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Supplementary Information: Differential capacitance of NaCl solution

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S1 Parallel Plate Capacitor

Without the NaCl solution between the gold plates, our system behaves as an empty parallel plate capacitor. We move a unit test charge across charged plates of an empty capacitor of the polarisable gold and record the corresponding interaction potential energy. This is shown in Fig. S2 where the surface charge density is $\pm 0.061\, e\,\mathrm{nm}^{-2}$. Ideally, the potential energy would be a combination of the potential energy due to a parallel plate capacitor and the potential energy of interaction between the test charge and the plates at zero surface charge, and is depicted in Fig. S1.

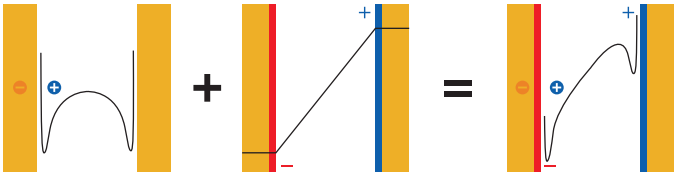

Fig. S1 Schematic depiction expected potential energy within the parallel plate capacitor. The blue dots represent a unit test positive charge and its image charge in the metal.

By removing the linear slope in Fig. S2, we obtain Fig. S3 which is what is expected as the interaction potential between the test charge and the polarisable gold at zero surface charge density.

S2 Poisson potential

We performed simulations at different surface charge densities. For each surface charge density, the corresponding potential drops

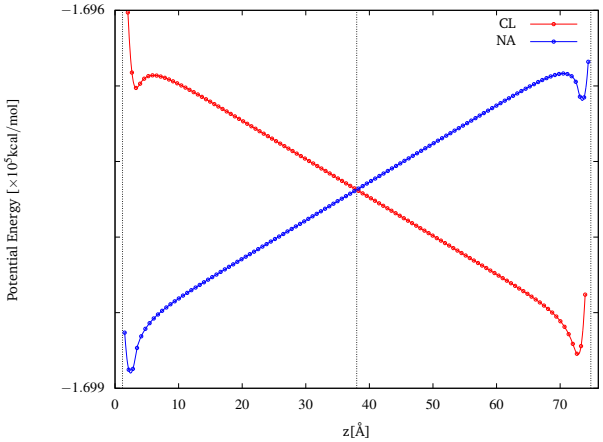

Fig. S2 Potential energy of Na (blue) or Cl (red) with $-0.061\, e\,\mathrm{nm}^{-2}$ on left electrode and $0.061\, e\,\mathrm{nm}^{-2}$ on right electrode.

were obtained according to the Poisson's equation

$$\Phi = \Phi(\zeta) - \frac{1}{\varepsilon_0}\int_{\zeta}^{z} \mathrm{d}z' \int_{-\infty}^{z'} \mathrm{d}z''\, \rho_q(z'') \qquad (1)$$

where ζ is a reference point in the gold slab whose potential is $\Phi(\zeta)$ and $\rho_q(z)$ is the charge density. Fig. S4 shows the potential drops in the NaCl solution for various set surface charges on the non-polarisable gold.

In Fig. S5 we show that at the cathode, at higher surface charge, the hydrogens of water at the interface form a distinct peak. This suggests a transformation in the orientation of interfacial water, such that the hydrogens point towards the surface. To further establish this, we show in Fig. S7 the cosine of the angle between the normal to the surface and the dipole moment of water at varying potentials.

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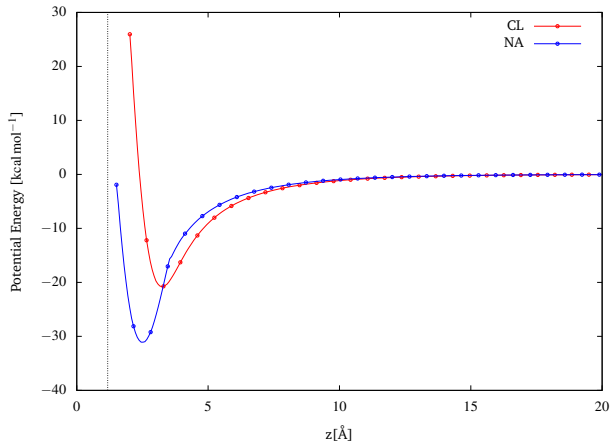

Fig. S3 Potential energy of Na (blue) or Cl (red) less the slope in Fig S2

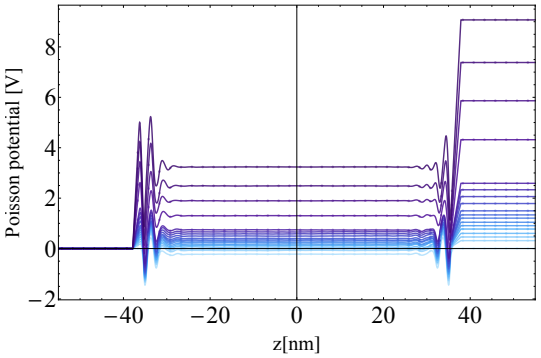

Fig. S4 Poisson potential drops at different surface charges at a non-polarisable gold surface. Increasing magnitude of surface charge is shown by increasingly darker lines.

