Principles of Electronic Nanobiosensors

Unit 3: Sensitivity

Lecture 3.4: Potentiometric Sensors: ISFET as a pH-Meter

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Outline

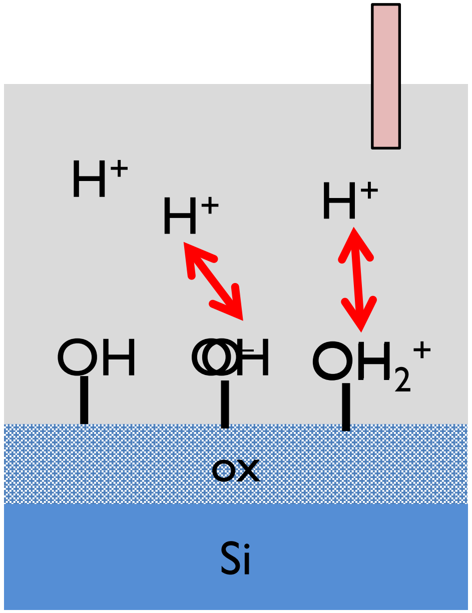
- Background: what is pH ?
- pH and surface charge of an ISFET
  - Surface binding model
- Nernst Limit of an ISFET
- Conclusions

MOSFET as a pH sensor

What is pH? $pH = -\log_{10} [H^+]_B$ Example: $[H^+]_B = 10^{-7}$ M → $pH = 7$

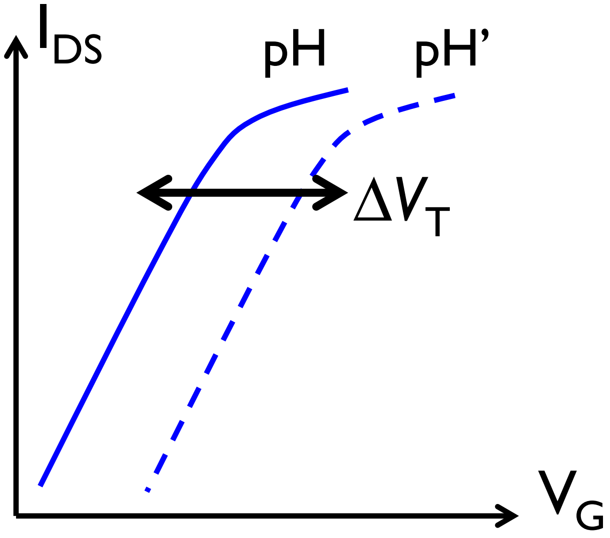
Human blood: $7.35 < pH < 7.45$

pH off the range is fatal to human body!



$$-OH \longleftrightarrow -O^- + H^+$$

$$-OH_2^+ \longleftrightarrow -OH + H^+$$



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Basics of pH control: pH of Pure Water

$$H_2O \rightleftharpoons [H^+] + [OH^-]$$

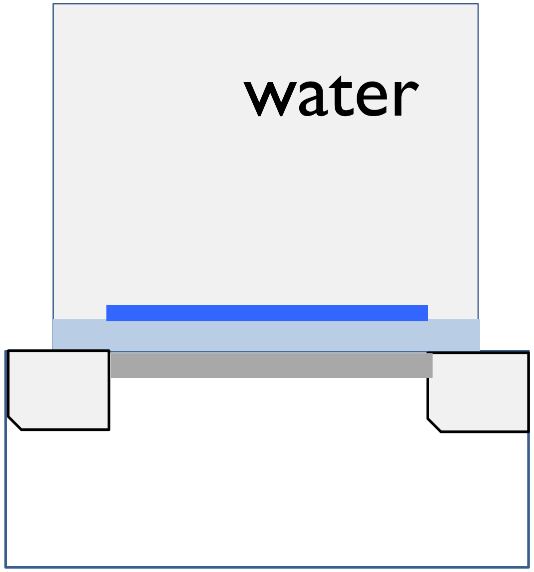
$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = 10^{-14}$$

