Electronic Supplementary Information for

Correlation between Mobility and Hydrogen Bonding Network of Water at Electrified-Graphite Electrode Using Molecular Dynamics Simulation

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Determination of the cell size.

Fig. S1: Potential profiles calculated by using Poisson equation.

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Determination of the cell size

We designed the condenser-type cell so that the water density in the bulk region matches the density of corresponding bulk liquid as follows,

(a) First, we performed MD calculation of 0.5 mol / L aqueous solution (without electrodes) under NPT conditions for 10 ns. Number density was estimated from the equilibrated cell.

(b) Next, we performed an MD calculation of a condenser-type cell at pzc under NVT conditions for 20 ns (The first 10 ns was for equilibration and the next 10 ns was for analysis). A position at least 2 nm away from the outermost surface of each electrode was defined as a bulk, and the average number density in the bulk region was calculated. The distance between the graphite electrodes was adjusted so that this value and the number density of (a) coincided by rounding to the first decimal place (in unit of nm^{-3}), and repeated until convergence.

(c) MD calculation in the case where the electrode surface has a charge is performed with the same cell size as the pzc condition. As shown in Table S1, we confirmed that the density in the middle region is within the range when a potential is applied.

Table S1 Comparison of the number density of water (/ nm^{-3}) for determining the simulation cell size.

salt	Bulk liquid	Number density (/ nm^{-3}) at the middle region (~20 < z < ~70 Å)					Distance between graphite /Å
		0 /μC cm^{-2}	1.83 /μC cm^{-2}	3.66 /μC cm^{-2}	5.49 /μC cm^{-2}	7.32 /μC cm^{-2}	
pure	33.33	33.00	33.02	33.03	33.03	33.01	90.50
LiCl	33.16	33.21	33.20	33.25	33.21	33.21	89.94
NaCl	32.59	32.55	32.54	33.56	32.54	33.53	91.34
CsCl	32.55	32.66	32.64	32.67	32.68	32.72	91.05
NaF	33.46	33.44	33.48	33.51	33.52	33.50	90.07
NaBr	33.09	32.68	32.70	32.72	32.71	32.69	91.91
NaI	32.47	32.00	31.98	32.01	32.01	31.99	92.88

