Electronic Supplementary Information for: Controlling Swelling/Deswelling of Stimuli-Responsive Hydrogel Nanofilms in Electric Fields

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Comments on the Theoretical Approach

In this work, we study the swelling of hydrogel nanofilms in the presence of an external electric field. For this purpose, we use a theory that accounts for size, shape, conformation and charge distribution of all molecular components, in particular the polymer backbone. This molecular theory is described in our recent work, where we have considered the swelling of the same hydrogel nanofilms under no external electric fields.¹ The only difference in the theoretical formalism that we have introduced here to investigate film behavior under an applied voltage is the boundary condition of the Poisson Equation at the grafting surface. An applied voltage, ΔV , fixes the value of the electrostatic potential at the grafting electrode,

$$\Psi(z=0) = \Delta V \tag{S1}$$

where $\Psi(z)$ is the local electrostatic potential. The Cartesian coordinate z measures the distance from the grafting electrode, which is placed at z = 0. We make the assumption that the system is homogeneous in the x-y plane. The second boundary condition that we impose when solving the Poisson Equation is

$$\lim_{z \to \infty} \Psi(z) = 0 \tag{S2}$$

which implies that the distant electrode is far from the film, in the bulk solution.

The area density of charge that establishes on the metallic surface of the grafting electrode, σ_M , can be calculated using Gauss' law and the fact that the electric filed is zero inside the conducting material, which leads to

$$\sigma_M = \epsilon_w \left. \frac{d\Psi(z)}{dz} \right|_{z=0} \tag{S3}$$

where ϵ_w denotes the dielectric permittivity of the medium (water). Note that we do not explicitly impose the charge density on the surface, but it results from the solution to the Poisson equation subject to the boundary conditions given by Eq. S1 and S2.

On the contrary, when no external electric field is applied to a film supported by a dielectric surface, the density of charge at the grafting surface must be zero. In this situation, assuming that the dielectric medium extends deep

enough under the film, the first boundary condition for the Poisson equation results from setting $\sigma_M \equiv 0$ in Eq. S3,

$$\left. \frac{d\Psi(z)}{dz} \right|_{z=0} = 0 \tag{S4}$$

Full description of the theoretical framework and the numerical methodology employed to solve the resulting equations can be found in the Supporting Information for Longo et al.¹, not only for zero surface charge conditions but also for an applied voltage. Numerical calculation of results using this method requires defining a molecular model for all species that compose the system, including the polymer network. Here, we use the same molecular model described in our previous work.¹

Additional Results

Figure S1 shows film thickness, h_{gel} , as a function of pH and applied potential for low and high salt concentration solutions. These three-dimensional plots represent the same results as Fig. 2A and D of the article, respectively.



Fig. S1 Plot of film thickness as a function of solution pH and applied voltage for two different salt concentrations.

The ionic strength inside the hydrogel film can be calculated using the concentrations adsorbed ions,

$$I_{s} = \sum_{i \in \{H^{+}, OH^{-}, +, -\}} \frac{1}{h_{gel}} \int_{0}^{h_{gel}} [i](z) \, dz \,, \tag{S5}$$

where [i](z) is the local molar concentration of ionic species *i*. In the last equation, we have omitted charge numbers because all ionic species are monovalent. Similarly, we can calculate the average concentration of adsorbed sodium ions as

$$[Na^+] = \frac{1}{h_{gel}} \int_0^{h_{gel}} [Na^+](z) \, dz \,. \tag{S6}$$

Figure S2 shows the ionic strength inside the hydrogel, and average concentration of adsorbed sodium ions as a function of *pH* for different applied voltages and zero surface charge. Within the range of voltages considered in this work, the ionic strength inside the film is relatively similar to that established for zero surface charge (see Figs. S2A and C). The most significant differences can be observed at low *pH* and $c_s = 0.1M$ for both the most positive and negative applied voltages, $\Delta V = 100mV$ and -100mV, respectively (black and purple lines in Fig. S2C). However, relative differences in I_s under these conditions are less than 5% (= $\frac{(0.105M - 0.1M)}{0.1M} \times 100\%$).

When *pH* increases above pKa = 5, ionic strength of the film increases. At low salt concentration, the relative change from the local minimum around *pH* 4 to the plateau at higher *pH*, ranges from roughly 1567% (from 0.003*M* to 0.05*M*) for $\Delta V = -100mV$ to 2567% (from 0.0015*M* to 0.04*M*) for $\Delta V = 100mV$, and 3233% (from 0.0015*M* to 0.05*M*) for $\sigma_M \equiv 0$ (see Fig. S2A). At high salt concentration, these relative changes are roughly 11% (from 0.105*M* to 0.117*M*) for $\Delta V = -100mV$, 6% (from 0.105*M* to 0.112*M*) for $\Delta V = 100mV$, and 12% (from 0.1*M* to 0.112*M*) for $\sigma_M \equiv 0$ (see Fig. S2C).