$$[\mathrm{H}^+] = [OH^-] = 10^{-7}\,M$$

$$x_0 = x + 2y$$

$$\frac{y^2}{x} = 10^{-14} = \frac{y^2}{x_0 - 2y}$$

$$\Rightarrow y = 10^{-7}$$



$$\mathrm{pH} = -\log_{10}[H^+] = 7$$

$$\mathrm{pOH} = -\log_{10}[\mathrm{OH}^-] = 7$$

$$\mathrm{pH} + \mathrm{pOH} = 14$$

Basics of pH Control: Acid/Base

$$\text{pH of 0.040M of HClO}_4\text{?}$$

Strong acid: fully ionized

$$[\mathrm{HClO_4}] = \left[H^+\right] + [ClO_4^{-1}]$$

$$x_0 = x + \left(h + y\right)/2$$

$$x \to 0, \quad h = y$$

$$x_0 \sim y = h$$

$$pH = -\log(0.04) = 1.4$$

$$\text{pH of 0.028M of NaOH?}$$

Base: fully ionized in water

$$[NaOH] = [Na^+] + [OH^-]$$

$$x_0 = x + \left(n + o\right)/2$$

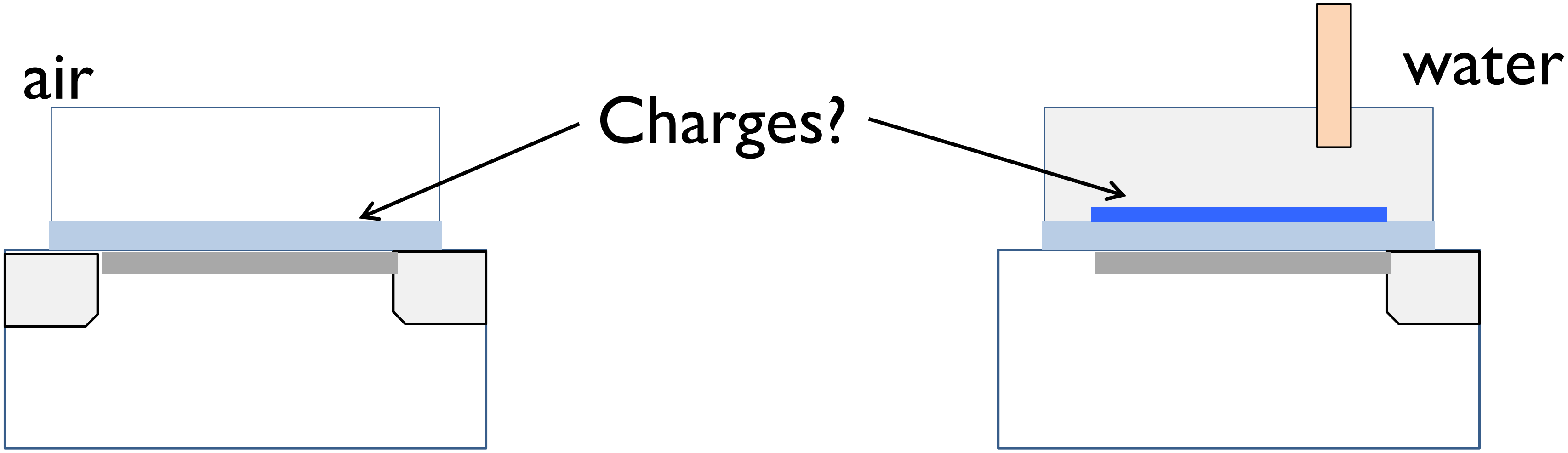
$$x \to 0, \quad n = o$$

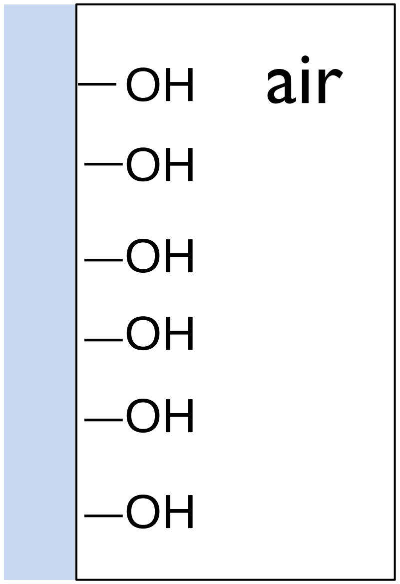
$$x_0 \sim n = o$$

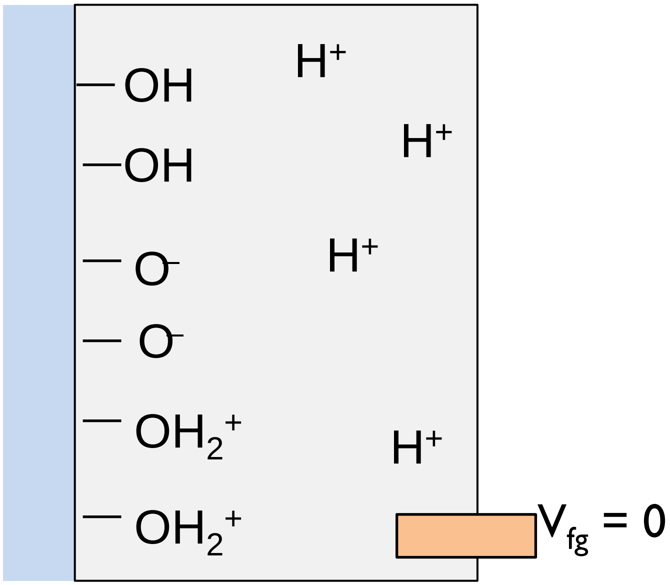
