Regulating Electronic Double Layer to Prevent Water Electrolysis

for Wet Ionic Liquids with Cheap Salt

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Supplementary Figure 1. Schematic of molecular dynamics (MD) simulation. a, Snapshot of the wet ionic liquids with adding salt between two planar electrodes. b, Molecular structure of cation ($[Emim]^+$), anion ($[TFSI]^-$), water (H₂O) and sodium ion (Na⁺). c, Mass density distribution along the z direction between two electrode surfaces. Black dash line represents the density of wet ionic liquid in bulk-state. the density deviation within the central region of the simulation box (3 ~ 7 nm from the electrode surface) remains -0.78% compared with that of bulk wet IL, suggesting that the sizes of simulated systems were sufficiently extensive to reproduce the bulk-like behavior of the electrolytes in the region central to the two electrodes.

Supplementary Table 1. Setup parameters of simulations. Number of cations, anions, water molecules, and $M^+(Li^+, Na^+, and K^+)$, the molar salt-water ratio, and the distance, L, between the electrodes, as well as the mass density error relative to the bulk state in each molecular dynamics system. Cation in the table means the cation in ionic liquids (ILs), i.e., 1-ethyl-3-methylimidazolium ([Emim]⁺); anion in the table means bis(trifluoromethylsulfonyl)imide ([TFSI]⁻) in this work.

	system	cation	anion	water	M ⁺	salt- water ratio	L (nm)	Density Error (%)
Wet IL	System1	454	454	80	0	0	10.0	-0.78
Salt-in - wet-IL	System2 (Na ⁺)	454	534	80	80	1:1	11.0	-0.89
	System3 (Li ⁺)	454	534	80	80	1:1	11.0	-0.98
	System4 (K ⁺)	454	534	80	80	1:1	11.0	-0.93



Supplementary Figure 2. Hygroscopicity of RTILs in the humid air. Water content in [Emim][TFSI] as a function of time. Red lines are to guide the eyes; Blue lines represent the averaged humidity during the measurements. After a 48-hours exposure to air, the water content of [Emim][TFSI] reaches to ~8326 ppm.



Supplementary Figure 3. Coordination number distribution of water around water in different electrolytes. Coordination number distribution of water around water in wet [Emim][TFSI] (red bar), in sodium salt-in-wet IL (blue bar), and in potassium salt-in-humid IL (purple bar)



Supplementary Figure 4. Coordination number distribution of water around alkali ions in different electrolytes. Coordination number distribution of water around Na⁺ (red bar), and K⁺ (purple bar) in salt-in-wet [Emim][TFSI] electrolyte.



Supplementary Figure 5. Solvation structure using non-scaled-charge force field and scaled-charge force field. a, RDF of water with Na⁺ ion in salt-in-wet [Emim][TFSI]. b, Proportion of free water in wet [Emim][TFSI] and salt-in-wet [Emim][TFSI]. c, Hydrogen bond between water molecules. d, Hydrogen bond between water and IL.

To address the issue of polarization effects, we explored an alternative approach using a scaled-charge force field, which has been widely employed in simulation of ionic liquid.¹⁻⁴ This approach involves scaling the charges on the ions are to approximately account for electronic polarization and/or charge transfer, which has been proved to greatly improve the structure and dynamic properties of the electrolyte, close to the ab initio counterparts and experiments.^{1, 2} We adopted a common practice of setting the scaling factor to 0.8, consistent with previous research.^{3,4} The solvation structure with different force fields was shown in Supplementary Figure 5. Notably, the radial distribution function (RDF) of water and Na⁺ exhibited minimal alterations with the scaled-charge force field compared to the non-polarizable one (Supplementary Figure 5a). While there were slight deviations in the proportion of free water under different force fields, both showed a substantial decrease with the addition of alkali metal ions (Supplementary Figure 5b). A similar trend was observed in the disruption of hydrogen bonds between water molecules, indicating a significant perturbation of the hydrogen bond network upon the introduction of alkali salts (Supplementary Figure 5c-d).



Supplementary Figure 6. Coordination environment effect on the oxidation stability of alkali-ion free/bound water. HOMO energy levels (a) and vertical potentials (b) of H_2O and $M(H_2O)^+$ within SMD model.



Supplementary Figure 7. Number density distribution of ionic liquid under negative polarization. a-b, The number density profiles of $[\text{Emim}]^+$ and $[\text{TFSI}]^-$ as a function of distance from the negative electrode surface in wet [Emim][TFSI] (a) and salt-in-wet [Emim][TFSI] (b). The pink-shaded region (z < 0.35 nm) is considered to be the interfacial region. The graphs from top to bottom represent the applied 0 V, -1 V, -2 V, and -3 V, respectively.



Supplementary Figure 8. Number density distribution of ionic liquid under positive polarization. a-b, The number density profiles of $[\text{Emim}]^+$ and $[\text{TFSI}]^-$ as a function of distance from the negative electrode surface in wet [Emim][TFSI] (a) and salt-in-wet [Emim][TFSI] (b). The pink-shaded region (z < 0.35 nm) is considered to be the interfacial region. The graphs from top to bottom represent the applied 0 V, 1 V, 2 V, and 3 V, respectively.



Supplementary Figure 9. Number density distribution of water and Na⁺ ion under negative polarization. a-b, The number density profiles of H₂O and Na⁺ as a function of distance from the negative electrode surface in wet [Emim][TFSI] (a) and salt-in-wet [Emim][TFSI] (b). The pink-shaded region (z < 0.35 nm) is considered to be the interfacial region. The graphs from top to bottom represent the applied 0 V, -1 V, -2 V, and -3 V, respectively.



Supplementary Figure 10. Number density distribution of water and Na⁺ ion under positive polarization. a-b, The number density profiles of H₂O and Na⁺ as a function of distance from the negative electrode surface in wet [Emim][TFSI] (a) and salt-in-wet [Emim][TFSI] (b). The pink-shaded region (z < 0.35 nm) is considered to be the interfacial region. The graphs from top to bottom represent the applied 0 V, 1 V, 2 V, and 3 V, respectively.



Supplementary Figure 11. Salt effect on the Electrosorption of water. a-b, Electrosorption of interfacial water in wet [Emim][TFSI] and salt-in-wet [Emim][TFSI] electrolyte with addition LiTFSI (**a**) and with addition KTFSI (**b**). The top and bottom panels are the total, and free /bound adsorbed water, respectively.



Supplementary Figure 12. Tendency for Na⁺ electrosorption at electrodes. a-b, Potential of mean force (PMF) of Na⁺ in [Emim][TFSI] as a function of distance from the electrode under negative polarization (-2 V) (a), and under positive polarization (2 V) (b). The PMF curves are calculated via umbrella sampling along the distance from the electrode surface. The pink-shaded region (z < 0.35 nm) is considered as the interfacial region.

Reference

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