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Kinetic enhancement in nanoscale electrochemical systems caused by non-normal distributions of the electrode potential

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We have recently shown [Proc. Natl. Acad. Sci. U.S.A. **107**, 4528 (2010)] that the discreteness and stochasticity of an electron transfer event on a resistively coupled nanoelectrode causes mesoscopic fluctuations in time of the electrode potential. These fluctuations give rise to a time-average faradaic current density substantially larger than in the macroscopic limit. The deviations result to a large extent from the potentiostatic control, which imposes a constraint on the evolution of the electrode potential that leads to non-normal distributions. The degree of freedom of the electrode potential requires a resistance between nanoelectrode and metallic support. In this article, we study the dependence of the mesoscopic stochastic dynamics on this resistance (assumed to be ohmic). We show that the enhancement of the reaction rate vanishes in both limits, zero and infinite resistance. The distribution of the electrode potential continuously transforms from a normal distribution at infinite resistance (the galvanostatic limit), through a more and more peaked distribution with increasingly important rare events to the deterministic behavior at zero resistance. © *2011 American Institute of Physics*. [doi:10.1063/1.3604950]

The increasing number of studies in nanotechnological applications has led to a growing interest in chemical and electrochemical reactions in mesoscopic systems. Considering chemical systems, the situation is much simpler than in electrochemical systems. The evolution of the number of reacting chemical species in a small volume is described by the chemical master equation;[1–7] the individual reaction events are Markovian, and the resulting stationary state obeys a normal distribution. An electrochemical reaction is usually controlled from the outside, which causes the reaction events to be non-Markovian and the distributions non-normal.[8]

Let us consider a nanoelectrode. This can, for example, be a metallic nanoparticle of some ten nm in diameter. When the nanoparticle is in an electrolyte solution which contains a redox couple, it will exchange electrons with the redox couple, thereby changing the electrostatic potential of the electrode, until an equilibrium situation is established. In this situation the electrode is at open circuit potential. The electrochemical reaction can be controlled, when a voltage is applied externally. Therefore, the nanoelectrode has to be linked to a macroscopic support, which, for example, can be accomplished by some molecular entities, such as alkyl chains.[9–11] If the electrostatic potential of the support is different from the one of the nanoparticle, a current will flow across the spacer. Here, for simplicity, we assume the spacer to behave as an ohmic resistor. This assumption may seem rather crude at first sight and, in general, when considering mesoscopic elements, tunneling resistances (as discussed, for example, in the framework of the so-called orthodox theory[12]) might provide a more accurate description. Yet, the effect we are investigating here is independent of the precise model for the series resistance, and it is instructive to first consider the simplest case, namely, a constant (ohmic) resistance. The essential point is that the electrode potential constitutes a degree of freedom that can fluctuate, as we discuss next.

There are two sources changing the electrostatic potential of the nanoparticle, the redox reactions and the potentiostatic control. The redox reactions are stochastic events causing fluctuations of the electrode potential. Note that the fluctuations are only *in time*, there are *no local fluctuations*, the electrostatic potential of the nanoparticle being always *uniform* on the nanoelectrode. Thus, we adopt here a mesoscopic description of the redox processes. The potentiostatic control, on the other hand, imposes a deterministic constraint on the electrostatic potential of the nanoparticle, driving it towards the one of the support. In a physical system, one has of course not just one nanoparticle but many of them. As long as they are laterally isolated the picture remains exactly the same. We envisage that the metal electrode is covered by an insulating layer which constitutes a series resistance R_e for a nanoparticle being anchored to it. The spacer layer can be, e.g., a self-assembled monolayer of some long-chain alkyl, or an oxide layer with some small electronic conductivity. In the first case, the lateral isolation of the nanoparticles is guaranteed (regardless of the value of R_e) when the distance of the nanoparticles is larger than a few Debye lengths, since laterally the alkyl chains are completely insulating. The Debye lengths can be lowered by increasing the concentration of the electrolyte and is typically not larger than a nm. In the second

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case, the interparticle distances should be an order of magnitude larger than the thickness of the insulating layer.