$$pOH = -\log(0.028) = 1.55$$

$$pH = 14 - 1.55 = 12.45$$

pH and Surface Charge







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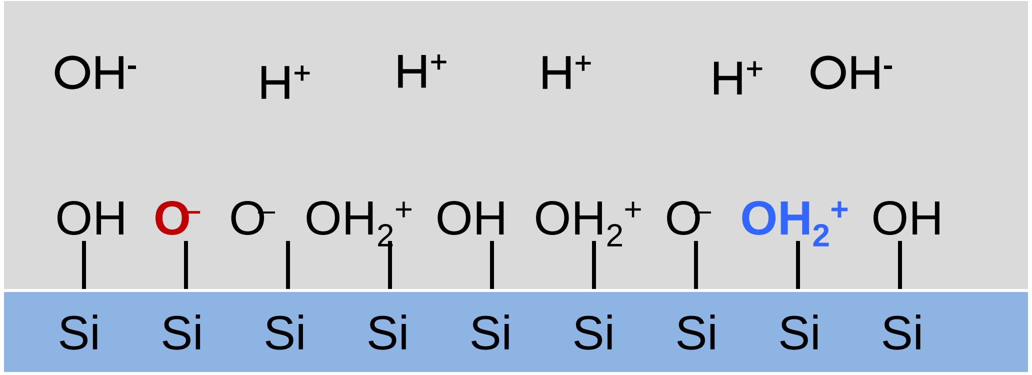
Surface Charging with pH



de-protonation

$$\mathrm{SiOH} \Leftrightarrow \mathrm{SiO^-} + \mathrm{H^+}$$

$$\frac{[\mathrm{SiO^-}][\mathrm{H^+}]_S}{[\mathrm{SiOH}]} = K_b$$

protonation

$$\mathrm{SiOH_2^+} \Leftrightarrow \mathrm{SiOH} + \mathrm{H^+}$$

$$\frac{[\mathrm{SiOH}][\mathrm{H^+}]_S}{[\mathrm{SiOH_2^+}]} = K_a$$

$$Q = q\,([\mathrm{SiOH_2^+}] - [\mathrm{SiO^-}])$$

$$[\mathrm{H^+}]_\mathrm{S} = [\mathrm{H^+}]_\mathrm{B}\, e^{-q\psi_0/k_BT}$$

Surface Binding Model

$$[\mathrm{SiO}^-] = K_b \frac{[\mathrm{SiOH}]}{[\mathrm{H}^+]_S} \qquad [\mathrm{SiOH}_2^+] = \frac{[\mathrm{SiOH}][\mathrm{H}^+]_S}{K_a}$$