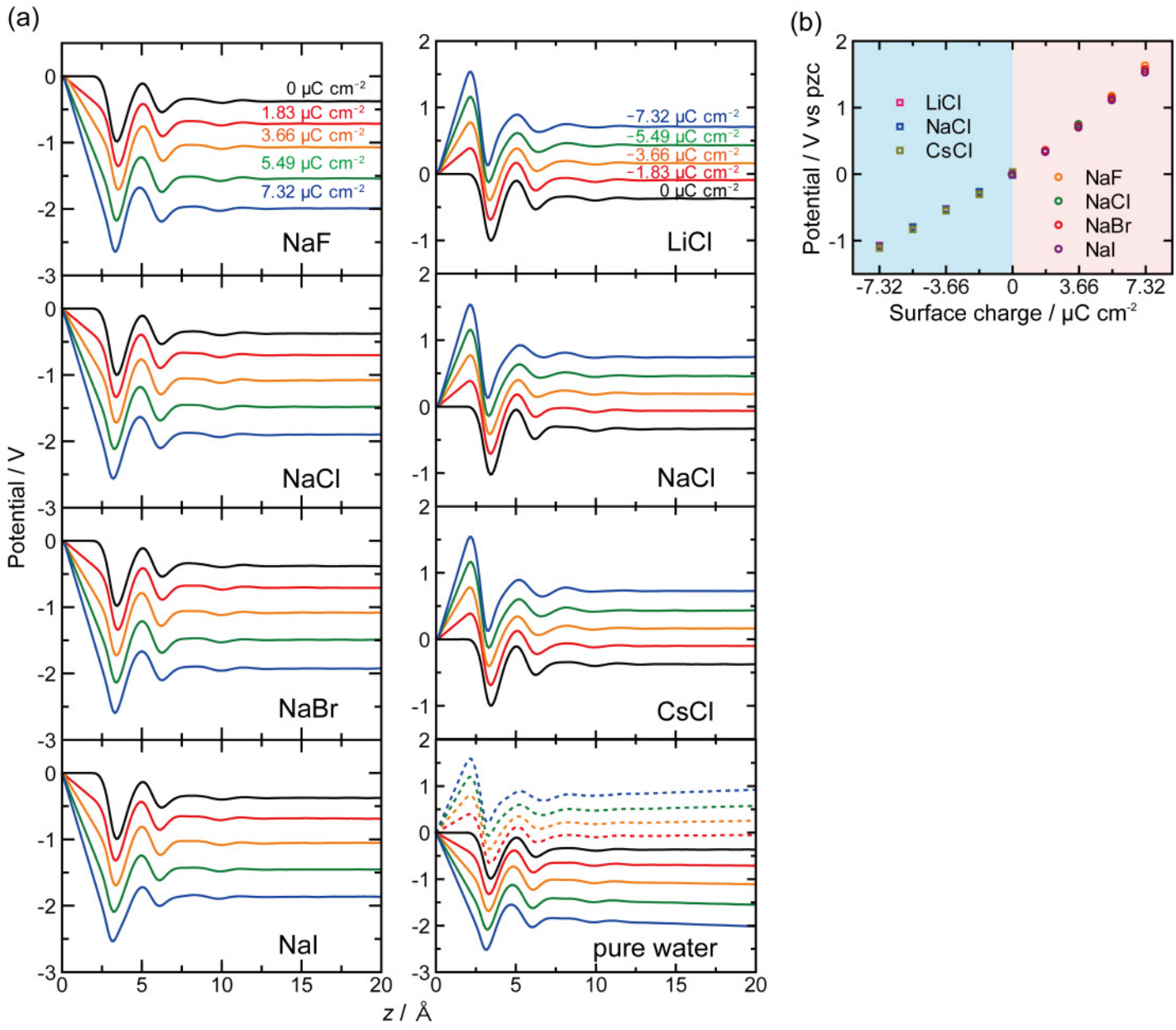

Fig. S1 Potential profiles calculated by using Poisson equation at positively (NaF, NaCl, NaBr, and NaI) and negatively charged (LiCl, NaCl, and CsCl) interfaces. For the pure water/graphite electrode, the results of both the positively (solid lines) and negatively (dotted lines) charged interfaces are shown. The potential drop with respect to the bulk region for the pure water/graphite interface at pzc was −0.363 V (black solid line in pure water). (b) Potential vs. surface charge plots reconstructed from (a). Potentials are relative values with respect to pzc of the pure water/graphite interface.

