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# pH Dynamics During Concentration Polarization

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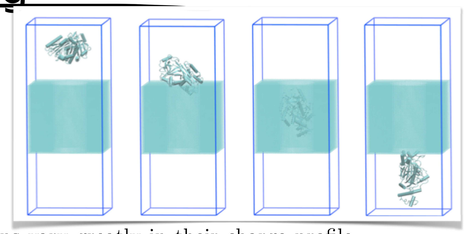
## Motivation

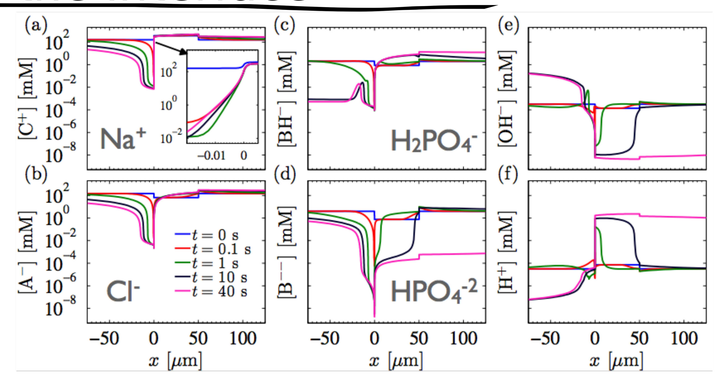
- Biological toxins are often difficult to detect because of their high activity, but low count.
- There is a real need to detect these in cases of suspected outbreaks, rather than waiting to see if symptoms occur.
- Nanofluidic electrophoretic sensing methods make ideal sensors:
  - can be mass produced and used in the field
  - can pre-concentrate samples to increase sensitivity
  - are easily integrated with other sensors
  - offer some ability for customization

## Protein Sensing



- Based on their sequence, proteins vary greatly in their charge profile, and ability to unfold.
- A membrane with well-defined, nanometer size pores requires partial unfolding for large proteins to pass.
- Voltage and solution makeup at both interfaces can be tuned to detect protein toxins or cellular distress signals.

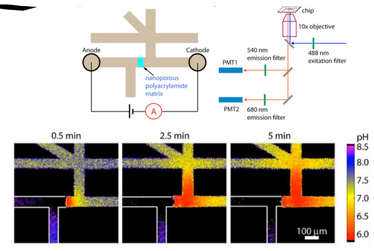
## At the Interface




$\vec{E} \longrightarrow$

## Experimental Setup

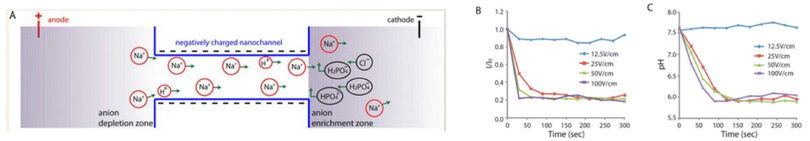
- In-situ polymerization creates pores.
- Experiment
  - 25-100 V/cm applied
  - 50 $\mu$m channel passes cations
  - Concentration enriches at cathode
  - Proton transport creates pH imbalance
  - Balance of forces at membrane is highly variable
- probe mode: ratiometic pH-sensitive dye (SNARF) quantitatively measures concentration and pH dynamics near membrane




Mai, Miller and Hatch, ACS Nano 2012.

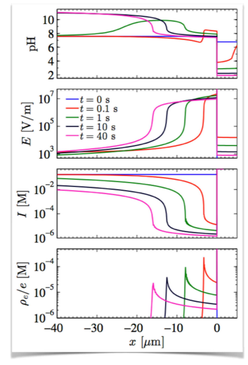
$\vec{E}$

## Concentration Polarization



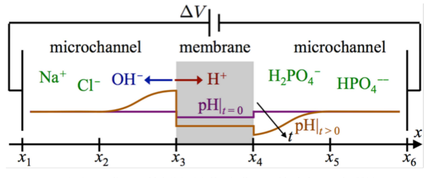

- Cations flow toward the cathode, but are rejected by the membrane.
- Those remaining form the enrichment zone, where concentrations can soar to O(100×).
- The amount of CP is described by the Dukhin number (the ratio of bulk to surface ion mobility) and the bulk diffusion of the co-ion.

## Time and Parameter Dependence




- Total device length affects voltage at the membrane.
- Net space-charge builds up on the $\mu$m scale away from the channel (conduction faster than reaction)
- The $10^5$ V/cm field moves with the charge front.
- violates electroneutrality, local equilibrium, and EDL theory ($lambda_D \sim$ 1nm)

## Numerical Model




Andersen, Rogers, Mai, Schudel, Hatch, Rempe, Mani. Langmuir, 2014.

$\vec{E} = 25$ V/cm
I = 160 mM (6 mM buffer)

| Diffusivity ($10^{-5}$ cm/s) | |
|---|---|
| $Na^+$ | 1.3 |
| $Cl^-$ | 2.0 |
| $H_2PO_4^-$ | 0.96 |
| $HPO_4^{2-}$ | 0.76 |
| $OH^-$ | 5.3 |
| $H^+$ | 9.3 |

| Dimensions (mm) | |
|---|---|
| Membrane Length | 0.05 |
| Resolved Simulation Length | 1.55 |
| Total Microchannel Length | 41.55 |

$$\mathrm{BH}^{z_{\mathrm{buf}}}_{(\mathrm{aq})} \underset{k_{\mathrm{b,buf}}}{\overset{k_{\mathrm{f,buf}}}{\rightleftharpoons}} \mathrm{B}^{z_{\mathrm{buf}}-1}_{(\mathrm{aq})} + \mathrm{H}^+_{(\mathrm{aq})}$$

pK 7.2, rate $\sim 10^7$ /mM-s

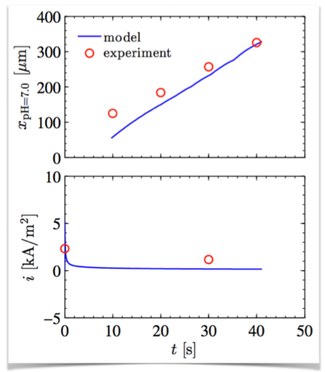
$$\mathrm{H_2O}_{(\mathrm{aq})} \underset{k_{\mathrm{b,w}}}{\overset{k_{\mathrm{f,w}}}{\rightleftharpoons}} \mathrm{OH}^-_{(\mathrm{aq})} + \mathrm{H}^+_{(\mathrm{aq})}$$

$K_w$ 14, rate $\sim 10^9$ /mM-s

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial x}\left[D_i(x)\left(-\frac{\partial c_i}{\partial x} - \frac{z_i c_i}{V_T}\frac{\partial \phi}{\partial x}\right)\right] = r_i$$

$$\frac{\partial}{\partial x}\left(-\varepsilon(x)\frac{\partial \phi}{\partial x}\right) = e\sum_i z_i c_i$$

## Key Comparison (pH Dynamics)




- pH dye is most sensitive at pH 7 – so we check the progression of the front
- Near-perfect fit requires adjusting only the water splitting rate.
- The strong ionic environment of the membrane catalyzes this process 10×.
- Total current agrees qualitatively, but few experimental data points.

## Conclusions

- CP allows very nonlinear tuning of the electric field and buffer concentration near an interface.
- Numerical modeling is required to capture these complex driving forces.
- $H^+$ and $OH^-$ directly contribute ∼3% to net charge transport.
- Electrostatics is still the dominant driving force for protein unfolding at the interface, but varies greatly with membrane charge and hydrolysis properties.
- These provide boundary conditions for molecular simulations.