Supplementary information for:

Modulating Interfacial Energy-dissipation via Potential-controlled Ion Trapping

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**Figure S1.** A. Schematic of the Surface Force Balance (SFB), with the principle components labeled, and a picture of the interference fringes of equal chromatic order from whose wavelengths and shape the surface separation D and curvature radius R are determined. Gold and mica are mounted on fused silica lenses in a crossed-cylinder configuration, equivalent to the geometry of sphere on a flat, with the lower lens mounted on a leaf spring of spring constant $K_n = 81.5 \pm 2.7$ N/m. The top lens is moved to a distance D between the surfaces by a 3-stage mechanism with the most sensitive stage being a sectored piezoelectric tube (PZT), and the normal force $F_n$ between the surfaces is monitored through the bending of the spring. Shear forces $F_s$ transmitted to the bottom surface when the top surface is moved laterally by the sectored PZT are monitored via the bending of the shear spring (of spring constant $K_s=300$N/m) measured with a sensitive capacitance probe (see also in figure S4). The inset, left, shows the 3-electrode configuration where the gold surface is mounted on the upper cylindrical lens facing the mica surface on the lower lens. B. Schematic of the custom-designed three electrode cell used in the SFB. In this setup, gold acts as a working
(W) electrode and two platinum wires as the (quasi) reference (R) and counter (C) electrodes. The boat is made from quartz to prevent leakage of current to the ground and the lower lens is placed on a leaf spring. During an experiment, all three electrodes are immersed in the quartz boat potential is applied to the gold surface using a potentiostat (CHI600C, CH Instruments, Inc.) which serves as the control unit.

![Interaction profiles F(D)/R between gold and mica under different applied potentials](image)

**Figure S2.** Interaction profiles F(D)/R between gold and mica under different applied potentials \(\Psi_{\text{app}}\) and across 1mM LiClO\(_4\). Empty grey symbols represent an out (retraction) profile taken immediately after approach (filled grey symbols) while maintaining an applied potential of -0.35V. Gold surface potentials \(\Psi_{\text{gold}}\) were extracted from fits (black curves) to numerical solutions of the non-linear Poisson-Boltzmann (PB), augmented by vdW attraction \(A_H = 9 \times 10^{-20} \text{J}\). Inset: Normal force Fn(D) vs surface separation D profiles in 1mM LiClO\(_4\) between gold and mica taken via a quasi-static stepwise approach at applied potential \(\Psi_{\text{app}} = -0.35\text{V}\), where full and empty symbols represent Fn(D)/R profiles during approach and retraction.
**Figure S3. A.** An atomic force microscope image of a gold surface 5 μm × 5 μm showing its surface height distribution profile (B) along a 5 μm cross section (white line).
Figure S4. Schematic illustration of the approach taken to measure shear forces (F_s) in the SFB in cases where strong applied lateral forces F_{app} (stronger than provided by the PZT) are needed to overcome the static friction between the surfaces (see F_s vs. F_n measurements in regime I shown in figure 2B under pure water and 1mM LiClO_4). To measure the shear force, at a given load, a lateral force F_{app} is applied, using a micrometer, to push the upper lens (upper panel) while recording the signal obtained a capacitance probe (lower panel). The applied lateral force F_{app} bend the leaf springs (process 1) until the spring restoring force overcomes the static friction between the surfaces (process 2, F_{app} \approx F_s), relaxing the leaf springs to their equilibrium position through sliding the upper surface. The sliding changes the distance measured by the probe from d_1 to d_2. From the distance change \Delta d = |d_1 - d_2|, the maximum static friction force F_s = K_s \Delta d can then be measured.
Variation of frictional forces following a potential step

The ability to trap hydrated counterions between two surfaces (gold and mica) while regulating surface potentials is crucial for controlling frictional forces in our system. Hence, we have explored whether counterions diffuse out of the intersurface gap over a period of ca. 100sec, as expected theoretically and experimentally\(^1-^3\) once the gold surface potential is toggled from regime II to regime I.

To this end, we applied a step potential between \(-0.3\)\(\text{V}\) (regime II) and \(-0.15\)\(\text{V}\) (regime I) (corresponding to gold surface potentials of \(-0.18\)\(\text{V}\) and \(0.004\)\(\text{V}\), respectively) while measuring the variation of the frictional force over a period of 130sec; then, the potential was toggled back to \(-0.3\)\(\text{V}\) (figure S5). As depicted, following a potential change from \(-0.3\)\(\text{V}\) to \(-0.15\)\(\text{V}\), the frictional force gradually (over a time scale of 20 sec or more) increased up to a point where it exceeded the maximal applied shear force \(F_{s,\text{max}}\) so that the surfaces did not slide (i.e., their lateral motion was coupled). Such an increase upon transition from regime II to regime I suggests that counterions may indeed slowly diffuse out of the gap. Once the potential was changed back to \(-0.3\)\(\text{V}\) (regime II) the frictional force decreased close to its initial value (i.e. its value prior to toggling the potential to \(-0.15\)\(\text{V}\)). It is of interest that in both cases an initial rapid change was followed by a much slower change over a time scale of 20 sec or longer. This suggests that a slow ion diffusion both in and out of the gap contributes to the dissipation on sliding, but that other dissipative mechanisms such as plastic deformation of gold asperities and gradual increase of nominal contact area may also play a role.
**Figure S5.** Variation of *in situ* frictional force $F_s$ between mica and gold across 2mM LiClO$_4$ (trace iii) as the upper gold surface is moved laterally (trace i) and a potential step -0.3V to -0.15V is applied to the gold (trace ii).