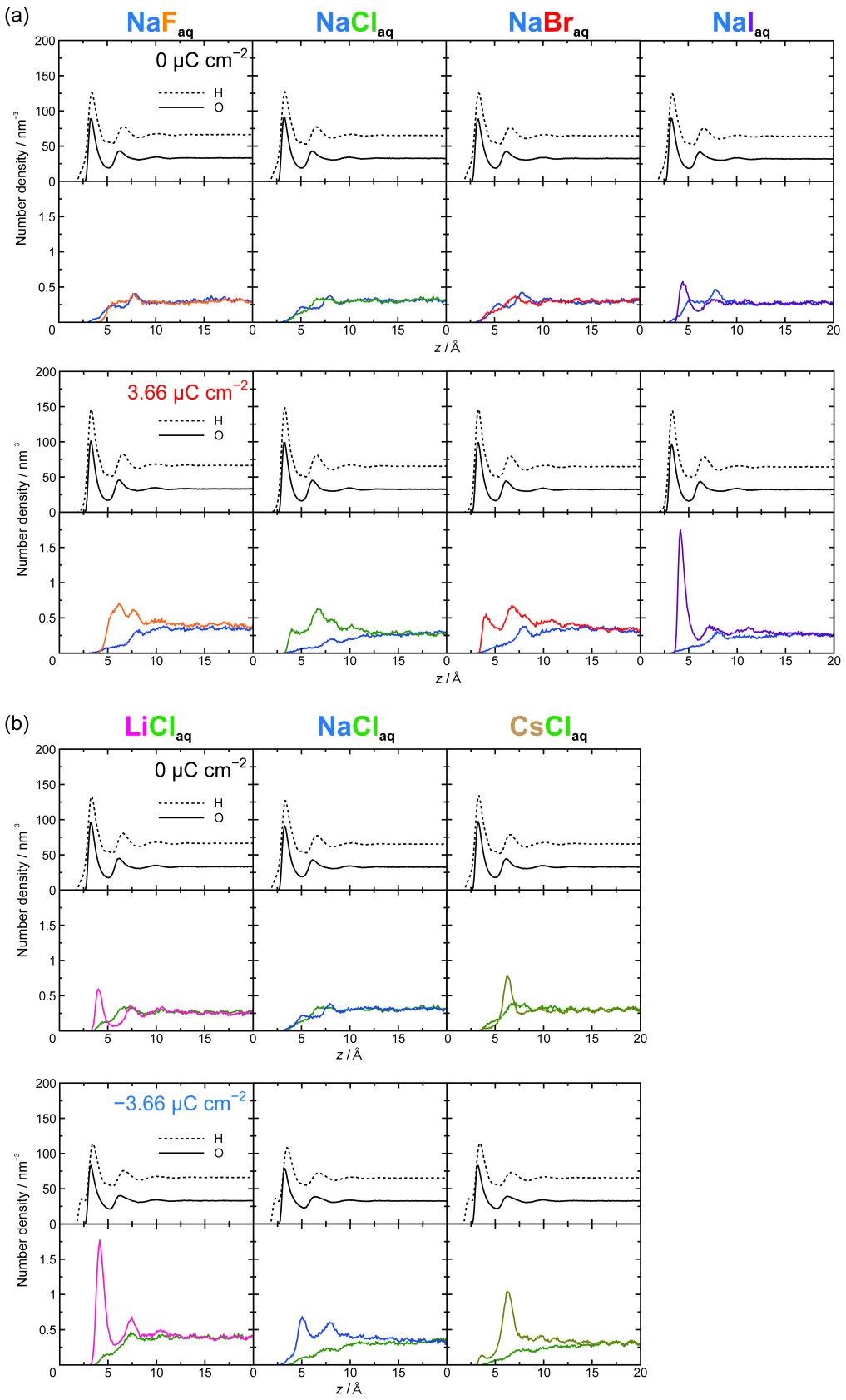

Fig. S2 Number density profiles of O and H atoms of water and ions. (a) 0.5 M NaX/graphite electrode interfaces. (b) 0.5 M MCl/graphite electrode interfaces. Different colors indicate the corresponding ions.