$$[\mathrm{SiO}^-]+[\mathrm{Si}OH]+[\mathrm{SiOH}_2^+] = N_0$$

$$[\mathrm{Si}OH]\left(1+K_b \big/ [\mathrm{H}^+]_S + [\mathrm{H}^+]_S \big/ K_a\right) = N_0$$

$$\begin{aligned} Q &= q\left([\mathrm{SiOH}_2^+]-[\mathrm{SiO}^-]\right) \\ &= qN_0 \left\{ \frac{[\mathrm{H}^+]_S / K_a - K_b / [\mathrm{H}^+]_S}{\left[1+K_b / [\mathrm{H}^+]_S + [\mathrm{H}^+]_S / K_a\right]} \right\} \end{aligned}$$

$$K_a = 10^{-pK_a}, K_b = 10^{-pK_b}$$

$$pK_a = -2, pK_b = 6$$

All information known, the surface charge can be calculated for any pH.

$$\begin{aligned} [\mathrm{H}^+]_\mathrm{S} &= [\mathrm{H}^+]_\mathrm{B} e^{-q\psi_0/k_B T} \\ &= 10^{-pH} e^{-q\psi_0/k_B T} \end{aligned}$$

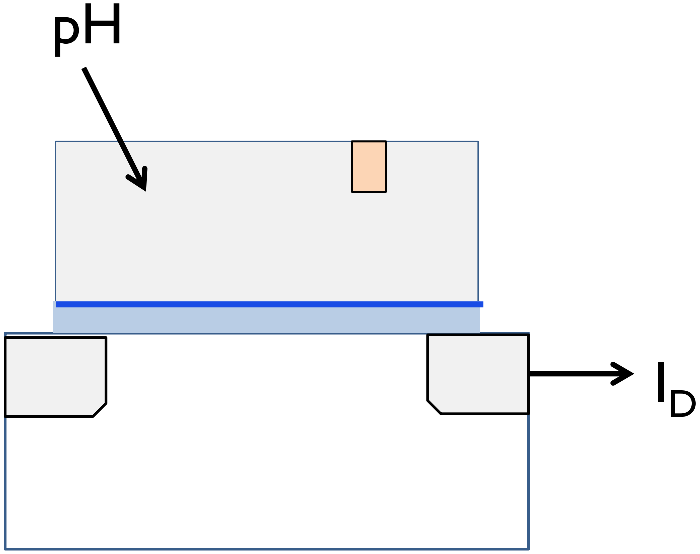
Point of Zero Charge

$$Q = 0 = qN_0 \left\{ \frac{\left[\mathrm{H}^+\right]_S / K_a - K_b / \left[\mathrm{H}^+\right]_S}{\left[1 + K_b / \left[\mathrm{H}^+\right]_S + \left[\mathrm{H}^+\right]_S / K_a\right]} \right\}$$

$$K_a K_b = \left[\mathrm{H}^+\right]_S^2 = \left[\mathrm{H}^+\right]_B^2$$

$$K_a = 10^{-pK_a}, K_b = 10^{-pK_b}$$

$$pzc = \frac{pK_a + pK_b}{2}$$



$$pK_a = -2, pK_b = 6$$

For SiO2

Self-consistent surface charge

$$Q(pH) = qN_0 \left\{ \frac{\left[\mathrm{H}^+\right]_S / K_a - K_b / \left[\mathrm{H}^+\right]_S}{\left[1 + K_b / \left[\mathrm{H}^+\right]_S + \left[\mathrm{H}^+\right]_S / K_a\right]} \right\}$$

$$Q = Q_{DL} + Q_{MOS}$$

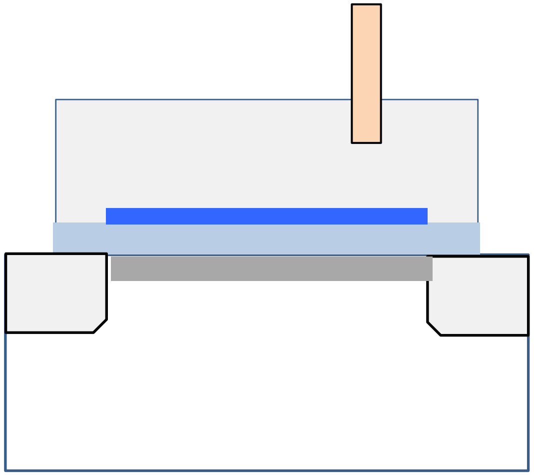
$$\sim Q_{DL} = Q_0 \exp\left(\frac{zq\psi_0}{k_B T_L}\right)$$

