



An impedance model for the low-frequency noise originating from the dynamic hydrogen ion reactivity at the solid/liquid interface



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ARTICLE INFO

Article history:

Received 19 April 2017

Received in revised form 16 June 2017

Accepted 9 July 2017

Available online 16 July 2017

Keywords:

Low frequency noise

Solid/liquid interface

Ion-sensor

Site-binding model

Electrochemical impedance

ABSTRACT

Understanding the dynamics of hydrogen ion reactivity at the solid/liquid interface is of paramount importance for applications involving ion sensing in electrolytes. However, the correlation of this interfacial process to noise generation is poorly characterized. Here, the relationship is unveiled by characterizing the interfacial process with impedance spectroscopy assisted by a dedicated electrochemical impedance model. The model incorporates both thermodynamic and kinetic properties of the amphoteric hydrogen ion site-binding reactions with the surface OH groups. It further takes into consideration the distributed nature of the characteristic energy of the binding sites. The simulated impedance matches the experimental data better with an energy distribution of the kinetic parameters than with that of the thermodynamic ones. Since the potentiometric low-frequency noise (LFN) originating from the solid/liquid interface correlates excellently with the real part of its electrochemical impedance spectrum, this work establishes a method for evaluating sensing surface quality aimed at mitigating LFN.

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1. Introduction

The successful semiconductor genome sequencing [1] and emerging semiconductor quantitative polymerase chain reaction [2] technologies employ ion-sensitive field-effect transistors (ISFETs) as electronic sensors for detection of pH variations in electrolytes. The sensing layer of an ISFET interfacing with the electrolyte under study is usually an insulating oxide present on a semiconductor conduction channel [3]. A change in pH leading to protonation (H^+ adsorption) or deprotonation (H^+ desorption) of the oxide surface can alter the surface charge state and electrical potential (φ_s) at the oxide/electrolyte interface, which in turn can cause a change in electrical current in the semiconductor channel [4]. Understanding the H^+ adsorption/desorption processes at this interface is, hence, of crucial importance in developing the ISFET technology for a variety of emerging applications [3,5]. The static behavior of the H^+ adsorption/desorption has been well accounted for, and the sensitivity of ISFETs is defined as a figure of merit that quantifies the variation of φ_s with that of pH in the electrolyte [6]. Concurrently, low-frequency noise (LFN) of ISFETs has been studied extensively [7–16], and our recent work

[16] concludes that noise originating from the electrical double layer (EDL) at the oxide/electrolyte interface is of thermal nature and comparable with that from the semiconductor/oxide interface. However, in which manner the dynamic properties of the H^+ adsorption/desorption can affect the interfacial noise remains poorly understood. Unveiling the physics of the dynamic H^+ reactivity at the solid/liquid interface as well as its correlation to LFN is especially relevant for detection of target ions of extremely low concentrations (i.e., single or few events). The present study aims at establishing an impedance model that can assist our investigation of noise behavior at the solid/liquid interface.

The excellent agreement between the potentiometric LFN and the real part of electrochemical impedance spectrum of solid/liquid systems [16,17] confirms the availability of electrochemical impedance spectroscopy (EIS) as an efficient tool to study the interfacial noise. Of particular prominence with EIS is its capability to effectively probe the dynamic information of the interfacial H^+ adsorption/desorption [18,19]. Therefore, it is highly viable to develop an impedance model that relates the interfacial noise to the dynamic properties of the H^+ adsorption/desorption. In EIS analysis, a commonly used approach is to construct an appropriate equivalent electrical circuit that can accurately describe the experimental impedance data. The dynamic information of the system under investigation can, then, be obtained based on the parameters extracted in accordance to the impedance model. For a blocking

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non-Faradaic system, such as the insulating oxide/liquid interface that is the focus of this study, the impedance in a Nyquist diagram often exhibits a straight line rotated around the high-frequency endpoint (lower end), with a phase angle smaller than 90° [20], instead of a vertical line represented by a series R-C circuit. This distorted impedance behavior cannot be accounted for by any simple R-C network, and is often represented by a phenomenological circuit component referred to as the constant phase element (CPE) [19,20].

The physical interpretation of the CPE behavior is still under debate, although it is generally accepted [19,21] to be rooted either in spatial structural inhomogeneity of electrodes or to arise from varying time constants associated with different physical processes distributed at the electrode surface. The electrode inhomogeneity may, in turn, arise from surface roughness [22,23] or disorder at atomic level [18,24]; but none of which have proven their validity to account for CPE for the oxide/liquid system. The state-of-the-art atomic layer deposition (ALD), employed in this study to grow oxide films, is known to yield thin films with excellent conformality and uniformity [25], which could help reduce the risk of having structural inhomogeneity such as varying composition [26] and electrode porosity [27]. However, the probable distributed nature of time constants, along and normal to the electrode surface [28], is more likely to be related to material properties than to structural imperfections. This distribution can be of current and/or potential type [28,29] or ascribed to distributed surface reactivity [28]. The former can be trivial for a blocking electrode, because of negligible DC current. The distribution normal to the electrode surface can involve either dielectric dispersion [30] or conductive dispersion for an oxide-coated electrode [26,31–34]. Since the former is much narrower than the latter, it will not contribute to CPE. Therefore, the conductive dispersion, i.e., the variation of local resistivity of the dielectric in the normal direction, has been frequently used to interpret the CPE phenomenon encountered in oxide/liquid systems [33]. The distribution of surface reactivity of the oxide, on the other hand, is seldom considered for interpretation of the CPE behavior that appears in an oxide/electrolyte system. However, surface reactions such as H^+ adsorption/desorption can remarkably modulate the surface charging status and contribute to the impedance. Therefore, it is logical to take the surface reactivity into account concerning the interpretation of the CPE behavior of an oxide/liquid interface.