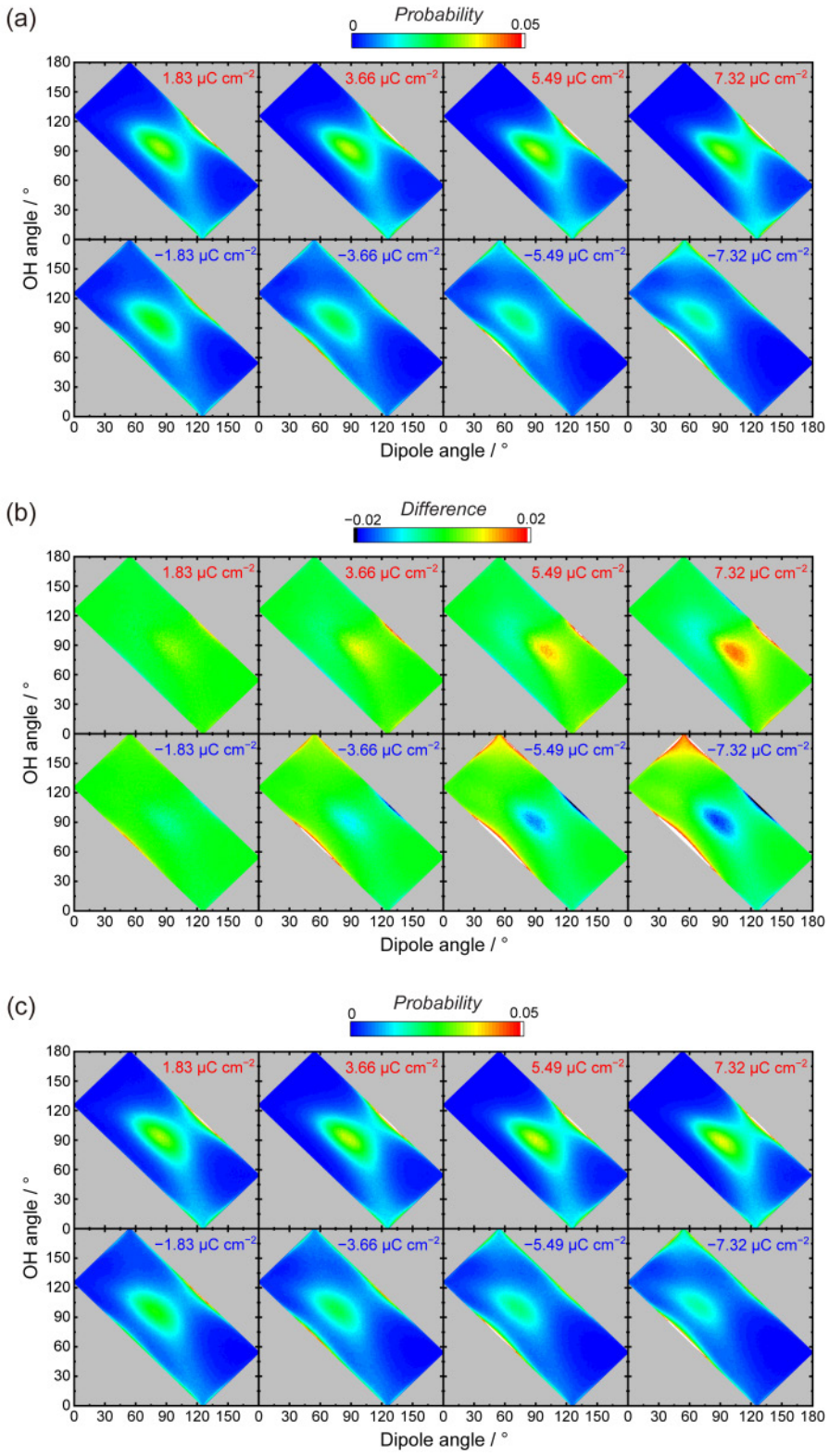

Fig. S3 Comprehensive 2D angular mappings of O–H bond and dipole vectors of the 1st layer water molecules. (a) Raw probability mapping for the pure water/graphite electrode interface. The differences of probability shown in Fig. 3(b) were calculated by subtracting the probability of Fig. 3(a) from (a). (b) Difference and (c) raw probability mappings for the 0.5 M NaCl/graphite electrode interfaces.