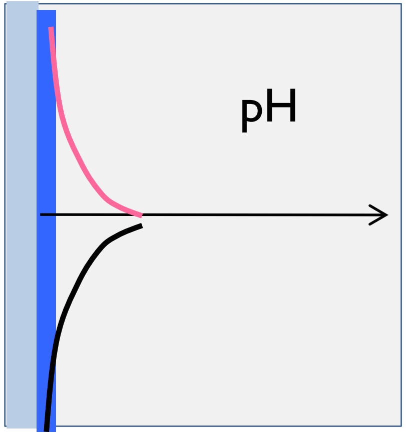
$$\psi_0 = \frac{k_B T_L}{zq} \ln Q / Q_0$$

$$[\mathrm{H}^+]_\mathrm{S} = [\mathrm{H}^+]_\mathrm{B}\, e^{-q\psi_0/k_B T}$$

$$\frac{\delta Q}{\delta\left(pH_s\right)} \equiv -q\beta_{\mathrm{int}}$$

Intrinsic buffer capacity



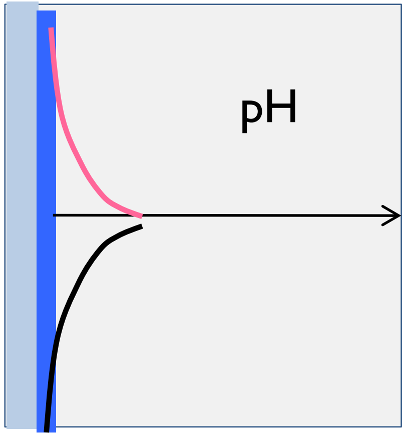


Aside: Surface potential and Buffer capacity

$$[\mathrm{H}^+]_\mathrm{S} = [\mathrm{H}^+]_\mathrm{B}\, e^{-q\psi_0/k_BT}$$

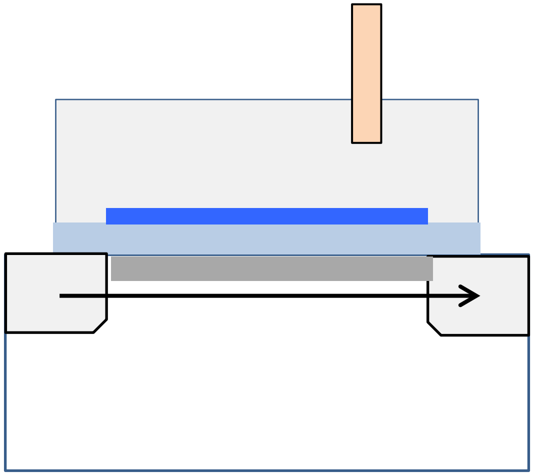
$$pH_s = pH_B + q\psi_0/2.3k_BT$$

$$\frac{\delta\psi_0}{\delta pH_s} = \frac{\delta\psi_0}{\delta\left(pH_B\right)+\delta\left(q\psi_0/2.3k_BT\right)}$$



$$\frac{\delta\psi_0}{\delta pH_s} = \frac{\delta\psi_0}{\delta Q}\times\frac{\delta Q}{\delta\left(pH_s\right)} = \frac{1}{C_{DL}}\times\left(-q\beta_{\mathrm{int}}\right)$$

$$\frac{\delta\psi_0}{\delta pH_B} = -2.3\frac{kT}{q}\left(1+\frac{2.3k_BTC_{DL}}{q^2\beta_{\mathrm{int}}}\right)^{-1}$$



Outline

1) How to calculate pH
2) pH and surface charge
   - Surface binding model
3) Nernst Limit of an ISFET
4) Conclusions

