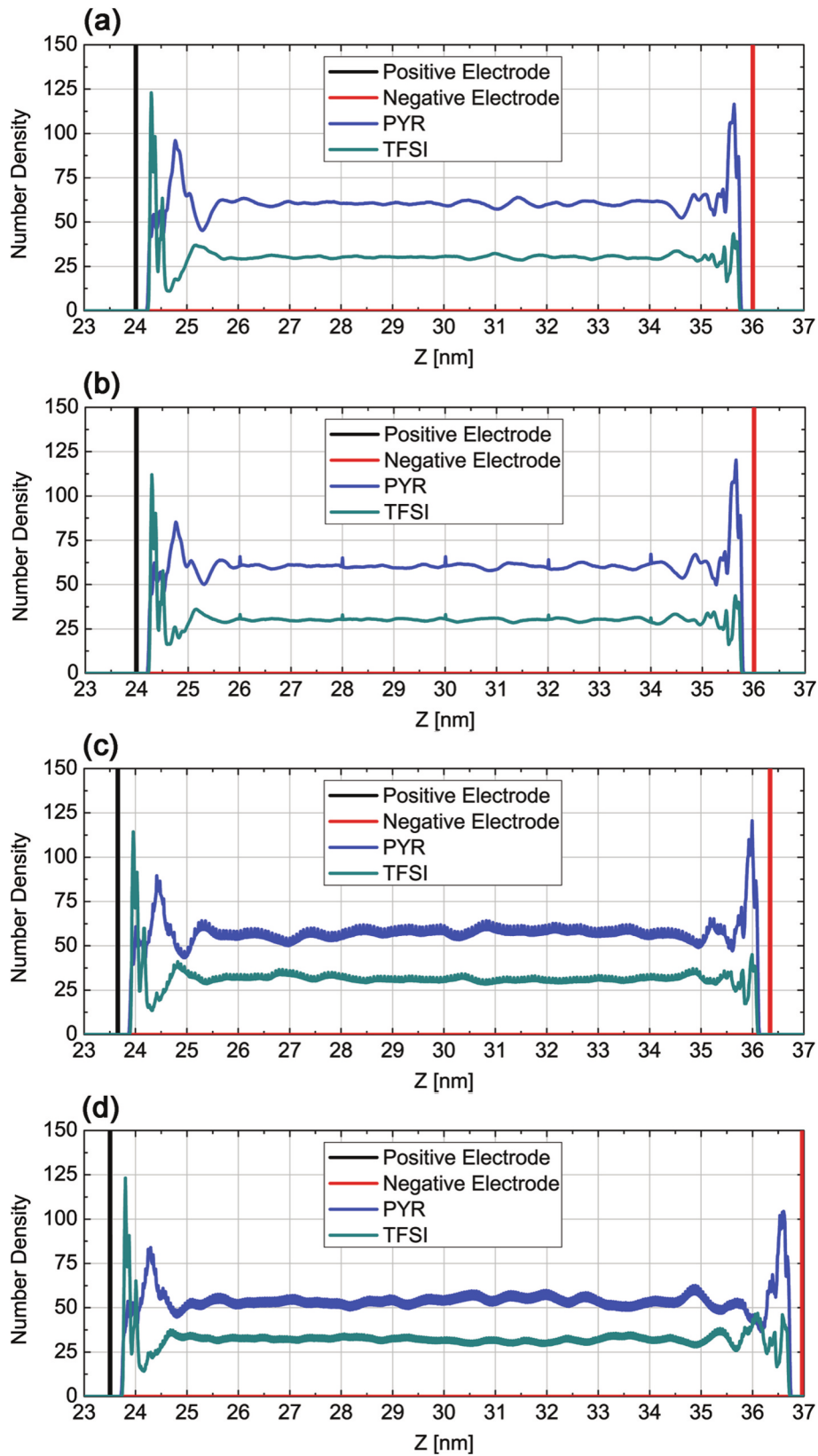


Fig. 2. Number density [nm^{-3}] profiles along the z-axis [nm] for the surface charge density of $\pm 4.81 \mu\text{C}/\text{cm}^2$. The panels show $[\text{Pyr}_{14}]^+$ and $[\text{TFSI}]^-$ distributions in (a) Model-1: dry IL, (b) Model-2: humid IL, (c) Model-3: humid IL with $[\text{Li}][\text{TFSI}]$ (1:1 salt-to-water ratio) and (d) Model-4: humid IL with $[\text{Li}][\text{TFSI}]$ (2:1 salt-to-water ratio).

