Controlling Interfacial Structural Evolution in Aqueous Electrolyte via Anti-Electrolytic Zwitterionic Waterproofing

Zheng Bo,* Meiqi Zhou, Shiyuan Zhou, Yajing Song, Zhu Liu, Honggang Liao,* Huachao Yang, Jianhua Yan, Kefa Cen, Xiulin Fan, Qian Yu, Kostya (Ken) Ostrikov, and Ju Li

Aqueous electrolytes are considered as an alternative to flammable and toxic organic electrolytes, whose broad applications in electrochemical energy storage (EES) devices unfortunately suffer from low electrochemical stability due to the easy electrolysis of water. Here, by performing in situ transmission electron microscope electrochemical characterizations at atomic resolution during charging/discharging, an anti-electrolytic strategy is revealed in aqueous electrolytes via physical zwitterionic waterproofing. It is found that the zwitterionic molecules can be directionally adsorbed to the negative electrode’s surface under the applied electric field, forming strings of zwitterionic molecules that extract water out from the electrode. More zwitterionic molecules further aggregate at the outer end of the strings through intermolecular electrostatic interactions, forming a waterproof layer that successfully expels water from the electrode’s surface. Meanwhile, the self-aggregation of zwitterionic additives in the bulk liquid successfully minimizes the influence on ion transport. Being intrinsically distinct from the solid electrolyte interphase concept associated with certain electrochemical reactions in organic or super-concentrated electrolytes, the strategy is effective in improving the electrochemical stability while maintaining high ionic conductivity in various aqueous electrolytes even with a dilute concentration, shedding light on developing sustainable EES devices with high performance.

1. Introduction

Electrolyte plays an essential role in tuning the overall performance of electrochemical energy storage (EES) devices.[1] The synergetic combination of wide voltage window, high ionic conductivity, non-flammability, and large temperature range is required for liquid electrolyte used for high-performance and sustainable EES technologies.[2] Aqueous electrolytes, which are intrinsically non-flammable, highly conductive, environmentally friendly and low-cost, have always been considered as a potential alternative to flammable and toxic liquid organic electrolytes.[3] Unfortunately, free water in aqueous electrolytes has quite high reactivity with charged electrodes, whose thermodynamic electrochemical stability window is only 1.23 V that is ~30% that of the organic electrolyte.[4] Building a protective solid-electrolyte interphase (SEI) layer at the electrode–electrolyte interface has been demonstrated as an effective route to prevent the continuous electrolysis of electrolytes.[5,6] However, such strategy is difficult to be applied in aqueous electrolytes since the easy electrolysis of free water continuously defeats the formation of robust SEI layer.[6,7]

Adding high concentration or certain type of salts had been proposed to facilitate the formation and repair of SEI layer on the electrode surface in aqueous electrolytes by enhancing chemical reaction of ions, especially the decomposition of anions, to overwhelm water electrolysis reaction.[7] However, issues including the consumption of electrolytes, poor environmental adaptability, and...
badly controllable kinetics remain unsolved.[62,8] In addition, since the competition between different chemical reactions (water electrolysis and decomposition of ions) relies on kinetics and is highly sensitive to environmental factors such as temperature and concentration, phase change of electrolyte in the form of gassing, freezing, or salt precipitation may occur even at ambient temperature.[9]

As an alternative strategy, nonionic additives (e.g., sucrose molecules and polyethylene glycol) are used to directly confine the free water structure to suppress water electrolysis and expand the electrochemical stability windows via strong electrostatic interactions between water molecules and hydrophilic functional groups.[10] However, the amount of free water in the bulk liquid phase is indiscriminately decreased, resulting in serious ion pairing and low conductivity of only 0.8–3.376 mS cm$^{-1}$.[10] Such a trade-off is detrimental to the rate performance and power density of EES devices.[11]