Fig. S2 Plot of ionic strength inside the film (top panels, A and C) and concentration of adsorbed counterions (bottom panels, B and D) as a function of pH for different applied voltages (solid lines) and zero surface charge (dashed black line). Low and high salt concentration solutions are shown in the left- and right-hand side panels, respectively. These plots correspond to the same conditions as Fig. 2.



Fig. S3 Plot of local pH as a function of distance from the grafting surface at pH 7 and $c_s = 0.001M$. Solid lines represent different applied voltages, while the dashed black line corresponds to zero surface charge.

We define local pH using:

$$pH(z) = -\log_{10}[H^+](z),$$
(S7)

where $[H^+](z)$ is the local concentration of protons. Figure S3 shows pH(z) at pH 7 and low salt concentration for different applied potentials and zero surface charge. We have arbitrarily chosen these solution conditions, but the following discussion is completely general.

We see four distinct regions (intervals of z) in Fig. S3. Far from the surface (large z), local pH approaches solution pH (*pH* 7). Inside the film but sufficiently far from the surface ($z > z_0$), a lower local pH establishes, which can be quantified using its average,

$$pH_{gel} = \frac{1}{h_{gel}} \int_{z_0}^{h_{gel}} pH(z) \,.$$
(S8)

Between the interior of the film and the bulk solution, an interfacial region is observed where pH(z) smoothly transitions from pH_{gel} to bulk pH. The extension and other features of this interfacial region depend strongly on the salt concentration.² In all these regions (*i.e.*, $z > z_0$), local pH is not very sensitive to a voltage applied between the grafting electrode and the bulk solution. However, in the region nearest the surface the situation is completely different. Local pH strongly depends on the applied voltage as seen in the upper inset of Fig. S3. In particular, immediately above the electrode, pH can be controlled using the applied voltage (as seen in Fig. 5) without altering pH_{gel} . Note that when $\sigma_M \equiv 0$, pH(z = 0) and pH_{gel} must be similar, within the local fluctuation occurring inside the film, which can be seen in Fig. S3.

Figure S4 shows the drop in pH inside the hydrogel, $\Delta pH = pH_{gel} - pH$, as a function of pH and applied potential for low and high salt concentration solutions. These plots are three-dimensional representations of the same results as Fig. 4 of the article.



Fig. S4 Plot of the drop in pH inside the film as a function of solution pH and applied voltage for low (top) and high (bottom) salt concentration. These plots are a different representation of the results presented in Fig. 4. The transparent yellow surface represents the drop in pH when the surface boundary condition is $\sigma_M \equiv 0$, which is independent of ΔV (black dashed line in Fig. 4).

Figure S5 shows the excess surface pH with respect to the bulk solution, $\Delta pH_{surf} = pH(z = 0) - pH$, as a function of *pH* and applied potential for low and high salt concentration solutions. These plots are three-dimensional representations of the same results as Fig. 5 of the article.



Fig. S5 Plot of excess surface pH (with respect to the bulk solution), $\Delta p H_{surf}$, as a function of applied voltage and solution pH. The transparent red surface corresponds to $\sigma_M \equiv 0$ boundary conditions, where $\Delta p H_{surf}$ is independent of ΔV (black dashed line in Fig. 5).

The excess surface pH seems to have a (roughly) linear dependence on the applied potential. This behavior can be easily explained using a simple model. For the free species, let us assume that all density changes are due to variations of the electrostatic potential. Then, these densities can be calculated using the Maxwell-Boltzmann distribution. In particular, the density of protons immediately above the surface, $\rho_{surf}^{H^+}$, we be expressed as

$$\rho_{surf}^{H^+} = \rho_{bulk}^{H^+} e^{-\beta \Delta V e} \tag{S9}$$

where $\rho_{bulk}^{H^+}$ is the proton density in the bulk solution. Following the definition given by Equation S7, we obtain:

$$pH_{surf} = pH + C\Delta V \tag{S10}$$

where C is a positive constant. Then,

$$\Delta p H_{surf} = C \Delta V \tag{S11}$$

which explains the roughly linear dependence of the excess surface pH on the applied potential.

References

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