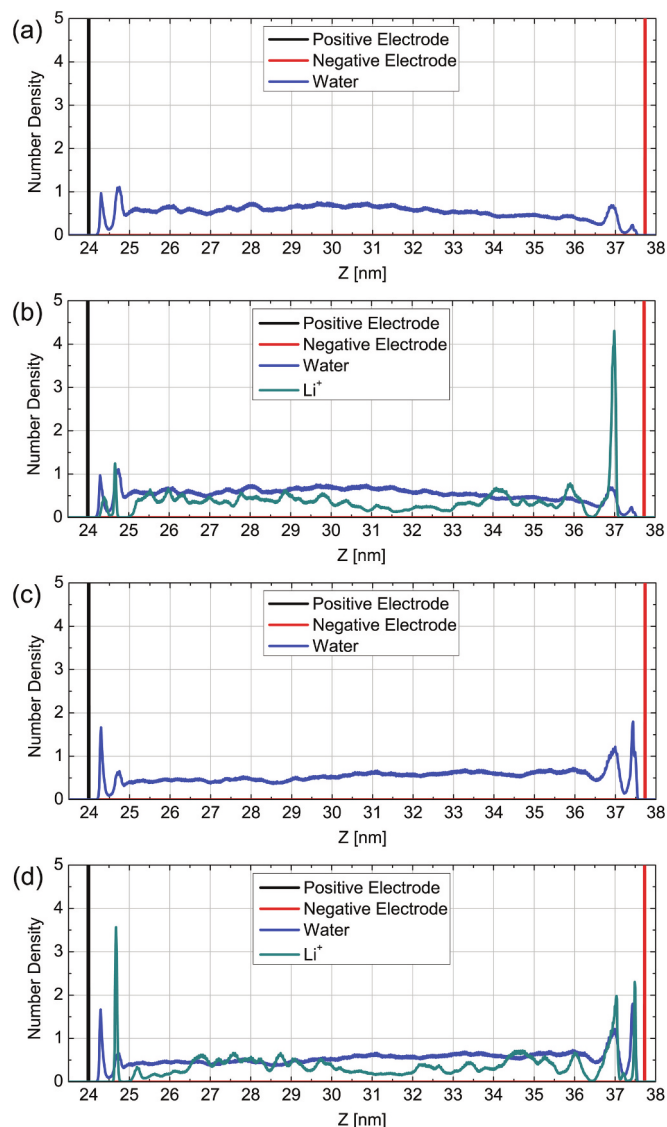


Fig. 3. Number density profiles along the z -axis for H_2O (blue line) and Li^+ (green line) at the humid $[\text{Pyr}_{14}][\text{TFSI}]/\text{graphene}$ interface. Panels (a) and (b) correspond to $\sigma = \pm 4.81 \mu\text{C}/\text{cm}^2$, while panels (c) and (d) correspond to $\sigma = \pm 9.62 \mu\text{C}/\text{cm}^2$. Panels (a) and (c) show the humid IL without added Li salt, whereas panels (b) and (d) show Model 4, corresponding to humid $[\text{Pyr}_{14}][\text{TFSI}]$ with $[\text{Li}][\text{TFSI}]$ at a 2:1 $\text{Li}^+:\text{H}_2\text{O}$ ratio. The positive and negative electrodes are indicated by black and red bars, respectively. Identical vertical-axis scales are used for directly comparable H_2O profiles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mixtures of $[\text{Li}][\text{TFSI}]$ with imidazolium- and pyrrolidinium-based ILs remain fully miscible at molar ratios of 1:1, 2:1, and even 4:1, confirming that solubility does not impose restrictions within this concentration range. Thus, the salt concentrations explored here lie well within the experimentally validated domain for humid ionic liquids. The 1:1 ratio was chosen because it represents the standard condition commonly employed to assess whether Li^+ complexation is sufficient to suppress interfacial water activity. Previous studies reported that a 1:1 ratio can partially mitigate water-driven narrowing of the electrochemical stability window; however, our simulations indicate that this concentration is insufficient for $[\text{Pyr}_{14}][\text{TFSI}]$, as a fraction of free water remains available to screen the electrode potential. In contrast, the 2:1 ratio produces a qualitatively distinct regime: Li^+ complexation becomes strong enough to sequester nearly all interfacial water, leading to

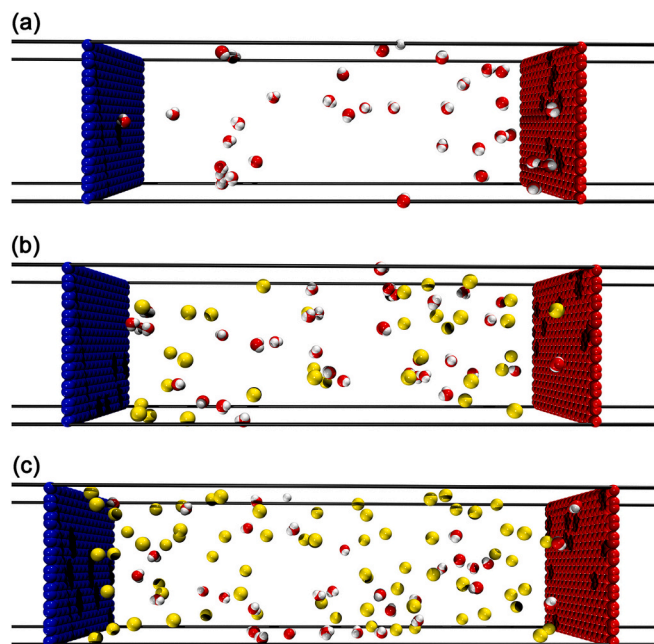


Fig. 4. Snapshots showing the distribution of (a) water molecules in humid ionic liquid and the distribution of (b) Li^+ ions and water molecules in salt-in-humid ionic liquid (Model-3, 1:1 salt-to-water ratio) and (c) Li^+ ions and water molecules in salt-in-humid ionic liquid (Model-4, 2:1 salt-to-water ratio) between two planar carbon electrodes at $\sigma = \pm 4.81 \mu\text{C}/\text{cm}^2$. Positive Electrode = red sphere; Negative Electrode = blue sphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pronounced depletion of H_2O in the contact layer and full restoration—or even overcompensation—of the potential difference relative to the dry ionic liquid.

In addition, elevated concentrations of lithium salts are known to increase the viscosity of ionic liquid electrolytes, which may hinder ion mobility. Nonetheless, the experimental study [14] has shown that 1:1, 2:1, and 4:1 mixtures remain processable and electrochemically stable, despite the expected rise in viscosity at higher salt fractions. Therefore, the viscosity increases associated with the salt concentrations examined here do not compromise the validity of the structural and electrostatic insights reported in this work. Overall, the chosen salt-to-water ratios allow us to probe the transition between partial and complete interfacial dehydration and to identify a composition, among those tested, that most effectively restores the electrostatic response toward the dry-IL limit.