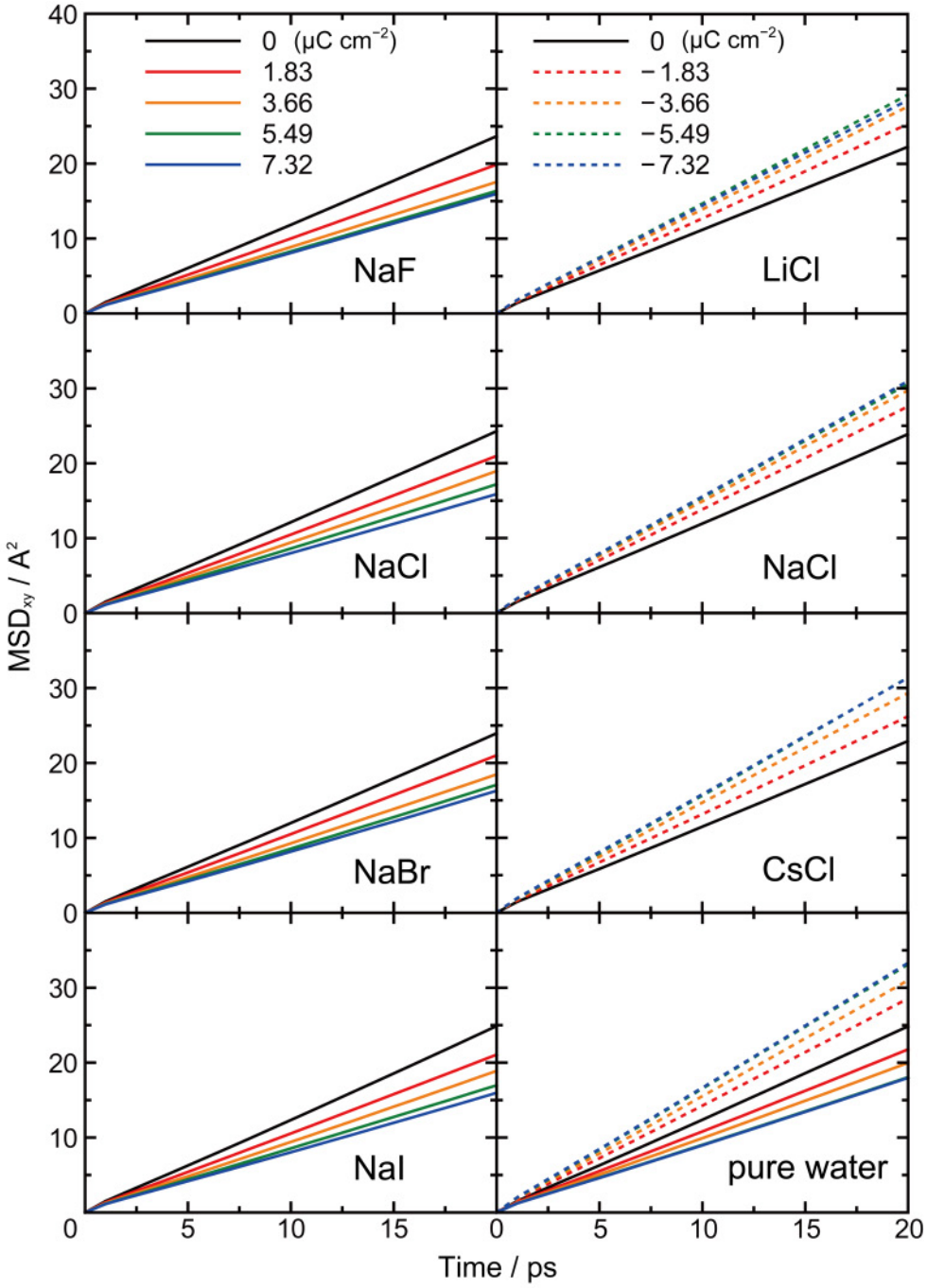

Fig. S4 MSD plots of 1st layer water molecules along the *x*-*y* plane.

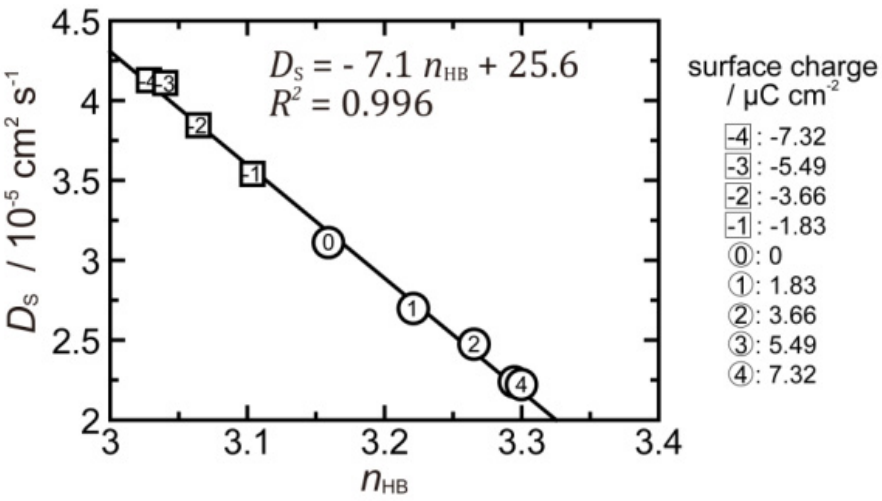

Fig. S5 D_S vs. n_{HB} plot for the pure water/graphite electrode interface, reproduced from Fig. 4(c). The black solid line is a linear fitting line.