Here, by performing in situ transmission electron microscope electrochemical characterizations at atomic resolution upon charging/discharging, we revealed a mechanism for breaking the trade-off between electrochemical window and ionic conductivity in aqueous electrolytes via antielectrolytic zwitterionic waterproofing at the electrode surface with negligible influence on ion transport in bulk liquid. The formation mechanism of the nanometers’ thick waterproof layer was studied by visualizing the dynamic behaviors of zwitterionic molecules near the electrode surface during charging/discharging at atomic resolution. Meanwhile, the zwitterionic molecules self-assembled into circular clusters, displaying negligible influence on ion transport. Consequently, the electrochemical stability window of the aqueous electrolyte was significantly increased to $≈2.83$ V accompanied with high ionic conductivity up to 26 mS cm$^{-1}$. Being intrinsically distinct from the SEI mechanism associated with certain electrochemical reactions in organic or super-concentrated electrolyte, our mechanism is applicable to various aqueous electrolytes (e.g., NaNO$_3$, LiNO$_3$, KNO$_3$ and Li$_2$SO$_4$) even with a dilute concentration, shedding light on developing sustainable EES devices with high performance.

2. Results and Discussion

The zwitterionic additive here refers to a family of materials possessing anionic and cationic groups with different wettability, characterized by high dipole moments but are still charge neutral. As a typical example, betaine ($C_5H_11NO_2$), has a negatively charged, hydrophilic carboxyl (−COO$^-$) group on one end, and a positively charged but hydrophobic trimethyl ammonium (−N$^+$(CH$_3$)$_3$) group on the other end of the same monomeric unit (Figure 1a).[13] Considering the unique zwitterionic nature of betaine additive, we expect that, as the electrode is negatively polarized, the hydrophilic positively charged −N$^+$(CH$_3$)$_3$ groups of betaine would move toward the electrode surface due to the strong counterion–electrode coulombic interactions, while the water molecules could be expelled from the electrode surface since they favor the hydrophilic negatively charged −COO$^-$ groups. Moreover, driven by the intermolecular electrostatic interaction, more betaine aggregations would continuously connect to the ones preferentially adsorbed on the electrode surface at another end with hydrophilic negatively charged −COO$^-$ group. Based on our density functional theory (DFT) calculations (see Experimental Section), the binding energy of the betaine molecule to itself is larger than that of the betaine to water, and the binding energy of betaine/ions is lower than that of the water/ions, indicating that clustering of betaine molecules should occur (The detailed results of the binding energy calculation are listed in Table S1, Supporting Information).

In this way, an anti-electrolytic waterproof layer would physically form at the surface of the negatively charged electrode to reduce the free water in the interfacial region and suppress water electrolysis, which would be beneficial to the expansion of voltage window. On the other hand, the self-aggregated structure would rarely affect the original electrolyte environment in the bulk liquid phase and thus impart sufficient free water as solvent to transport charged ions.

Such a hypothesis is primarily supported by our molecular dynamics (MD) simulation. A simulation cell containing 189 Na$^+$ ions, 189 NO$_3^-$ ions, 726 betaine, and 5,252 water molecules was built to formulate the 2 m NaNO$_3$−0.9Betaine/H$_2$O electrolyte (Experimental Section), which was sandwiched between two graphene sheets as the negative and positive electrodes. An electric field $E_z = 0.2$ V nm$^{-1}$ was imposed along the z-axis of the electrolyte solutions with a thickness of $≈7.5$ nm to mimic the experimental electrochemical condition. As shown in Figure 1b, high density of betaine molecules gathered at the interface, resulting in an obvious water-avoiding region between the negative electrode and the electrolyte. Consequently, the number density of water molecules at the interface was estimated to be $≈78%$ lower than that of the bulk liquid region (detailed calculation can be found in Experimental Section). Such effect was absent at the positive electrode. Further increase of the electric field led to the penetration of cations through the waterproof layer (Figure S1, Supporting Information), realizing electrostatic adsorption at both electrodes and energy storage. With such an antielectrolytic zwitterionic water-proof layer, the cathodic limit potential and the overall electrochemical stability window of electrolyte should be expanded. Meanwhile, the solvation shell of Na$^+$ or NO$_3^-$ ions was maintained, leaving free water to separate ion pairing as shown in the right magnified window of Figure 1b. Following such principle, other zwitterionic additives, such as sulfobetaine (3-Dimethyl-oxylazaniuniyl)propane-1-sulfonate, $C_5H_{35}NO_S$, should also perform the same (The relative binding energy calculation are listed in Table S2, Supporting Information).