We stress that the present classical MD simulations cannot directly determine whether Li^+ -bound water has a lower oxidation or reduction rate than free water, because electron transfer, bond breaking, and chemical reactions are not included in the force field. Our conclusion is therefore structural and electrostatic: Li^+ addition reduces the population of free water molecules at the electrified interface and converts part of the residual water into Li^+ -coordinated species. This reduced free-water availability is consistent with mitigation of water-driven ESW narrowing, but it should not be interpreted as a direct calculation of redox kinetics or reaction barriers. In summary, our results show that increasing the salt:water ratio to 2:1 (Model-4) strongly excludes H_2O from the electrode interface—up to complete depletion at certain negative polarizations and substantial removal under strong fields—consistent with $\text{Li}^+(\text{H}_2\text{O})_n$ complexation and mitigated ESW narrowing.

To quantitatively evaluate the interaction energy of interfacial water molecules with Li^+ ions in polarized electrodes as a function of the EDL potential—and, crucially, to separate the effects of water-electrode and

Li^+ -electrode interactions—the total interaction energy was decomposed into four components: (1) LJ water-electrode interactions, (2) Coulombic water-electrode interactions, (3) LJ ion-electrode interactions, and (4) Coulombic ion-electrode interactions. Table 2 reports the normalized electrostatic (Coulomb) and LJ energies, calculated per interaction pair. This decomposition clarifies the relative magnitude and character of the interactions that govern electric double-layer formation.

The results for the interaction energy between Li^+ and the positive graphene electrode (GRP) indicate that the LJ contributions are small (± 0.1 – 0.6 kcal/N.mol) and even change sign, while the Coulomb term increases strongly with σ , shifting from -0.41 at 1.6 to $+4.70$ kcal/N.mol at ± 7.2 $\mu\text{C}/\text{cm}^2$. This trend reveals an increasing electrostatic repulsion of Li^+ as the positive electrode becomes more polarized. In contrast, H_2O exhibits large and negative LJ contributions (≈ -2.3 to -4.1 kcal/N.mol), reflecting strong dispersion-driven binding. The Coulombic term remains weak and close to zero, but shifts slightly negative at higher σ , suggesting mild stabilization. Overall, water adsorption strengthens with increasing surface charge, primarily due to LJ interactions.

For the negative graphene electrode (GRN), the LJ contributions for Li^+ remain small (≈ -0.2 to -0.4 kcal/N.mol) up to $\sigma = \pm 7.2$ $\mu\text{C}/\text{cm}^2$, while Coulomb energy interactions are consistently negative (≈ -0.36 to -0.89 kcal/N.mol), pointing to a progressively stronger electrostatic attraction of Li^+ to the cathode. At $\sigma = \pm 9.6$ $\mu\text{C}/\text{cm}^2$, a sharp transition is observed, with Coulomb energy interaction reaching -42.7 kcal/N.mol (LJ = $+1.14$ kcal/N.mol), indicating a very strong Coulombic stabilization of Li^+ under this high-polarization condition. For H_2O , LJ contributions become increasingly negative (-3.5 to -7.1 kcal/N.mol), evidencing stronger physical adsorption, while Coulombic terms also grow more negative, particularly at $\sigma \geq 7.2$ $\mu\text{C}/\text{cm}^2$, showing electrostatic stabilization of interfacial water.

Taken together, these results demonstrate distinct behaviors: in GRP, Li^+ is repelled electrostatically as σ increases, whereas water is stabilized mainly through LJ forces—consistent with the tendency of hydrophobic ILs to allow water accumulation even under positive bias. In GRN, both Li^+ and H_2O are stabilized electrostatically; under high charge density ($\sigma = -9.62$ $\mu\text{C}/\text{cm}^2$), Li^+ undergoes dramatic Coulomb attraction, suggesting strong interfacial trapping. Except for the extreme high-polarization case at the negative electrode, H_2O generally shows stronger overall electrode association dominated by LJ interactions, whereas Li^+ binding is mainly governed by Coulombic attraction and

becomes dominant only under the highest negative polarization.

The potential difference between the electrodes was obtained as $\Delta\Phi = \Phi_+ - \Phi_-$, where Φ_+ and Φ_- are the electrostatic potentials for the positive and negative electrodes, respectively. The EDL potential is defined relative to its value at the potential of zero charge (PZC), which in MD simulations is well determined from the Poisson potential drop across the EDL when the electrode surface charge is zero. The corrected potential difference is then expressed as $\Delta\delta\Phi = \delta\Phi^{\text{charged}} - \delta\Phi^{\text{discharged}}$ (Table 3). The corrected potential difference $\Delta\delta\Phi$ is used here as an electrostatic descriptor of EDL polarization relative to the PZC. It should not be interpreted as a direct electrochemical stability window. This distinction is particularly important for $\sigma = \pm 7.20$ and ± 9.62 $\mu\text{C}/\text{cm}^2$, for which $\Delta\delta\Phi$ exceeds the approximate low-potential regime where fixed-charge graphene models are most reliable. Thus, the high- σ data are discussed qualitatively as polarization trends, whereas the low- σ data provide the most reliable quantitative comparison among the electrolyte compositions.