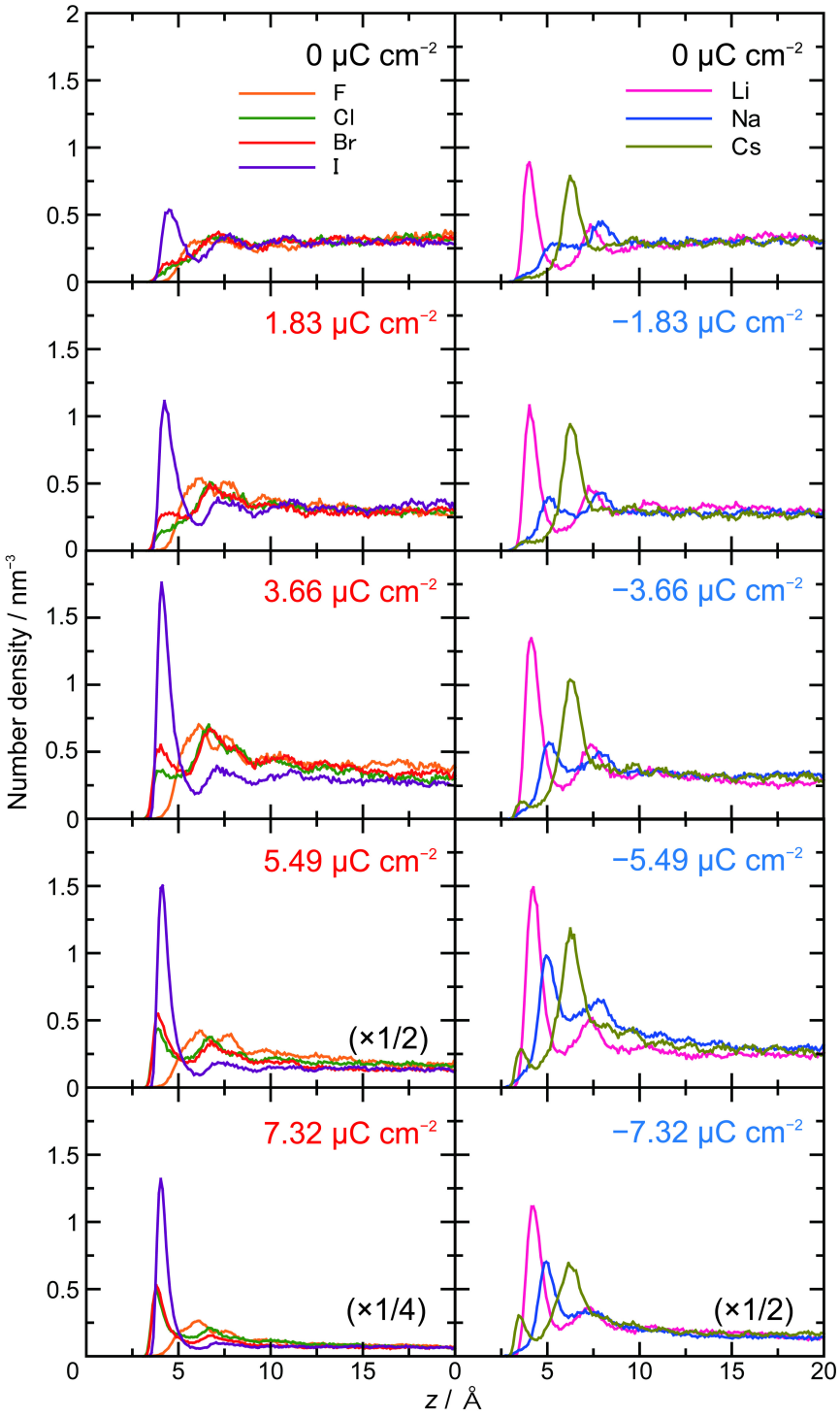

Fig. S6 Number density profiles of (left) anions at positively charged interfaces and (right) cations at negatively charged interfaces. Density profiles for 5.49, 7.32, and −7.32 μC cm^{-2} charge densities are rescaled by values in the parenthesis.