**Estimation of the total load and friction coefficient**

We define the total load ($F_n$) applied to the surfaces as the sum of the external mechanical load $F_{ext}$ applied by the surface force balance motor and the pull-off force $F_{pull-off}$ required to separate the surfaces while under adhesive interaction (in regime II). Following our estimation of the total load ($F_n = F_{pull-off} + F_{ext}$) after altering the gold surface potential, the friction coefficient is then $\mu = (F_s/F_n)$.

For figure 3A(ii) and 3A(iii): $\Psi_{app} = -0.2$ V and -0.15 V, and thus from figure 1A the corresponding gold surface potential values are $\Psi_{gold} = -0.058$V and 0.004V, respectively. From figure 1B we can extract the adhesion energy in 2 mM LiClO$_4$ at these surface potential values to obtain $W_A = 3.9$ mJ/m$^2$ and 6.9 mJ/m$^2$, respectively, and from $F_{pull-off} = (3\pi R W_A/2)$ we expect $F_{pull-off} \approx 183$ mN and 325 mN, and (with $F_n = 314$ and 255 $\mu$N) so $F_n = 497$ and 580 $\mu$N respectively. For $F_s \approx 49$
and 67 μN respectively, this gives μ ≈ 0.09 and 0.1 respectively; this is closely comparable with
the friction deduced from the shear traces just before the toggling of the potential, namely m(trace
ii)=27/314=0.085 and μ(trace iii)=22/255=0.086, but clearly much lower than the CoF ≈ 0.8 for
regime I; therefore, strongly indicates Li+ trapping.

For figure 3B(i): Ψ_{\text{gold}} = +0.095 V, and thus from figure 1B (for 1 mM Li concentration) we expect
W_A ≈ 37 mJ/m^2 and F_{\text{pull-off}} = (3\pi RW_A/2) ≈ 1750 μN ; thus F_n = 2000 μN and (for F_s ≈ 190 mN)
this yields μ > 0.095.

For figure 3B(ii): After toggling to Ψ_{\text{app}} = -0.3 V (corresponding to Ψ_{\text{gold}} = -0.165 V), the pull-off
force is reduced to F_{\text{pull-off}} ≈ 500 μN (W_A ≈ 10 mJ/m^2 at Ψ_{\text{gold}} = -0.165 V in 1 mM Li+ solution).
Therefore, F_n = 456 μN + F_{\text{pulloff}} ≈ 960 μN, so in case Li+ penetrated to the intersurface gap (i.e.,
switching from regime I to II) we expect that F_s ≈ μ(II) \times F_n ≈ 50 μN. However, since from figure
3B(ii) the magnitude of F_s is in fact > 228 μN, clearly hydrated ions did not penetrate into the gap.
Moreover, even if we assume that after toggling the potential to Ψ_{\text{app}} = -0.3 V there is no adhesion
energy (W_A = 0 mJ/m^2) then F_n = F_{\text{ext}} = 462 μN and thus F_s ≈ μ(II) \times F_n ≈ 25 μN (assuming μ(II)
≈ 0.05 if hydrated ions were trapped), much smaller than F_s > 228μN. In terms of the friction
coefficient, μ > ca. 0.5 and 0.23 respectively (for the 2 assumptions of F_{\text{pull-off}} = 0mN or F_{\text{pull-off}} ≈
500 μN, respectively), much greater than when hydrated ions are trapped in regime II.

**Effect of ion concentration of on adhesion energy in regime I (fig. 1B) and on frictional
dissipation in regime II (fig. 2B):**

The adhesion energy W_A between gold and mica is dictated by vdW and electrostatic forces and
can written as W_A=W_e+W_{vdW} where, W_e(D) = 1/A \int_0^D F_e(D)dD is the electrostatic energy and
$W_{vdW}$ is the vdW interaction energy between the surfaces\textsuperscript{4}. In principle, while $W_{vdW}$ is hardly affected by small changes in electrolyte concentration the electrostatic force per unit area $F_e(D)/A$ – and thus $W_e(D)$ – will be lower at any given D for higher salt concentration because of the shorter Debye screening length (see figure 1 and S2). This, in turn, reduces the magnitude of the adhesion energy $W_A$ at higher electrolyte concentration in regime I, as observed in figure 1B. This effect was not observed in our friction measurements where similar friction coefficient values were obtained in regime II for 1mM and 2mM, as can be seen in figure 2B. This is because at both salt concentrations Li\textsuperscript{+} counterions are trapped between the surfaces and frictional dissipation is modulated by hydration lubrication.

**References**

1. Tivony, R.; Safran, S.; Pincus, P.; Silbert, G.; Klein, J., Charging dynamics of an individual nanopore. *Nature Communications* 2018, 9 (1), 1-8.

2. De Levie, R., On porous electrodes in electrolyte solutions: I. Capacitance effects. *Electrochimica Acta* 1963, 8 (10), 751-780.

3. Biesheuvel, P.; Bazant, M., Nonlinear dynamics of capacitive charging and desalination by porous electrodes. *Physical Review E* 2010, 81 (3), 031502.

4. Tivony, R.; Klein, J., Modifying surface forces through control of surface potentials. *Faraday Discussions* 2017, (199), 261-277.