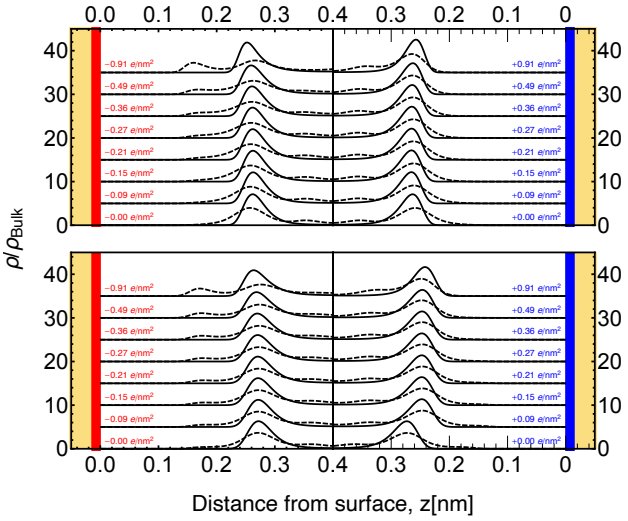

Fig. S5 Number densities ρ of O (solid), H (dashed) normalised with their bulk densities ρ_{Bulk}, at the cathode (left) and at the anode (right) at varying surface charge. The top and bottom panels correspond to non-polarisable and polarisable gold respectively. The number densities are shifted up in steps of 5 in ascending surface charge for clarity.

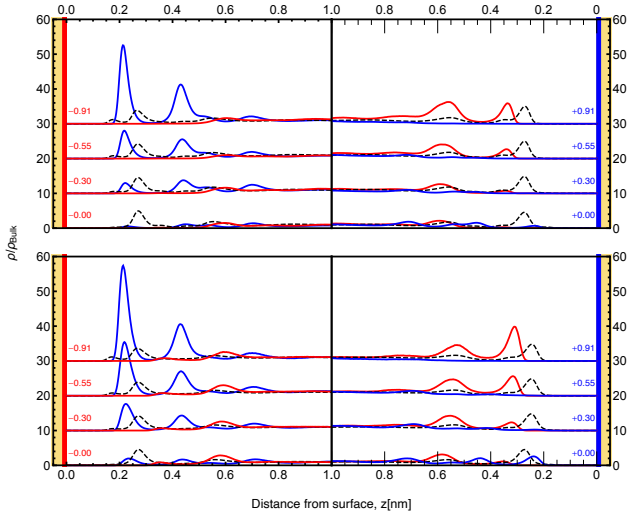

Fig. S6 Number densities ρ of Na^+ (blue), Cl^- (red) and water (black, dashed) normalised with their bulk densities ρ_{Bulk}, at the cathode (left, with red surface) and at the anode (right, with blue surface) at varying surface charge in $e\,\mathrm{nm}^{-2}$ (shown in small fonts). The top and bottom panels correspond to systems with SWM4-NDP water and SPC/E water respectively, confined in polarisable gold slabs. The number densities are shifted up in steps of 10 in ascending surface charge.

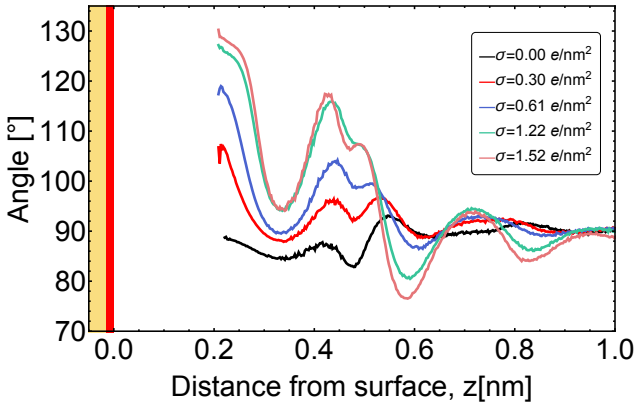

Fig. S7 Orientation of water at the cathode of the nonpolarisable gold. The schematic diagrams show how a water molecule may appear at the grid line it is placed on.

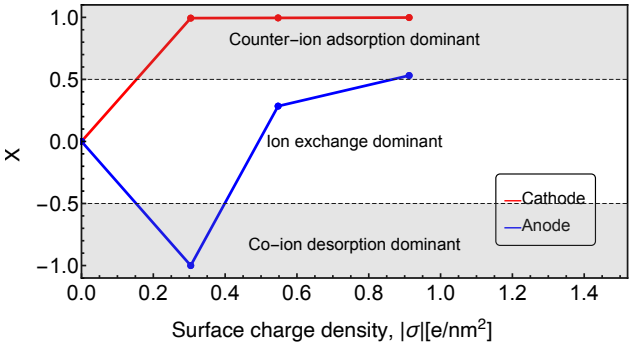

Fig. S8 X-parameter calculated within the first layer of solution at the interface, during charging at the cathode (red) and at the anode (blue) system with polarisable water and polarisable gold.