Being distinct from the previous SEI concept relying on the chemical reactions of electrolytes, the above strategy is based on the formation of an anti-electrolytic waterproof layer through a physical process. Realizing this concept and describing it in real at molecular resolution, we constructed a micro-supercapacitor system in a liquid cell in high-resolution transmission electron microscope (HRTEM) for real-time observation by using acetylene black electrode and NaNO$_3$−Sulfobetaine/H$_2$O electrolyte, as schematically shown in Figure 1c. To enhance the mass-thickness contrast of TEM images and facilitate observations,[13] sulfobetaine with heavier element (S) is used for in situ observations instead of betaine containing only light elements (C, H, O, and N). Similar to betaine, sulfobetaine also has a negatively
charged hydrophilic group and a positively charged but hydrophobic group on the same monomeric unit, which meets our concept of design. More details of the methods are presented in Experimental Section. In Figure S2, we present a series of HRTEM images showing the change of morphology of the electrode with atomic resolution during the negative polarization process. The corresponding in situ HRTEM movie was provided as Movie S1. Significant shrinkage of the electrode material was observed under electric field. Meanwhile, the surface of the electrode material became rough with a gel-like structure attached to the crystalized acetylene black electrode. Figure 2a demonstrated the atomistic pictures of this evolution in details by showing the dynamic behaviors of sulfobetaine molecules upon charging. As a negative potential was applied on the electrode, we observed that considerable sulfobetaine molecules were attached to the surface of the loose acetylene black electrode, as marked by the white arrows in Figure 2a. It is noted that the length of one sulfobetaine molecule is \( \approx 1 \) nm, therefore the black linear contrast here should refer to a string of several...
sulfobetaine molecules’ connection head to tail. The volume of acetylene black shrank as that clearly presented in Movie S2 (Supporting Information). This can be explained by the fact that the zwitterionic sulfobetaine molecules attach to the negatively charged electrode with its positive hydrophobic group and is capable of expelling water stored in the loose structure of acetylene black. The string of sulfobetaine molecules attached to the surface of electrode further grew in length by connecting additional molecules until at certain moment nano-clustering of sulfobetaine molecules occurred at the near surface with frequent reshaping (as marked by the blue arrows in Figure 2a). Later the clusters of sulfobetaine molecules wrapped around the surface of the carbon electrode, forming a waterproof layer. Therefore, as shown in the schematic in Figure 2b, our in situ HRTEM observations indicate that the formation of the waterproof layer seems to involve three stages of structural evolution: the initial directional adsorption of sulfobetaine molecules to the electrode surface, the lengthening of the molecules’ string, and the clustering of the sulfobetaine molecules. The morphology of the waterproof layer depends on the surface roughness of the electrode. Protrusions would appear at the salient points on the electrode. However, if the electrode surface is relatively flat, the waterproof layer can be quite uniform in thickness. Figure 2c and Movie S3 (Supporting Information) show the dynamic process of the formation of the waterproof layer at atomic resolution on an individual acetylene black particle with diameter at \( \approx 30 \) nm. It was observed that except one protrusion, the waterproof layer gradually formed at different places and further connected with each other and paved around the surface of the electrode particle. The thickness of the waterproof layer was only \( \approx 5 \) nm. The shrink rate of the carbon electrode’s diameter is calculated as 0.0315 nm s\(^{-1}\) (Figure S3, Supporting Information). During the entire process, the atomic structure of the acetylene black near the...
surface maintained the same and no gas bubble was observed, indicating that no chemical reaction occurred during the successful impediment of water electrolysis.

