Oscillations at the Si/electrolyte contact: Relation to Quantum Mechanics

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Abstract. The basic process at the surface of the Si electrode is characterized by a cyclic oxidation of a thin silicon layer and the subsequent removal of the oxide by etching. Here, the oxide thickness evolves not uniformly due to cracks and nanopores. The mathematical model used to describe the phenomenon is based on a sequence of time dependent (oxide thickness) oscillator density functions that describes the passing of the (infinitesimal) oscillators through their minimum at each cycle. Two consecutive oscillator density functions are connected by a second order linear integral equation representing a Markov process. The kernel of the integral equation is a normalized Greens Function and represents the probability distribution for the periods of the oscillators during a cycle. Both, the oscillator density function and the two-dimensional probability density for the periods of the oscillators, define a random walk. A relation between the oscillator density functions and solutions of the Fokker-Planck equation can be constructed. This allows a connection of the oscillations, originally considered only for the description of a photo-electrochemical observation, to the Schrödinger equation. In addition, if the trajectory of a virtual particle, located at the silicon oxide electrode surface, is considered during one oscillatory cycle, then it can be shown that the displacement of the particle measured at the electrode surface performs a Brownian motion.

1. Introduction
Oscillation phenomena of silicon electrodes in electrochemical systems have been known for a long time [1]. In photo-electrochemistry and electrochemistry, oscillatory behaviour has been extensively studied on Si photo-electrodes [2]. Various models for the oscillation phenomena were discussed based on self-oscillating domains [3], the so-called current bursts [4], and oxide-induced interfacial stress [5] where the latter model explains sustained current oscillations with the existence of two types of oxides with different nanopore densities. The observation of nano-dimensioned pores, fluctuating with the phase of the oscillating (photo) current of Si electrodes immersed in dilute ammonium fluoride solutions motivated the further development [6-8] of the original stress model, also to spatial resolution, by applying cellular automates [7]. If the model is presented by a special phase space analysis based on the holographic principle [9-10], then an analogy between the spectral energy densities of the black body radiation and that obtained from the model for current oscillations can be shown [10]. We first describe (section 2) the mathematics of the model and the relation to the Fokker-Planck and Schrödinger equation. The Brownian motion of a virtual particle, which position is defined by an infinitesimal point located at the silicon surface, is discussed in section 3.
2. Mathematical model and the Fokker-Planck equation

The basic process at the electrode surface domain $\Omega \subseteq \mathbb{R}^2$ is characterised by a cyclic oxidation of a small silicon layer and the following removal of the oxide by etching (figure 1). Lattice mismatch between silicon and its oxide leads to stress, cracks, and nanopores resulting in a not uniformly evolution of the oxide thickness. The oxide thickness $d(t, x, y)$ is considered at a fixed point $(x, y)$ at the electrode surface in dependence on the time $t$. Here the phase $\varphi = \varphi(t, x, y)$ propagates nonlinearly and monotonically increasing for $2\pi \leq \varphi(t, x, y) \leq (i + 1)2\pi$, $i = 0, 1, 2, \ldots$. The so called phase oscillator $\varphi$ is discretized by using the holographic principle [9-10]. Therefore the oxide thickness is registered periodically only once during one cycle. In the phase space $\Phi = \{(x, y, \varphi) | (x, y) \in \Omega, \varphi \in \mathbb{R} \}$ that corresponds to a registration of the phase $\varphi$ at the so-called snap-shot (holographic) screens $S^\phi_i = \{(x, y, \varphi + i \cdot 2\pi) | (x, y) \in \Omega \}$ for $i = 0, 1, 2, \ldots$. The result is the time dependent oscillator density function $p^\phi_i(t)$ [9] defining the differential number of phase oscillators $\varphi$ passing $S^\phi_i$ at the time $t$ at the $i$-th time. Here the fixed parameter $\phi$ ($0 \leq \phi < 2\pi$) determines the position of the $S^\phi_i$ in the phase space. For instance, $\phi = 0$ ($\phi = \pi$) corresponds to the registration of the oxide thickness at its minimum $d_{\min}$ ($d_{\max}$) at the times $t_i(x, y)$, $i = 0, 1, 2, \ldots$ (figure 1 right). Assuming that all oscillators $\varphi$ pass $S^\phi_i$ during the time interval $[t_i^{\min}, t_i^{\max}]$ at the $i$-th cycle, then two consecutive oscillator density functions are connected by a Markov process represented by a linear integral equation (figure 2 left)

$$
\int_{t_i^{\min}}^{t_i^{\max}} p^\phi_{i+1}(s) q^\phi_{i,s}(t-s) \, ds \quad \text{for} \quad 0 \leq \phi < 2\pi, \quad t_i^{\min} \leq t \leq t_i^{\max} \quad \text{and} \quad i = 1, 2, 3, \ldots
$$

(1)

The kernel $q^\phi_{i,s}(t-s)$ of the integral equation is a normalized Greens Function [8] and represents the probability density for the periods $t-s$ of the oscillators in dependence on the starting times $s$ of the oscillators during the $i$-th cycle. Both together, the oscillator density function $p^\phi_i(s)$ and the two-dimensional probability density $q^\phi_{i,s}(t-s)$ for the periods of the oscillators, define a random walk [10]. By equation (1), a temporal evolution of the probability density function $p^\phi_i(t)$ is given (figure 2 right). Moreover, this probability density function is also a solution of the Fokker-Planck equation [11]

$$
\frac{\partial}{\partial t} p^\phi_i(t) = -\frac{\partial}{\partial \phi} \left[ A(\phi) p^\phi_i(t) \right] + \frac{1}{2} \frac{\partial^2}{\partial \phi^2} \left[ B(\phi) p^\phi_i(t) \right] \quad \text{for} \quad 0 \leq \phi < 2\pi, \quad t_i^{\min} \leq t \leq t_i^{\max}, \quad i = 0, 1, 2, \ldots
$$

(2)
with time-independent drift coefficient $A(\phi)$ and diffusion coefficient $B(\phi)$. In this case the Fokker-Plank equation can be transformed to the Schrödinger equation \[11\].