$\Delta\delta\Phi$ increases steadily with σ in all systems, consistent with stronger polarization of EDL. The presence of water and Li^+ modifies this behavior in distinct ways, depending on charge density and salt/water ratio. Effect of water (Model-2: humid IL): at low σ (± 1.6 and ± 3.2 $\mu\text{C}/\text{cm}^2$), humid ILs show reduced $\Delta\delta\Phi$ compared to Model-1: dry IL (0.72 V vs. 0.80 V at ± 1.6 $\mu\text{C}/\text{cm}^2$; 1.29 V vs. 1.62 V at ± 3.2 $\mu\text{C}/\text{cm}^2$). This reduction reflects water's dielectric screening, which lowers the potential drop by solvating ions and disrupting ionic layering. At higher σ (± 4.81 and ± 9.62 $\mu\text{C}/\text{cm}^2$), the difference narrows (2.24 V vs. 2.16 V; 4.58 V vs. 4.35 V), as strong electrode polarization dominates over water's moderating effect. Effect of Li^+ addition: at low σ , introducing Li^+ increases $\Delta\delta\Phi$ relative to humid IL without salt (Model-2), partially recovering the values toward those of dry IL (Model-1). This indicates Li^+ -water complexation, which sequesters water molecules and reduces their screening effect. At higher σ , the outcome depends on concentration: with Model-3 (1:1 salt:water), $\Delta\delta\Phi$ is slightly lower than Model-2 (humid IL) at ± 4.81 $\mu\text{C}/\text{cm}^2$ (2.07 V vs. 2.16 V) but nearly identical at ± 9.62 $\mu\text{C}/\text{cm}^2$ (4.40 V vs. 4.35 V). With Model-4 (2:1 salt:water), $\Delta\delta\Phi$ surpasses both Model-1 and Model-2 (dry IL and humid IL) values (2.45 V at 4.81 $\mu\text{C}/\text{cm}^2$; 4.62 V at 9.62 $\mu\text{C}/\text{cm}^2$), suggesting that high Li^+ concentration reduces water-induced screening and increases the electrostatic potential drop within the limits of the fixed-charge model.

3.2. Strategy of selective Li^+ placement on the water redistribution at electrified interfaces and electrostatic potential difference

To assess the sensitivity of interfacial water organization to the initial Li^+ distribution, additional simulations were performed in which Li^+ ions were selectively placed either in the bulk region or near the polarized electrode interfaces. These simulations are not used as the primary basis for the main conclusions, but rather as sensitivity tests to evaluate how local Li^+ enrichment can influence water redistribution within the EDL. We next examined how selectively adding (and positioning) Li^+ in the humid ionic liquid evolves under different electrode polarizations after thermalization, considering the same proportion used in Model-4 (2:1 salt-to-water ratio). Fig. 5 shows the Li^+ number-density profiles when ions are initialized either in the bulk center of the electrolyte or at the polarized interfaces. The production simulations were carried out for 100 ns at 450 K. For $\sigma = \pm 4.81$ $\mu\text{C}/\text{cm}^2$, a Li^+ layer

Table 2

Interaction energy (in kcal/N.mol), normalized per interaction pair, between electrolyte species and the positive graphene electrode, GRP, or negative graphene electrode, GRN. Electrostatic (Coulomb) and Lennard-Jones (LJ) contributions are reported for all surface charge densities σ , in $\mu\text{C}/\text{cm}^2$.

σ	GRP			
	Li^+		H_2O	
	LJ	Coulomb	LJ	Coulomb
1.6	0.0663	-0.4105	-2.3862	0.0442
3.2	-0.1717	0.4293	-2.3238	0.0630
4.8	-0.6472	3.6591	-3.4861	-0.0151
7.2	-0.5295	4.7037	-4.0222	-0.3523
9.6	-0.1716	1.2982	-4.1121	-0.5263

σ	GRN			
	Li^+		H_2O	
	LJ	Coulomb	LJ	Coulomb
1.6	-0.4106	-0.5829	-3.5046	-0.1695
3.2	-0.1643	-0.3620	-3.0241	-0.3113
4.8	-0.2938	-0.8906	-1.3854	-0.2559
7.2	-0.1883	-0.7594	-2.9072	-1.2856
9.6	1.1356	-42.7136	-7.0889	-4.6512

Table 3

Reported values (in V) for the potential difference corrected by the PZC, $\Delta\delta\Phi$.

$\sigma(\mu\text{C}/\text{cm}^2)$	Model-1	Model-2	Model-3	Model-4
± 1.6	0.8043	0.7200	0.7762	0.8386
± 3.2	1.6222	1.2930	1.4876	1.5758
± 4.81	2.2401	2.1685	2.0744	2.4492
± 7.20	3.3170	3.2118	3.1431	3.4618
± 9.62	4.5786	4.3551	4.4021	4.6251