Nernst Limit of an Ion Sensitive FET

$$\Delta I_D \propto Q_s = Q_s^+ - Q_s^- = f\left\{[H^+]_S\right\}$$

$$[\mathrm{H}^+]_S = [\mathrm{H}^+]_B\, e^{-q(\psi_0 - V_{FG})/k_BT} \qquad [\mathrm{H}^+]_B \equiv e^{-2.303\,pH}$$

$$= e^{-2.303\,pH - q(\psi_0 - V_{FG})/k_BT}$$

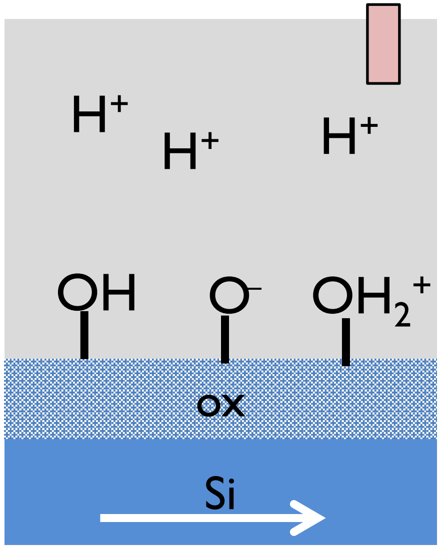
$$I_{D1} \propto Q_{s1} \sim f(x_1) \quad x_1 = e^{-2.303\,pH_1 - q(\psi_{01} - V_{FG1})/k_BT}$$

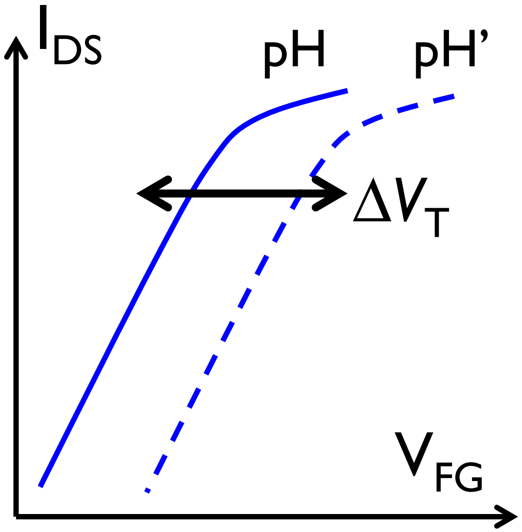
$$I_{D2} \propto Q_{s2} \sim f(x_2) \quad x_2 = e^{-2.303\,pH_2 - q(\psi_{02} - V_{FG2})/k_BT}$$

$$I_{D1} = I_{D2} \Rightarrow \psi_{0,1} = \psi_{0,2}$$

$$\Delta V_G \approx 2.303(k_BT/q)\Delta \mathrm{pH}.$$

$$\Delta V_G / \Delta \mathrm{pH} = 59\,mV/pH$$





Conclusions

- pH sensors involve one of the simplest biosensors. pH reflects the concentration of protons in a solution, and is often an excellent marker of health of an individual.

- The pH sensor relies on modification of surface charges in response to changes in pH.

- The maximum pH sensitivity of(59 mV/pH) is called the Nernst limit.

- The first pH-meter measured acidity of various types of orange juices. It used a different type of special ion-sensitive electrodes coupled with a vacuum tube amplifier.

Review Questions

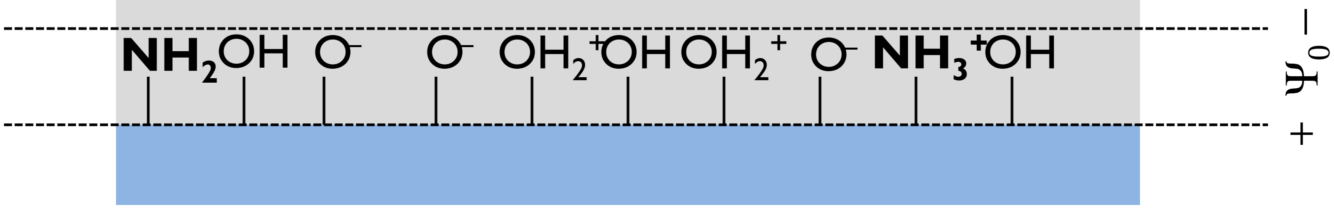
- There is a minimum background conductivity of water that cannot be changed by adding acid or base. Explain.
- If the noise of a sensor is 10 mV, what fundamental limit to pH resolution can the sensor achieve?
- What is pzc? Will it change if the oxide is changed from SiO2 to SiN?
- Why is it necessary to control pH of human body so precisely? Make a guess.