The distribution of zwitterionic additives and charged ions on the electrode surface at different working voltages were systematically studied by using high-resolution scanning transmission electron microscope (HRSTEM) and energy-dispersive X-ray spectroscopy (EDS) to provide chemical information that complemented the in situ observations on structural evolution. The cross-section TEM samples of the electrode in the bulk counterparts were lift-off from the surface of 0.5 V charged, 1.0 V charged and discharged negative electrode materials in NaNO₃–Sulfobetaine/H₂O electrolytes, respectively. The signal of C, Na, and S represents the information of electrode, positive ion in electrolyte and sulfobetaine additive, respectively. The signal of O can come from sulfobetaine additive and NaNO₃ solution to 2 m NaNO₃ electrolyte was observed (Figure 4d). According to the electrochemical stability window of bulk water. Meanwhile, as shown in Figure 4b, the ionic conductivity is up to 26 mS cm⁻¹, much higher than those of conventional nonionic additive approaches (0.8–3.736 mS cm⁻¹). In addition, one can even expand the cathodic limit potential to −1.53 V and the overall electrochemical stability window to 2.83 V (Figure S4, Supporting Information) by further increasing the concentration of betaine (2 m NaNO₃–1.3Betaine/H₂O). The same electrochemical testing was performed on NaNO₃–Sulfobetaine/H₂O electrolyte as well. The overall electrochemical stability window was expanded to 2.76 V (Figure S5, Supporting Information) with the ionic conductivity remaining high (10.42 mS cm⁻¹). Besides, two additional zwitterionic additives 3-[Decyl(dimethyl)ammonio]-1-propanesulfonate (C₁₃H₂₅NOS) and 3-[Dodecyl(dimethyl)ammonio]-1-propanesulfonate (C₁₇H₃₅NOS) are tested as well, the detailed methods are presented in Experimental Section. The electrochemical stability windows and ionic conductivities of the two electrolytes with zwitterionic additives are measured as 2.71 V/40.1 mS cm⁻¹ and 2.67 V/45 mS cm⁻¹, respectively (Figures S6 and S7, Supporting Information).

Benefiting from the above merits, the zwitterion-based electrolyte enables the construction of high-performance supercapacitors. The electrochemical performances using betaine-based and nonionic additive-based electrolytes (2 m NaNO₃–0.9Betaine/H₂O and 2 m NaNO₃/66.7 wt.% sucrose) are comprehensively compared. Symmetric supercapacitor coin cells using commercial activated carbon YP-50F electrodes are assembled, and the detailed fabrication process can be found in Experimental Section. Importantly, due to the moisture-tolerant and environmentally friendly properties of the electrolytes, the assembly process of supercapacitor cells can be conveniently performed in the ambient atmosphere without a glove box. The supercapacitors using 2 m NaNO₃–0.9Betaine/H₂O electrolyte displayed significant optimization in terms of both capacitance and resistance. The cyclic voltammogram (CV) curve of 2 m NaNO₃–0.9Betaine/H₂O electrolyte at a scan rate of 200 mV s⁻¹ shows an approximately rectangular shape, indicating a good capacitive behavior (Figure 4c). The CV curves at other scan rates can be found in Figures S8 and S9 (Supporting Information). Smaller IR drop of the galvanostatic charge/discharge (GCD) curves of 2 m NaNO₃–0.9Betaine/H₂O electrolyte is observed (Figure 4d). According to the electrochemical impedance spectroscopy (Figure 4e) and equivalent circuit fitting results (Figure S10, Supporting Information), the charge...
Figure 3. HAADF-STEM images and EDS mapping of the porous carbon electrodes with different charging conditions, and the HRTEM images showing the self-aggregation of sulfo betaine in the bulk liquid phase. a) HAADF-STEM images of carbon electrode at varying voltages and the corresponding EDS maps for typical elements involved of C, Na, O, and S. Significant accumulation of additives, and Na⁺ can be observed at the electrode surface when the electrode is polarized to near maximum potential. b) The time-series TEM images of the bulk liquid phase of the NaNO₃–Sulfo betaine/H₂O solutions under electric field. The sulfo betaine molecules were separated from the solution and formed the nanosized clusters with hydrophilic sulfur-containing groups on the periphery and other hydrophobic groups on the inner layer.
transfer resistance ($R_{ct}$) and equivalent series resistance ($R_s$) are 0.12 and 0.41 $\Omega\,\text{cm}^2$ for 2 m NaNO$_3$–0.9Betaine/H$_2$O systems, respectively, which are significantly lower than those of 2 m NaNO$_3$/66.7 wt.% sucrose (1.64 and 4.01 $\Omega\,\text{cm}^2$, respectively), confirming the smaller resistance for ion transportation. Consequently, upon a 40-fold current density increase from 0.5 to 20 A g$^{-1}$, a superior capacitance retention of 82.3% (from 36.2 to 29.8 F g$^{-1}$) is recognized for 2 m NaNO$_3$–0.9Betaine/H$_2$O systems, in contrast to the value of 16% (from 24.22 to 3.87 F g$^{-1}$) in 2 m NaNO$_3$/66.7 wt.% sucrose (Figure 4f). Due to the large electrochemical stability window and high ionic conductivity, supercapacitors using 2 m NaNO$_3$–0.9Betaine/H$_2$O electrolyte exhibit superior energy density and power density as evidenced by the Ragone plots in Figure 4g.