In the present study, we consider distributed H^+ reactivity on an oxide surface in order to account for the CPE behavior in the oxide/electrolyte system since the surface H^+ adsorption/desorption can predominantly modulate the surface charging conditions. This consideration leads to the development of an impedance model by incorporating the thermodynamic and dynamic properties of the surface H^+ reactivity. Investigation of the energy distribution of the surface reactivity renders a wide time constant dispersion that provides a sound physical basis for the CPE behavior of the oxide/electrolyte system. The developed impedance model can be a powerful tool for guiding our sensing interface design towards minimizing the LFN contribution from the solid/liquid interface.

2. Theory

The Nernst equation predicts that the variation in ϕ_s of a metal electrode submerged in liquid is 59.2 mV per pH unit of solution at room temperature, i.e., $\Delta\phi_s/\Delta pH = 2.303kT/q$. In the case of oxide-covered electrodes, however, the observed $\Delta\phi_s$ is generally less than this theoretical sensitivity limit. This deviation prompted the development of the successful site-binding model [35] in an attempt to interpret the observed non-Nernstian behavior via

describing the charging/de-charging processes of the oxide/liquid interface. This model has been widely accepted as the primary theoretical tool for the oxide/liquid interfaces. In this model, oxide charging is attributed to the H^+ adsorption or desorption by surface hydroxyl (OH) groups to form negative or positive sites on the oxide summarized by the following reversible reactions:



The surface equilibria can thus be described by introducing two thermodynamic equilibrium constants with subscripts A and B to reactions 1a and 1b respectively:

$$K_A = \frac{a_S[M-O^-]}{[M-OH]}, \quad K_B = \frac{a_S[M-OH]}{[M-OH_2^+]} \quad (2)$$

where, $[M-O^-]$, $[M-OH_2^+]$, and $[M-OH]$ are the densities of deprotonated, protonated, and uncharged surface OH group, respectively, and a_S is the surface H^+ concentration in mol. The dynamic rate equations for the two reactions are given as

$$\frac{d[M-OH]}{dt} = c_A[M-O^-]a_S - r_A[M-OH], \quad (3a)$$

$$\frac{d[M-OH_2^+]}{dt} = c_B[M-OH]a_S - r_B[M-OH_2^+] \quad (3b)$$

where, c_A and r_A refer to the rate constants for protonation and deprotonation of the $M-O^-$ group, while c_B and r_B are those of the uncharged OH M-group. Using the principle of detailed balance in equilibrium we find $r_A = c_A K_A$ and $r_B = c_B K_B$.

In the context of impedance spectroscopy as the characterization method, the generated currents associated with the dynamic processes described with eqs 3a and 3b are:

$$I_A = q \frac{d[M-OH]}{dt} = qN_S(c_A\Theta^- a_S - r_A\Theta^0), \quad (4a)$$

$$I_B = q \frac{d[M-OH_2^+]}{dt} = qN_S(c_B\Theta^0 a_S - r_B\Theta^+) \quad (4b)$$

in which q represents the elementary charge, N_S the total density of surface OH group, and Θ^+ and Θ^- the fractions of N_S that carry positive and negative charge, respectively. Let Θ^0 denote the fraction of the neutral OH group of N_S , these fractional coverages can be expressed as [6]:

$$\Theta^+ = \frac{a_S^2}{D_1}, \quad \Theta^- = \frac{K_A K_B}{D_1}, \quad \Theta^0 = \frac{K_B a_S}{D_1}, \quad (5)$$

where, $D_1 = K_A K_B + K_B a_S + a_S^2$, and the net surface charge density in equilibrium can be calculated via $\sigma_0 = qN_S(\Theta^+ - \Theta^-)$. The solution to eqs 4a and 4b is of the form of a two-branch admittance that naturally corresponds to the dynamic rate reactions in eqs 3a and 3b. By adding an AC perturbation and making the small-signal approximation, they were solved as shown in Supporting Information (SI), and the final expression for the admittance is:

$$Y_{SB} = \frac{sC_{\text{buff}} \left[1 + s \frac{1}{D_2} \left(\frac{a_S}{c_A} + \frac{K_A}{c_B} \right) \right]}{1 + \frac{s}{D_1} \left(\frac{a_S + K_B}{c_A} + \frac{a_S + K_A}{c_B} \right) + \frac{s^2}{D_1 c_A c_B}} \quad (6)$$

in which $D_2 = K_A K_B + 4K_A a_S + a_S^2$, and $s = j\omega$ with j as the imaginary unit and ω as the angular frequency. C_{buff} is an equivalent capacitance calculated as:

$$C_{\text{buff}} = \frac{d\sigma_0}{d\phi_S} = \beta_{\text{int}} \frac{dpH_S}{d\phi_S} = \frac{q^2 N_S D_2 K_B a_S}{kT D_1^2} \quad (7)$$

where, $\beta_{\text{int}} = \frac{d\sigma_0}{dpH_S}$ is the intrinsic surface buffer capacity that quantifies the capability of an oxide surface to buffer the variation of the surface H^+ concentration [6].

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