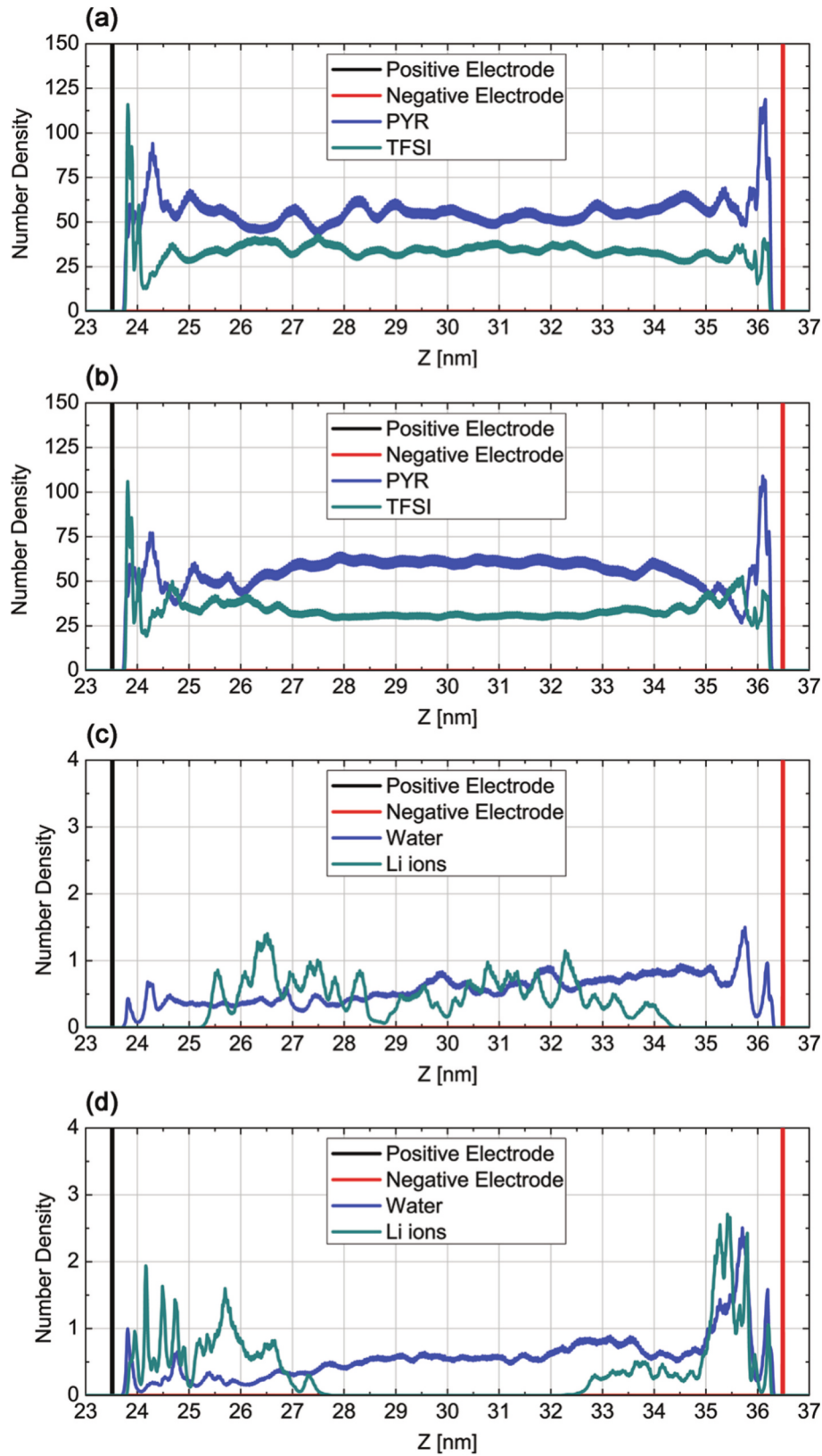


Fig. 5. Number density profiles along the z-axis at a surface charge density of $\pm 4.81 \mu\text{C}/\text{cm}^2$. The left panel (a and c) shows water and Li^+ distributions in humid $[\text{Pyr}_{14}][\text{TFSI}]$ with Li^+ initialized in the bulk center, while the right panel (b and d) shows the corresponding distributions with Li^+ initialized at the polarized interfaces (2:1 salt-to-water ratio). The positive electrode is indicated by a black bar and the negative electrode by a red bar. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

persists in its initial basin—either remaining in the central region or residing near the polarized interfaces. This behavior suggests that the viscosity and solvation structure of the humid IL impose energetic barriers that localize Li^+ . When initialized in the bulk, ions feel an electrostatic drive toward the charged electrode but must first overcome the viscous/solvation barriers to traverse the liquid and reach the surface, where they can mitigate water's impact on the ESW. Conversely, when Li^+ is placed directly at the polarized interfaces, viscous/solvation barriers hinder its redistribution, confining the salt near both electrodes, expelling H_2O from the surfaces, and complexing residual interfacial water as $\text{Li}^+(\text{H}_2\text{O})_n$. Therefore, we use these simulations only to show that local Li^+ enrichment near the interface can reduce free-water accumulation, not to claim that such a distribution is the unique equilibrium state. Again, the selective distribution of Li exerts little influence on the IL number density profiles, particularly in the interfacial contact adsorption region (Fig. 5a and b). Snapshots of the two simulated configurations showing Li^+ and water molecules from the selective addition of Li^+ atoms can be seen in Fig. 6.

In the configuration where Li^+ ions were initially positioned in proximity to the electrodes, no variation in potential was detected. The results reveal a $\Delta\delta\Phi$ value of 2.43 V at a 2:1 salt-to-water ratio, which is essentially consistent with the 2.45 V reported in Table 3 (Model 4). Although the simulation based on the selective addition of Li^+ ions did not induce significant electrical modifications in the device, this approach proved to be highly effective in mitigating the impact of water adsorption on the electrodes. The mechanism is straightforward: Li^+ positioned near the interfaces binds strongly to nearby water molecules, suggesting the formation of stable $\text{Li}^+(\text{H}_2\text{O})_n$ coordination complexes that cannot penetrate the dense ionic layer adjacent to the surface. As illustrated in Fig. 6b, this favors the confinement of water in the bulk region, preventing its migration toward the charged interfaces. This selective interfacial dehydration reduces the availability of free water at electrified interfaces, which is consistent with mitigation of water-related degradation pathways in real systems. However, because redox kinetics and bond-breaking events are not included in the present classical MD framework, this effect should be interpreted as structural and electrostatic rather than as direct evidence of suppressed electrochemical decomposition. The absence of significant variations in the interfacial potential further indicates that this local restructuring of the EDL does not perturb the overall electrostatic regime of the capacitor.