As shown in Figure S11 (Supporting Information), supercapacitors using 2 m NaNO$_3$–0.9Betaine/H$_2$O shows a high capacitance retention of 85% after 20,000 cycles at 5 A g$^{-1}$ with nearly 100% coulombic efficiency, demonstrating the advantages of our new method beyond the traditional SEI strategy. Meanwhile, since betaine is capable of destroying the hydrogen-bond network of water,[14] using betaine would put down the freezing point of water to even lower. Differential scanning calorimetry (DSC) measurements show that the thermogram of the 2 m NaNO$_3$–1.3Betaine/H$_2$O electrolyte is a completely flat
line, indicating that there is no obvious phase change within a wide temperature range of 80 to −90 °C (Figures S12a and S12b, Supporting Information). Considering that the temperature limit of WIS electrolyte employing traditional SEI layer is only ~10 °C,[10d] using zwitterionic betaine additives is obviously beneficial for energy storage at low-temperature environment (Figure 4h).

3. Conclusion

The results above demonstrated that the as-proposed antielec-

trolytic zwitterionic waterproofing strategy is capable of sup-

pressing interfacial electrolysis of aqueous electrolytes with

negligible influence on ion transport in bulk solution. The

qualified zwitterionic additives should contain the following

characters: 1) owning negatively and positively charged ends

with opposite wettability in monomeric unit, which can orien-

t themselves precisely in electrostatic adsorption to form the

waterproof layer that can suppress electrolysis at the solid-

liquid interface and 2) their self-aggregation in electrolyte is

energetically favorable and would not confine free water so

that ion pairing can be avoided in bulk liquid phase. Since our

strategy relies on physical electrostatic interactions not chem-

istry, it is applicable to not only sodium-contained electrolyte

but also lithium and potassium salt electrolytes (the data was

listed in Figure S13, Supporting Information) that are widely

used for aqueous electrolyte energy storage devices. Such a gen-

eral concept of controlling the interfacial structural evolution

is scientifically important since it is free of the issues associ-

ated with chemical reactions, which is less sustainable and is

generally not applicable to dilute aqueous electrolytes.[6,7,15] Our

results shed light on designing high-voltage and highly-conduc-

tive aqueous electrolytes with high adaptive capacity to environ-

ments for sustainable energy storage devices. One can expect

that, a series of zwitterion-based aqueous electrolytes can be

further explored based on this strategy, which may even push

the performance of EES devices to new high.