3. Brownian motion of a virtual particle

In the following the trajectory of a virtual particle located at the silicon oxide electrode surface is considered during one oscillatory cycle. The trajectory is determined (figure 3 left) using the microscopic nanopore model \[5, 9\] at which in dependence on the starting time $s$ the evolution of a nanopore as the mean of the evolution of real nanopores during one cycle is regarded. For simplicity, we set $d_{\min} = 0$, $\phi = 0$ and can omit $\phi$ in the corresponding notations. In the case of sustained oscillations we choose for $q$ a normalized Greens Function \[8, 10\] (figure 2 left) i.e.

$$q_{i,s}(t-s) = \begin{cases} 2(t - \bar{T})(L_s)^{-1}, & \text{for } \bar{T} \leq t \leq \bar{T} + s \\ 2(\bar{T} + L - t)L^{-1}(L - s)^{-1}, & \text{for } \bar{T} + s \leq t \leq \bar{T} + L \end{cases}$$ \(3\)

for $s \in [t_i^{\min}, t_i^{\max}]$, $L = t_i^{\max} - t_i^{\min}$ and $\bar{T}$ denotes the macroscopic oscillation period. Based on the oxide etching process \[7\], for a fixed $s \in [t_i^{\min}, t_i^{\max}]$ and $t \in [t_i^{\max}, t_i^{\min}]$ the hyperbolic oxide surface $d_{i,s}(r)$ and the always perpendicularly crossing hyperbolic particle trajectory $d_{i,s}^{-1}(r)$ are defined by

$$d_{i,s}(r) = (1 - r_s(t) r^{-1}) a^{-1} \text{ for all } r \text{ with } r_s(t) \leq r \leq r_s$$ \(4\)

and

$$d_{i,s}^{-1}(r) = a^{-1} - ((a^{-1})^2 + r^2 - r_s^{-2}(t))^{1/2} \text{ for all } r \text{ with } r_s(t) \leq r \leq r_s(t).$$ \(5\)

Here $r_s(t) = (r_s^2(t) - (a_{\max})^2)^{1/2}$ for $a_{\max} \leq r_s(t) \leq r_s$ and $r_s(t) = 0$ for $0 \leq r_s(t) \leq a_{\max}$ determine the radius of the starting point of the oxide surface. $r_s(t) = r_s(t) \left( \int_0^{\bar{T}_s} g_{i,s}(\tau - s) \, d\tau \right)^{1/2}$ defines the radius of the end point of the particle at the bottom of the nanopore where the oxide is removed at the time $t$ and $r_s = r_{\min} + (r_{\max} - r_{\min}) \left(1 - ((s - t_i^{\min}) (t_i^{\max} - t_i^{\min})^{-1})^{1/2}\right)$ reflects the decreasing of the (half) nanopore distance towards the end of the cycle \[9\]. Hence, the displacement $\Delta r$ of a particle is defined by

$$\Delta r_s(t) = r_s(t) - \bar{r}_s(t) \text{ for } s \in [t_i^{\min}, t_i^{\max}] \text{ and } t \in [t_i^{\max}, t_i^{\min}].$$ \(6\)
Figure 3. For a fixed oxide growth starting time \( s \) of a nanopore, the trajectory (blue line) of a virtual particle crosses the \( t \)-dependent oxide surfaces (red lines) always perpendicularly. Here, the oxide is etched away and hence the oxide surface decreases during the time \( t \) (left). The probability density for the displacement \( \Delta r \) of a virtual particle shows a Lévy like distribution (right).

Finally, using the nanopore model the probability density \( w \) for a displacement \( \Delta r \) of a particle located anywhere at the oxide surface during a cycle is given by

\[
w(\Delta r) = c \int_{(s,t) \mid |\Delta r_i(t)|=\Delta r, s \in [t_{i-1}^{\min}, t_i^{\max}), t \in [t_i^{\min}, t_i^{\max})} \bar{r}_i(t) q_{i,s}(t-s) \, dt \, ds \quad \text{for} \quad 0 \leq \Delta r \leq d_{\text{max}}^{\max}
\]

Here, for a fixed \( \Delta r \), the path of integration is given by the contour lines of \( \Delta r_i(t) = \Delta r \) for \( t_{i-1}^{\min} \leq s \leq t_i^{\max}, \quad t_i^{\min} \leq t \leq t_i^{\max} \) and \( c \) is a normalization factor. Figure 3 right shows the probability density for a particle displacement for \( L = T = 30 \text{s} \), \( d_{\text{max}}^{\max} = 10\text{nm}, \quad r_{\text{min}} = 20\text{nm}, \quad \text{and} \quad r_{\text{max}} = 60\text{nm} \).

4. Conclusions and Outlook
The mathematical concept of the discretization of phase oscillators is based on the holographic principle and leads to a linear integral equation representing a Markov process and a random walk. The solution of the integral equation is an oscillator density function whose relation to the Fokker-Planck equation and hence to the Schrödinger equation is shown. Further, a virtual particle located at the silicon oxide surface at the electrode performs a Brownian motion during one cycle. In summary, the model shows analogies to quantum mechanics. Because of the link to the Schrödinger equation and to particle trajectories, the relation to the Bohmian Mechanics [12] should be investigated in future.

5. References
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