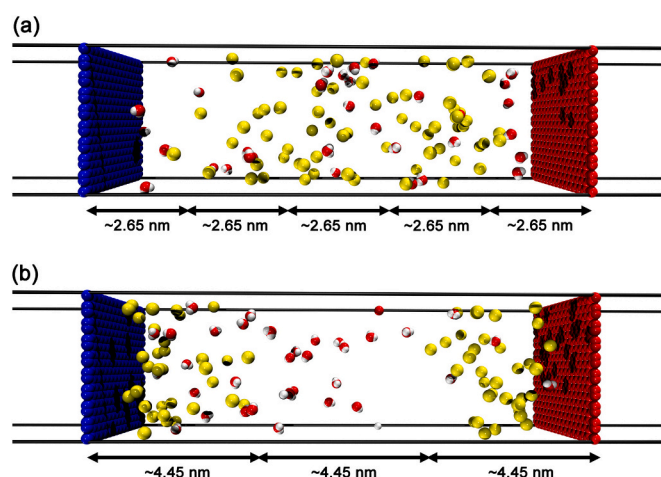


Fig. 6. Snapshots showing the distribution of Li^+ ions and water molecules in humid $[\text{Pyr}_{14}][\text{TFSI}]$ ionic liquid with (a) Li^+ ions initially positioned in the bulk center and (b) Li^+ ions initially positioned near the polarized electrodes. For both cases shown, the salt-to-water ratio is 2:1 and $\sigma = \pm 4.81 \mu\text{C}/\text{cm}^2$. Positive Electrode = red sphere; Negative Electrode = blue sphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Together, these results identify selective Li^+ addition as a promising and controllable route for engineering more stable, humidity-tolerant electrolytes, as well as for mitigating water-induced narrowing of the electrochemical stability window in humid ionic liquids. In summary, water alone lowers $\Delta\delta\Phi$, especially at low-to-moderate σ , by screening the electrode potential. Li^+ addition counterbalances this effect: at low σ , it restores $\Delta\delta\Phi$ toward dry IL values; at high σ and higher salt ratios, it can even overcompensate, leading to stronger electrode polarization than in dry ILs. Although the present study is restricted to the $[\text{Pyr}_{14}][\text{TFSI}]$ ionic liquid and the conclusions are more directly applicable to it, they may be relevant to closely related pyrrolidinium-TFSI-based electrolytes. Other ionic-liquid families, especially more hydrophilic imidazolium-based ILs, may display different water affinities, Li^+ solvation structures, viscosities, and optimal $\text{Li}^+:\text{H}_2\text{O}$ ratios.

4. Conclusion

This study addressed three central questions concerning the role of lithium-salt engineering in humid $[\text{Pyr}_{14}][\text{TFSI}]$: (i) whether Li^+ can modulate free-water availability and interfacial density profiles; (ii) whether this modulation can reduce the population of free interfacial water associated with water-induced ESW narrowing; and (iii) how these effects are related to Li^+ localization and mobility-related limitations within the confined environment of supercapacitor-like systems. Classical MD simulations revealed that water alone reorganizes the electrical double layer, accumulating near the electrode interfaces and reducing the corrected electrostatic potential difference due to dielectric screening. The introduction of lithium salt promotes $\text{Li}^+(\text{H}_2\text{O})_n$ coordination, which decreases the population of free interfacial water, especially at the 2:1 $\text{Li}^+:\text{H}_2\text{O}$ ratio. This behavior modifies interfacial water availability and redistributes number-density profiles across the EDL, supporting point (i).

At low surface charge densities, Li^+ addition partially restores $\Delta\delta\Phi$ toward dry IL values, while at higher polarizations — and particularly at a 2:1 salt-to-water ratio — displays larger $\Delta\delta\Phi$ values than those of the dry IL. These findings indicate that lithium-salt engineering reduces water-induced electrostatic screening and modifies the EDL polarization response, supporting point (ii). However, because the present simulations are classical and non-reactive, $\Delta\delta\Phi$ should be interpreted as an electrostatic descriptor of EDL polarization, not as a direct measure of the electrochemical stability window, redox stability or degradation kinetics.

Finally, sensitivity tests in which Li^+ ions were initially enriched near the interfaces showed reduced free-water accumulation and favored $\text{Li}^+(\text{H}_2\text{O})_n$ coordination, highlighting a possible route to mitigate water accumulation on electrified surfaces. Mechanistically, Li^+ addition decreases the availability of free water near the electrode surface and reduces dielectric screening within the EDL, thereby addressing point (iii).

Overall, this work supports a structural and electrostatic mechanism in which lithium-salt addition reduces the availability of free interfacial water and mitigates water-induced screening in humid $[\text{Pyr}_{14}][\text{TFSI}]$. This mechanism is consistent with reduced water-driven ESW narrowing, but it does not constitute a direct calculation of water redox reactions or absolute voltage limits. Because only $[\text{Pyr}_{14}][\text{TFSI}]$ was simulated, the optimal $\text{Li}^+:\text{H}_2\text{O}$ ratio identified here should not be assumed to be universal. Future studies involving other ionic-liquid families, lower-temperature control simulations, and longer sampling times will be important to establish the broader transferability of this lithium-salt engineering strategy.

CRediT authorship contribution statement

Leonardo B.A. Oliveira: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Tertius**

L. Fonseca: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Guilherme Colherinhas:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.est.2026.123574>.

Data availability

Data will be made available on request.