Appendix

Derivation of surface charge on SiN surface

HW: Find the pH dependent equilibrium concentration for NH_3 decorated surfaces.

Surface binding model (for OH group + modified by amide group Si_3N_4 system)



(protonation)

(de-protonation)

$$SiOH_2^+ \Leftrightarrow SiOH + H^+ \qquad NH_3^+ \Leftrightarrow NH_2 + H^+ \qquad SiOH \Leftrightarrow SiO^- + H^+$$

$$\frac{[SiO^-][H^+]_S}{[SiOH]} = K_b \qquad \frac{[SiNH_2][H^+]_S}{[SiNH_3^+]} = K_c \qquad \frac{[SiOH][H^+]_S}{[SiOH_2^+]} = K_a$$

$$Q_0 = q(N_1[NH_3^+] + N_2[OH_2^+] - N_2[O^-])$$

$$\approx q(N_1[NH_3^+] - N_2[O^-])$$

$$pH_{pzc} = -\log_{10}(K_a K_b)/2$$

HW solution: Surface binding model (for OH group)

$$[\mathrm{SiO^-}] = K_b \frac{[SiOH]}{[\mathrm{H^+}]_S} = \mathrm{N}_1 \left[1 + \frac{K_b}{[\mathrm{H^+}]_S}\right]^{-1} \frac{K_b}{[\mathrm{H^+}]_S}$$

$$\mathrm{SiO^-} + \mathrm{SiOH} = \mathrm{N}_1 \Rightarrow \mathrm{SiOH}\left[1 + \frac{K_b}{[\mathrm{H^+}]_S}\right] = \mathrm{N}_1$$

$$[\mathrm{NH_3^+}] = \frac{[NH_2][\mathrm{H^+}]_S}{K_c} = \mathrm{N}_2 \left[1 + \frac{[\mathrm{H^+}]_S}{K_c}\right]^{-1} \frac{[\mathrm{H^+}]_S}{K_c}$$

$$\mathrm{NH_2} + \mathrm{NH_3^+} = \mathrm{N}_2 \Leftrightarrow \mathrm{NH_2}\left[1 + \frac{[\mathrm{H^+}]_S}{K_c}\right] = \mathrm{N}_2$$

HW solution: Surface binding model (for OH group)

$$Q_0 = q\left[[\mathrm{NH}_3^+]-[\mathrm{SiO}^-]\right]$$

$$= qN_0\left\{N_1\frac{\left[\mathrm{H}^+\right]_S/K_c}{\left[1+\left[\mathrm{H}^+\right]_S/K_c\right]} - N_2\frac{K_b/\left[\mathrm{H}^+\right]_S}{\left[1+K_b/\left[\mathrm{H}^+\right]_S\right]}\right\}$$

$usually \Rightarrow$

$pK_a(SiOH_2^+) = -2,\qquad pK_b(SiO^-) = 6,\qquad pK_c(NH_2) = 3-4$

$$pH_{pzc} = \left(pK_a + pK_b\right)/2$$

References

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- Brown, Theodore Lawrence, Chemistry: the central science, Pearson Education, 2009.
- Van Hal, R. E. G., J. C. T. Eijkel, and P. Bergveld, "A novel description of ISFET sensitivity with the buffer capacity and double-layer capacitance as key parameters", *Sensors and Actuators B: Chemical* **24**.1 (1995): 201-205.
- Van der Schoot, Bart H., and Piet Bergveld, "ISFET based enzyme sensors", *Biosensors* **3**.3 (1988): 161-186.