4. Experimental Section

Materials and Characterizations: Electrolytes were prepared by molality

(mol kg⁻¹), abbreviated as m. Zwitterion-based electrolytes were prepared by

mixing betaine (C₅H₁₁NO₂) with deionized water at different weight

ratios (0.9 and 1.3), abbreviated as 0.9Betaine/H₂O and 1.3Betaine/

H₂O for simplicity. Then 2 m NaNO₃ were dissolved into the Betaine/

H₂O solution to formulate 2 m NaNO₃–0.9Betaine/H₂O and 2 m

NaNO₃–1.3Betaine/H₂O electrolytes. And 2 m KNO₃, 2 m LiNO₃, and 1 m

Li₂SO₄ were dissolved into the Betaine/H₂O solution to formulate 2 m

NaNO₃–0.9Betaine/H₂O, 2 m LiNO₃–0.9Betaine/H₂O, and 1 m

Li₂SO₄–0.9Betaine/H₂O, respectively. The NaNO₃–Sulfobetaine/H₂O electrolyte

was prepared by dissolving 2 m NaNO₃ and sulfobetaine-8 (3-[Dimethyl-

cyclaziniumyl]propane-1-sulfonate, C₁₃H₂₉NO₃S) in deionized water

at a Sulfobetaine/H₂O weight ratio of 1.4. 3-[Decyl(dimethyl)ammonio]-

1-propanesulfonate (C₁₃H₂₉NO₃S) was added into the 2 m NaNO₃

aqueous electrolyte at a betaine to water weight ratio of 0.7 to construct

NaNO₃–C₃H₇NO₃S/H₂O electrolyte. The 2 m NaNO₃/66.7 wt.% sucrose electrolyte

were fabricated by adding 2 m NaNO₃ in 66.7 wt.% sucrose aqueous

solution (5.84 mol kg⁻¹) according to the literature.[10b] Lithium bis

(trifluoromethane sulfonyl) imide (LiTFSI) was mixed with deionized

water to create a 21 m LiTFSI solution. All the aqueous solutions were

fabricated in the ambient atmosphere at room temperature. The ionic

conductivities of electrolytes were measured by a conductivity meter

(DDSJ-308F, Shanghai). The thermal properties of the electrolyte were

carried out by Differential scanning calorimetry Q2000 (TA Instruments)

within the −90 to 80 °C temperature range under a scan rate of 5 °C min⁻¹.

Electrochemical Measurements: The electrodes used for the assembly

of supercapacitor coin cells were prepared as follows: YP-50 commercial

activated carbon (AC, YP-50F, Kuraray Chemical, Japan), carbon black,

stereoy-butadiene rubber (SBR), and carboxymethyl cellulose (CMC)

were mixed homogeneously with a ratio of 85:10:3:2. The obtained

mixture was stirred in the vacuum and coated on stainless steel current

collectors, and then the electrodes were dried at 60 °C for 3 h under

vacuum. The mass loadings of the electrodes were ~2.6 mg cm⁻². The

supercapacitor coin cells were assembled by different electrolytes using

two AC electrodes separated with a glass fiber membrane. Contributing to

the eco-friendly and moisture-resistant property of the betaine-

based electrolytes, the entire preparation and assembly process of the

supercapacitors were completely carried out in the ambient atmosphere

without using any moisture-free treatments. Cyclic voltammetry (CV),

linear sweep voltammetry (LSV), galvanostatic charge/discharge (GCD)

and electrochemical impedance spectroscopy (EIS) tests were carried

out using an electrochemical workstation (PGCSTAT302N, Metrohm

Autolab B.V.). The electrochemical stability window of electrolytes was
determined using three-electrode devices with stainless steel electrodes

and Ag/AgCl (in a 3 M KCl aqueous solution) reference electrode. EIS

measurements were executed with 5 mV amplitude over the frequency

range from 0.01 Hz to 100 kHz. Low-temperature electrochemical

performance tests were carried out in a temperature and humidity

chamber (Donggung Kowin Testing Equipment).

Accordingly, the specific capacitance C (F g⁻¹) of the supercapacitor

was calculated based on GCD curves according to the following

Equation (1):

\[ C = \frac{I}{V} \]  

where \( I \) (A g⁻¹) is the discharge current density, \( t \) (s) is the discharge
time obtained in GCD measurements, and \( V \) (V) is the potential window

after voltage drop. The mass of electrodes is calculated by their total

mass.

The specific energy density \( E \) (Wh kg⁻¹) and power density \( P \) (W kg⁻¹)

based on GCD curves are calculated using Equation (2) and (3).

\[ E = \frac{0.5CV^2}{3.6} \]  

\[ P = \frac{E \times 3600}{t} \]

where \( t \) (s) is the discharge time, \( V \) (V) is the potential window after

voltage drop, \( C \) (F g⁻¹) is the total capacitance of supercapacitor.