References

- [1] L. Bruno Assis Oliveira, T.L. Fonseca, G. Colherinhas, Investigating ionic liquid hydration effects at high temperatures: insights from classic molecular dynamics simulations, *J. Mol. Liq.* 393 (2024) 123662, <https://doi.org/10.1016/j.molliq.2023.123662>.
- [2] F. Matroodi, C. Bottari, B. Rossi, A. Mannu, M. Paolantoni, A. Mele, Hydration water and ionic aggregation in aqueous solutions of imidazolium-based protic ionic liquids, *J. Mol. Liq.* 395 (2024) 123881, <https://doi.org/10.1016/j.molliq.2023.123881>.
- [3] D.H. Dagade, K.R. Madkar, S.P. Shinde, S.S. Barge, Thermodynamic studies of ionic hydration and interactions for amino acid ionic liquids in aqueous solutions at 298.15 K, *J. Phys. Chem. B* 117 (2013) 1031–1043, <https://doi.org/10.1021/jp310924m>.
- [4] M. McEldrew, Z.A.H. Goodwin, A.A. Kornyshev, M.Z. Bazant, Theory of the double layer in water-in-salt electrolytes, *J. Phys. Chem. Lett.* 9 (2018) 5840–5846, <https://doi.org/10.1021/acs.jpclett.8b02543>.
- [5] Z. Li, G. Jeanmairat, T. Méndez-Morales, B. Rotenberg, M. Salanne, Capacitive performance of water-in-salt electrolytes in supercapacitors: a simulation study, *J. Phys. Chem. C* 122 (2018) 23917–23924, <https://doi.org/10.1021/acs.jpcc.8b07557>.
- [6] T. Malaspina, G. Colherinhas, S.E. Weitzner, B.C. Wood, E. Eterno Fileti, Unraveling local structures of salt-in-water and water-in-salt electrolytes via ab initio molecular dynamics, *J. Mol. Liq.* 383 (2023) 122097, <https://doi.org/10.1016/j.molliq.2023.122097>.
- [7] A. D'Alessandro, S. Bellani, A. Gamberini, V. Mastroradi, M.I. Zappia, M. Abruzzese, S. Thorat, E. Calcagno, F. Bonaccorso, Water-based supercapacitors with amino acid electrolytes: a green perspective for capacitance enhancement, *Batteries Supercaps* 7 (2024), <https://doi.org/10.1002/batt.202300458>.
- [8] U. Schröder, J.D. Wadhawan, R.G. Compton, F. Marken, P.A.Z. Suarez, C. S. Consorti, R.F. de Souza, J. Dupont, Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(S)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids, *New J. Chem.* 24 (2000) 1009–1015, <https://doi.org/10.1039/b007172m>.
- [9] R. Qiao, Water at ionic liquids-solid interfaces, *Curr. Opin. Electrochem.* 13 (2019) 11–17, <https://doi.org/10.1016/j.coelec.2018.10.004>.
- [10] G. Feng, X. Jiang, R. Qiao, A.A. Kornyshev, Water in ionic liquids at electrified interfaces: the anatomy of Electrosorption, *ACS Nano* 8 (2014) 11685–11694, <https://doi.org/10.1021/nn505017c>.
- [11] K. Motobayashi, M. Osawa, Potential-dependent condensation of water at the Interface between ionic liquid [BMIM][TfSA] and an Au electrode, *Electrochem. Commun.* 65 (2016) 14–17, <https://doi.org/10.1016/j.elecom.2016.01.018>.
- [12] Y. Zhong, J. Yan, M. Li, L. Chen, B. Mao, The electric double layer in an ionic liquid incorporated with water molecules: atomic force microscopy force curve study, *ChemElectroChem* 3 (2016) 2221–2226, <https://doi.org/10.1002/celec.201600177>.
- [13] S. Bi, R. Wang, S. Liu, J. Yan, B. Mao, A.A. Kornyshev, G. Feng, Minimizing the electrosorption of water from humid ionic liquids on electrodes, *Nat. Commun.* 9 (2018) 5222, <https://doi.org/10.1038/s41467-018-07674-0>.
- [14] M. Chen, J. Wu, T. Ye, J. Ye, C. Zhao, S. Bi, J. Yan, B. Mao, G. Feng, Adding salt to expand voltage window of humid ionic liquids, *Nat. Commun.* 11 (2020) 5809, <https://doi.org/10.1038/s41467-020-19469-3>.
- [15] X. Zhao, K. Zhou, Y. Zhong, P. Liu, Z. Li, J. Pan, Y. Long, M. Huang, A. Brakat, H. Zhu, Hydrophobic ionic liquid-in-polymer composites for ultrafast, linear response and highly sensitive humidity sensing, *Nano Res.* 14 (2021) 1202–1209, <https://doi.org/10.1007/s12274-020-3172-3>.
- [16] S. Wu, J. Tang, F. Li, X. Liu, Y. Yamauchi, M. Ishida, H. Zhou, A synergistic system for lithium-oxygen batteries in humid atmosphere integrating a composite cathode and a hydrophobic ionic liquid-based electrolyte, *Adv. Funct. Mater.* 26 (2016) 3291–3298, <https://doi.org/10.1002/adfm.201505420>.
- [17] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries, *Science* (1979). 350 (2015) 938–943. doi:<https://doi.org/10.1126/science.aab1595>.
- [18] F.M.N.U. Khan, M.G. Rasul, A.S.M. Sayem, N.K. Mandal, Design and optimization of lithium-ion battery as an efficient energy storage device for electric vehicles: a comprehensive review, *J. Energy Storage* 71 (2023) 108033, <https://doi.org/10.1016/j.est.2023.108033>.
- [19] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, Molecular states of water in room temperature ionic liquids, *Phys. Chem. Chem. Phys.* 3 (2001) 5192–5200, <https://doi.org/10.1039/b106900d>.
- [20] O. Borodin, G.A. Giffin, A. Moretti, J.B. Haskins, J.W. Lawson, W.A. Henderson, S. Passerini, Insights into the structure and transport of the Lithium, sodium, magnesium, and zinc Bis(trifluoromethanesulfonyl)imide salts in ionic liquids, *J. Phys. Chem. C* 122 (2018) 20108–20121, <https://doi.org/10.1021/acs.jpcc.8b05573>.
- [21] L. Martínez, R. Andrade, E.G. Birgin, J.M. Martínez, PACKMOL: a package for building initial configurations for molecular dynamics simulations, *J. Comput. Chem.* 30 (2009) 2157–2164, <https://doi.org/10.1002/jcc.21224>.
- [22] W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids, *J. Am. Chem. Soc.* 118 (1996) 11225–11236, https://doi.org/10.1021/JA9621760.SUPPL_FILE/JA11225.PDF.
- [23] W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, M.L. Klein, Comparison of simple potential functions for simulating liquid water, *J. Chem. Phys.* 79 (1983) 926–935, <https://doi.org/10.1063/1.445869>.
- [24] H. de Araujo Chagas, G. Colherinhas, Temperature dependence of electric double-layer structure and electrochemical properties in graphene supercapacitors with [emim][BF₄] electrolyte: a molecular dynamics study, *Chem. Phys. Lett.* 877 (2025) 142325, <https://doi.org/10.1016/j.cplett.2025.142325>.
- [25] H. de Araujo Chagas, E.E. Fileti, G. Colherinhas, A molecular dynamics study of graphene-based electrode and biocompatible ionic liquid for supercapacitor applications, *J. Mol. Liq.* 360 (2022) 119494, <https://doi.org/10.1016/j.molliq.2022.119494>.
- [26] H. de Araujo Chagas, E.E. Fileti, G. Colherinhas, Comparing supercapacitors with graphene/graphene electrodes and [Bmim][PF₆] [Emim][BF₄] [Ch][Gly] and [Pyr][Tfsl] ionic liquids using molecular dynamics, *J. Mol. Liq.* 379 (2023) 121703, <https://doi.org/10.1016/j.molliq.2023.121703>.
- [27] L. de S. Silva, H. de A. Chagas, G. Colherinhas, Sustainable supercapacitors using advanced hydrated amino acid ionic liquids: a novel approach to biodegradable energy storage, *J. Mol. Liq.* 417 (2025) 126638. doi:<https://doi.org/10.1016/j.molliq.2024.126638>.
- [28] E.E. Fileti, H. de A. Chagas, G. Colherinhas, T. Malaspina, Quantum molecular dynamics approach to understanding interactions in betaine chloride and amino acid natural deep eutectic solvents, *ACS Phys. Chem. Au* 5 (2024) 72, <https://doi.org/10.1021/acsphyschemau.4c00072>.
- [29] G. Colherinhas, T. Malaspina, E.E. Fileti, Storing energy in biodegradable electrochemical supercapacitors, *ACS Omega* 3 (2018) 13869–13875, <https://doi.org/10.1021/acsomega.8b01980>.
- [30] L.B.A. Oliveira, L. de S. Silva, T.L. Fonseca, G. Colherinhas, Chloride substitution and hydration effects in [emim][bnz] electrolytes for lightweight supercapacitors, *J. Mol. Liq.* 443 (2026) 129142. doi:<https://doi.org/10.1016/j.molliq.2025.129142>.
- [31] L. de S. Silva, G. Colherinhas, Ester-based electrolyte mixtures for graphene supercapacitors: a molecular dynamics investigation, *J. Phys. Chem. B* 130 (2026) 2178–2193. doi:<https://doi.org/10.1021/acs.jpcc.5c06507>.
- [32] H. de Araujo Chagas, G. Colherinhas, E.E. Fileti, Unveiling the potential of natural deep eutectic solvents in electrochemical energy storage applications, *ACS Physical Chemistry Au* 6 (2026) 29–37, <https://doi.org/10.1021/acsphyschemau.5c00063>.
- [33] L. de S. Silva, G. Colherinhas, Evaluation of structural and electrochemical properties of supercapacitors with graphene electrodes and hydrated pure or mixed [bmim]-based ionic liquids via molecular dynamics, *ACS Phys. Chem. Au* 5 (2025) 519–532. doi:<https://doi.org/10.1021/acsphyschemau.5c00036>.
- [34] L.B.A. Oliveira, L. de S. Silva, H. de Araujo Chagas, T.L. Fonseca, G. Colherinhas, Impact of chloride and bromide composition in ionic liquid/water electrolytes on

