Correlation of Low-Frequency Noise to the Dynamic Properties of the Sensing Surface in Electrolytes

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This material includes:

1. Evaluation of static properties $\alpha_s$, $C_{\text{stem}}$, and $N_s$,

2. Simplified expression of $\tau$, $R_s$, and $R_p$,

3. Dependence of $f_c$ on surface properties,

as well as the following figures:

Figure S1. pH sensitivity depicted as function of binding site density $N_s$ with varying $C_{\text{stem}}$ at $pH=7$,

Figure S2. Equivalent circuit of the site-binding impedance $z_{SB}$.

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1. Evaluation of static properties $a_s$, $C_{\text{Stem}}$, and $N_s$

The variation of $\phi_s$ with that of $pH$, i.e. $\Delta \phi_s/\Delta pH$, is commonly defined as the sensitivity for the ISFETs, quantification of which has been well addressed by the site-binding model$^1$. To conquer the complexity of the original site-binding model, van Hal et al. develop a general approach$^2$ to calculate the $pH$ sensitivity, where, a key parameter is the surface $H^+$ buffer capacitance $C_{\text{buff}}$. Introduction of $C_{\text{buff}}$ brings a concise but physically meaningful expression for the $pH$ sensitivity $S_{\text{pH}}$ as follow$^2$:

$$S_{\text{pH}} = \frac{\Delta \phi_s}{\Delta pH} = \frac{59.2 \text{ mV/pH}}{C_{\text{DL}}/C_{\text{buff}} + 1}$$

(S1)

where, $\phi_s$ denotes the surface potential, and $C_{\text{DL}}$ the EDL capacitance. The calculations of $C_{\text{DL}}$ and $C_{\text{buff}}$ depend on the EDL model and charging mechanism applied, respectively. In the present work, $C_{\text{DL}}$ is calculated via Gouy-Chapman-Stern model, in which $C_{\text{DL}}$ is the series connection of Stern capacitance $C_{\text{Stem}}$ and the diffuse layer capacitance $C_{\text{diff}}$. On the other hand, $C_{\text{buff}}$ is accounted for by the original Yates el.’s site-binding charge mechanism$^2$, and calculated with:

$$C_{\text{buff}} = \frac{d\sigma_o}{d\phi_s} = \frac{q^2 N_s D_2 K_B a_s}{kT D_i^3}$$

(S2)

where, $\sigma_o$ denotes the surface charge density, $q$ the elementary charge, $N_s$ the density of surface OH group, $k$ Boltzmann constant, $T$ the temperature, $a_s$ surface $H^+$ concentration, $D_1 = K_A K_B + K_B a_s + a_s^2$, and $D_2 = K_A K_B + 4 K_B a_s + a_s^2$. Using eqs. S1 and S2 with a measured $S_{\text{pH}}$, $a_s$, $C_{\text{Stem}}$, and $N_s$ can be solved implicitly, provided value of any of three parameters is known.
C_{Stern}, with its nature taken into account, is determined by the structure of electrolyte and interfacial charging condition\(^3\), rather than the surface structure; therefore, it should be considerably similar, and thus assigned with the same value for the samples at a certain pH value in our modelling. In Figure S1, \(S_M\) is depicted a function of \(N_S\) at pH=7. In our modeling, \(C_{Stern}\) was searched within the reported range\(^2\) from 0.2 to 1.4 \(\text{F/m}^2\). To achieve a good fitting of \(S_N\) to the measurement and a reasonable value compared to the reported ones\(^2\), \(C_{Stern}\) was assigned as 0.34 \(\text{F/m}^2\), corresponding to the solid line in the figure, and the values of the derived \(N_S\) for the samples, depicted in the figure too, are listed in table 1 in the main text, where \(S_M\), \(K_A\) and \(K_B\) can also be found. Since the measured sensitivity \(S_m\) for the three samples is different, the derived \(N_S\) can be considerable variable for the samples too, as shown in the figure, which may arise from the uneven morphology and structure of the ALD oxide film at its early growth stage.

2. Simplified expression of \(\tau_p\), \(R_s\), and \(R_p\)

The site-binding impedance \(z_{SB}\) can be decomposed to a sum of first-order partial fractions:

\[
z_{SB} = \frac{1}{j \omega_{SB}} = \frac{1}{sC_{\text{buff}}} + \frac{R_p}{1 + s\tau_p} + R_s
\]

(S3)

where, buffer capacitance \(C_{\text{buff}}\), resistances \(R_s\) and \(R_p\) and time constant \(\tau_p = R_p C_{\text{w}}\) are associated with the site-binding reactions. They expressions have been detailed in our recent work\(^4\). Here we utilize \(K_B \gg a_s \gg K_A\) and \(K_B K_A \approx a_s^2\) to further simplify their expressions, as follows:

\[
C_{\text{buff}} = \frac{q^2 N_S}{kT} \frac{D_2 K_B a_s}{D_1} \approx \frac{q^2 N_S}{kT} \frac{2a_s}{K_B}
\]

(S4a)

S-3
\[ \tau_p = R_p C_{re} = \frac{1}{D_2} \left( \frac{a_s}{c_A} + \frac{K_\Lambda}{c_B} \right) \approx \frac{1}{D_2} \frac{K_\Lambda}{c_B} \approx \frac{1}{2K_B c_B} \] (S4b)

\[ R_s = \frac{kT}{q^2 N_s} \frac{D_1}{K_B a_s (a_s c_B + K_\Lambda c_A)} \approx \frac{kT}{q^2 N_s} \frac{1}{K_\Lambda c_A} \] (S4c)

\[ R_p = R_s \frac{a_s K_\Lambda \left[ a_s (c_A - 2c_B) + K_\Lambda (2c_\Lambda - c_B) \right]^2}{D_2 c_A c_B} \approx \frac{kT}{q^2 N_s} \frac{D_1}{K_B K_\Lambda a_s c_A} \frac{a_s K_\Lambda (a_s + 2K_\Lambda)^2 c_\Lambda^2}{D_2 c_A c_B} \approx \frac{kT}{q^2 N_s} \frac{D_1 a_s^2}{D_2 K_B c_B} \frac{1}{c_B} \approx \frac{kT}{q^2 N_s} \frac{1}{a_s c_B} \] (S4d)

\[ C_{re} = \frac{\tau_p}{R_p} = \frac{q^2 N_s}{kT} \frac{2a_s}{K_B} \] (S4e)

3. Dependence of \( f_c \) on surface properties

The site-binding \( z_{su} \) can be described with the equivalent circuit depicted in Figure S2. From the expressions of all the components in the circuit as formulated with eqs S4a-e, it can be found that

\[ C_{buff} = C_{re} \] (S5a)

\[ R_p \gg R_s, \text{ in the limit of } c_\Lambda \gg c_B \] (S5b)

Therefore, the circuit can be approximated with the \( \frac{1}{2} C_{buff} - R_s \) branch since the two capacitors are in series. The corner frequency \( f_c \) of the branch, i.e. \( f_c \) of the site-binding network, is found as:

\[ f_c = \frac{1}{2\pi R_s C_{buff} / 2} = \frac{K_\Lambda K_B c_\Lambda}{2\pi a_s} \approx \frac{a_s c_\Lambda}{2\pi} \] (S6)
Figures

**Figure S1.** $p$H sensitivity depicted as function of binding site density $N_S$ with varying $C_{\text{Stern}}$ at $p$H=7.

**Figure S2.** Equivalent circuit of the site-binding impedance $z_{SB}$.

Reference