The coulombic efficiency, \( \eta \), measured in GCD tests is estimated by

\[ \eta = \frac{t_2}{t_1} \times 100\% \]  

where \( t_1 \) and \( t_2 \) (s) represent the discharge and charge time, respectively.

DFT Calculations: The binding energy calculations between betaine

(sulfobetaine), water, and ions were performed using the GAUSSIAN

09 program with the 6–311 G base set[19] at the B3LYP level.[17] The

calculated values and optimized morphologies are collected in the

Tables S1 and S2 (Supporting Information), where the solvation shells

for \( Na^+ \) and \( NO_3^- \) ions are taken from the trajectory of the molecular

dynamics simulations.

Molecular Dynamics (MD) Simulations: All MD simulations were

carried out using the GROMACS 2016.2 simulation package[18] in

rectangular simulation boxes under 3D periodic boundary conditions.

The GROMOS54A7 force field[19] for betaine, water, and graphene sheets
were employed in the simulation. The force field parameters for all ions were taken from Xie et al.[20] The simulation cell contains 189 Na\(^+\) ions, 189 NO\(_3\)\(^-\) ions, 726 betaines, and 5252 water molecules. The dimensions of the cell after equilibration are \(L_x \times L_y \times L_z = 60.77 \times 60.77 \times 101.28 \) Å, including a thickness of \(\approx 25 \) Å vacuum in the \(z\)-axis beyond the electrolyte solutions to avoid the interactions between two graphene sheets. We imposed electric field \(E_z\) of 0.2, 0.3, 0.4, and 0.5 V nm\(^{-1}\) along the \(z\)-axis on the electrolyte solution with a thickness of \(\approx 75 \) Å to mimic the electrochemical condition in experiments. Energy minimization of the initial configuration was performed using a steepest descent algorithm. Then the energy minimized configuration was equilibrated in the isothermal-isobaric (NPT) ensemble for 135 ns with configurations recorded every 10 ps. Temperature was kept at the room temperature with the Nosé–Hoover thermostat[21] using a 0.4 ps coupling time. Pressure was set at 1 bar with the Parinell–Ramahran barostat[22] using a 2 ps coupling time. All simulations used a 1.5 nm Lennard–Jones and short-distance Coulombic interaction cutoff. Long-range electrostatics were computed using Particle–Mesh Ewald summation.[23] Dynamics were propagated with a leap-frog Verlet integrator[24] using a 2 fs time step.

In situ Liquid Cell High-Resolution Transmission Electron Microscope (HRTEM) Measurement: Liquid cells with a 10 nm-thick low-stress SiNx (HRTEM) Measurement

Liquid cells with a 10 nm-thick low-stress SiNx were employed in the simulation. The force field parameters for all ions were taken from Xie et al.[20] The simulation cell contains 189 Na\(^+\) ions, 189 NO\(_3\)\(^-\) ions, 726 betaines, and 5252 water molecules. The dimensions of the cell after equilibration are \(L_x \times L_y \times L_z = 60.77 \times 60.77 \times 101.28 \) Å, including a thickness of \(\approx 25 \) Å vacuum in the \(z\)-axis beyond the electrolyte solutions to avoid the interactions between two graphene sheets. We imposed electric field \(E_z\) of 0.2, 0.3, 0.4, and 0.5 V nm\(^{-1}\) along the \(z\)-axis on the electrolyte solution with a thickness of \(\approx 75 \) Å to mimic the electrochemical condition in experiments. Energy minimization of the initial configuration was performed using a steepest descent algorithm. Then the energy minimized configuration was equilibrated in the isothermal-isobaric (NPT) ensemble for 135 ns with configurations recorded every 10 ps. Temperature was kept at the room temperature with the Nosé–Hoover thermostat[21] using a 0.4 ps coupling time. Pressure was set at 1 bar with the Parinell–Ramahran barostat[22] using a 2 ps coupling time. All simulations used a 1.5 nm Lennard–Jones and short-distance Coulombic interaction cutoff. Long-range electrostatics were computed using Particle–Mesh Ewald summation.[23] Dynamics were propagated with a leap-frog Verlet integrator[24] using a 2 fs time step.

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