- the electrochemical performance of graphene-based supercapacitors: a molecular dynamics study, *J. Phys. Chem. C* 129 (2025) 13532–13541, <https://doi.org/10.1021/acs.jpcc.5c01816>.
- [36] G. Bussi, D. Donadio, M. Parrinello, Canonical sampling through velocity rescaling, *J. Chem. Phys.* 126 (2007) 014101, <https://doi.org/10.1063/1.2408420>.
- [37] T. Darden, D. York, L. Pedersen, Particle mesh Ewald: an N-log(N) method for Ewald sums in large systems, *J. Chem. Phys.* 98 (1993) 10089–10092, <https://doi.org/10.1063/1.464397>.
- [38] M.J. Abraham, T. Murtola, R. Schulz, S. Páll, J.C. Smith, B. Hess, E. Lindahl, Gromacs: high performance molecular simulations through multi-level parallelism from laptops to supercomputers, *SoftwareX* 1–2 (2015) 19–25. doi:<https://doi.org/10.1016/j.softx.2015.06.001>.
- [39] M. Abraham, A. Alekseenko, C. Bergh, C. Blau, E. Briand, M. Doijade, S. Fleischmann, V. Gapsys, G. Garg, S. Gorelov, G. Gouaillardet, A. Gray, M. E. Irrgang, F. Jalalypour, J. Jordan, C. Junghans, P. Kanduri, S. Keller, C. Kutzner, J.A. Lemkul, M. Lundborg, P. Merz, V. Miletić, D. Morozov, S. Páll, R. Schulz, M. Shirts, A. Shvetsov, B. Soproni, D. van der Spoel, P. Turner, C. Uphoff, A. Villa, S. Wingbermühle, A. Zhmurov, P. Bauer, B. Hess, E. Lindahl, GROMACS 2023 Manual, 2023, <https://doi.org/10.5281/ZENODO.7588711>.
- [40] B. Hess, H. Bekker, H.J.C. Berendsen, J.G.E.M. Fraaije, LINC: a linear constraint solver for molecular simulations, *J. Comput. Chem.* 18 (1997) 1463–1472, [https://doi.org/10.1002/\(SICI\)1096-987X\(199709\)18:12<1463::AID-JCC4>3.0.CO;2-H](https://doi.org/10.1002/(SICI)1096-987X(199709)18:12<1463::AID-JCC4>3.0.CO;2-H).
- [41] W. Humphrey, A. Dalke, K. Schulten, VMD: visual molecular dynamics, *J. Mol. Graph.* 14 (1996) 33–38, [https://doi.org/10.1016/0263-7855\(96\)00018-5](https://doi.org/10.1016/0263-7855(96)00018-5).
- [42] J.B. Haskins, J.J. Wu, J.W. Lawson, Computational and experimental study of Li-doped ionic liquids at electrified interfaces, *J. Phys. Chem. C* 120 (2016) 11993–12011, <https://doi.org/10.1021/acs.jpcc.6b02449>.