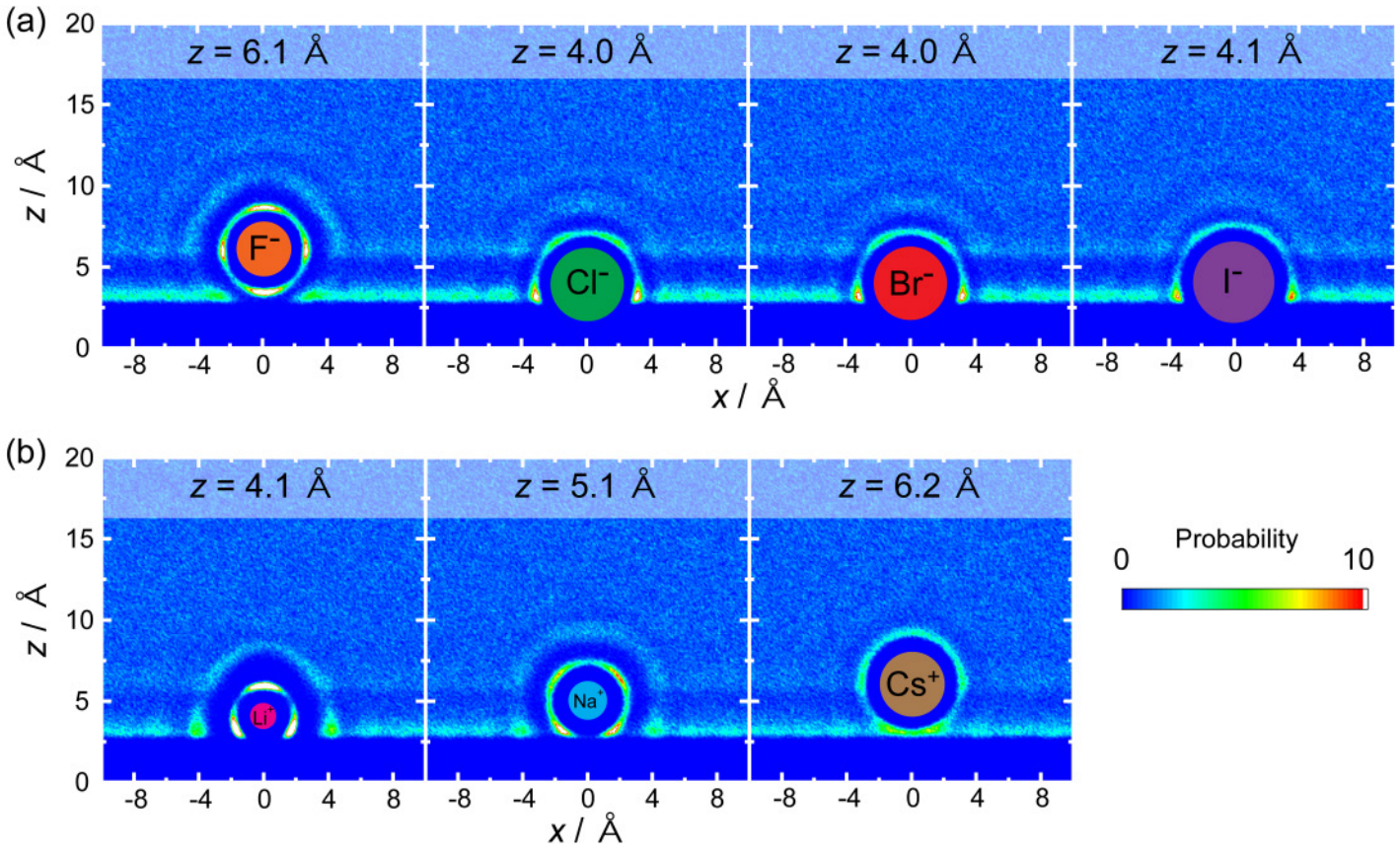

Fig. S7 Analyses of interfacial hydration structure by fixed-ion MD simulations at (a) 3.66 μC cm^{-2} (F^-, Cl^-, Br^-, and I^-) and (b) −3.66 μC cm^{-2} (Li^+, Na^+, and Cs^+). Each ion was vertically fixed at the 1st peak position of Fig. S6 and laterally at the center of the hexagonal carbon ring and 7200 water molecules were packed with another electrode to make a capacitor cell. The *x*−*z* density mappings of water O atoms were constructed with a width of 2 Å along the *y* axis and the density values were normalized by the bulk density. The values are larger than 10 in the white areas.