Clearly, the resistance of the spacer between the nanoparticles and the support weights the impact of the stochastic reaction events for the electrode potential. For negligible resistance the electrostatic potential of the nanoparticle is equal to the one of the support. Hence, in this limit the electrode potential of the nanoparticle is fully controlled by the externally applied voltage. In the other limit of infinite resistance and infinite voltage at the support the electrode potential has maximal freedom to vary, but the current is fully determined by the external parameters (applied voltage and series resistance). This limit corresponds to a constant current control. In between these two limits fluctuations of the electrode potential can lead to drastic changes of the current density at a nanoelectrode compared to the macroscopic case.

In this paper we discuss how the distribution of the electrostatic potential of the nanoelectrode can be tuned between the deterministic regime and a normal distribution by varying the magnitude of the ohmic resistor. The important implications on the reaction rate occur at intermediate values of resistance where the events are non-Markovian and the distributions are long-tailed.

Redox processes on macroelectrodes in an electrolyte solution are well described by the kinetic Butler-Volmer theory which treats the concentrations of chemical species and the faradaic current coming from redox processes as deterministic variables. This description is thus fully given by the specification of concentrations of chemical species, the electrode potential, and kinetic constants. According to the Butler-Volmer electrochemical equation, the rate constant of an electrochemical reaction ρ depends exponentially on the electrode potential:[13]

$$k_\rho^{(mac)}(E) = k_\rho^0 e^{c_\rho (E-E^0)}. \qquad (1)$$

Here E^0 is the redox potential of the reaction, the preexponential factor k_ρ^0 does not depend on the electrode potential and $c_\rho = \frac{-\alpha |n_\rho| F}{RT}$ for reduction reactions and $c_\rho = \frac{(1-\alpha)|n_\rho| F}{RT}$ for oxidation reactions, α is the transfer coefficient, n the number of electrons transferred, F the Faraday constant, R the ideal gas constant, and T the temperature. In this paper we will consider $\alpha = 0.5$ and $T = 300K$.

For nanoelectrodes as described above, this description does not hold any longer: Electrochemical reactions are essentially stochastic events[8] as is the case with purely chemical reactions where no electron transfer processes are present.[1,2] Hence, rigorously, the state of the system cannot be given in terms of concentrations and a fixed value of the electrode potential E, but is determined by probability distributions of numbers of particles and of the electrode potential and the electrochemical kinetics of the system is, consequently, described by the time evolution of the probability distributions. This description is provided by the electrochemical master equation[8] which is the generalization of the chemical master equation[3–5] to redox processes. For sufficiently large systems, the probability distribution of the variables coincides with the first moment of the distribution, and the deterministic description is valid. When the probabilistic nature of the reactions becomes significant, which, according to our investigations starts already at (disk) electrode sizes of a few ten nanometer in diameter,[8] the fluctuations in the electrode potential cause a drastic change of the average current density at a nanoelectrode. Thus, the Butler-Volmer rate constant Eq. (1) becomes meaningless, and the following definition of the rate constant on nanoelectrodes was introduced:[8]

$$k_\rho^{(nano)} \equiv k_\rho^0 \langle e^{c_\rho (E-E^0)} \rangle, \qquad (2)$$

where the cornered brackets denote time averages taken after the system has settled down to constant mean values of the variables. Note that in this paper only time averages are considered.

Furthermore, comparing Eqs. (1) and (2) and recalling that in the macroscopic limit the instantaneous electrode potential coincides always with the first moment of the distribution, it can be seen that because of the stochastic behavior of the electrode potential on a nanoelectrode, *every elementary electrochemical reaction occurs faster than predicted by the macroscopic Butler-Volmer kinetic theory*

$$k_\rho^{(nano)} \geq k_\rho^{(mac)}. \qquad (3)$$

The stronger the fluctuations, the stronger the inequality holds, the equality being valid in the macroscopic limit $\Omega \to \infty$, where Ω is the system size of the nanosystem. Note that the inequality implies that the reaction rates are compared at equal mean electrode potential $\langle E \rangle$, however, the fluctuations may lead also to a shift of $\langle E \rangle$.[8]

To compare reaction rates on nanoelectrodes to the ones on macroelectrodes we introduce the enhancement factor Q_ρ of reaction ρ as

$$Q_\rho \equiv \frac{k_\rho^{(nano)}}{k_\rho^{(mac)}} = \frac{\langle e^{c_\rho E} \rangle}{e^{c_\rho \langle E \rangle}} \geq 1. \qquad (4)$$

In this article, we study how $k_\rho^{(nano)}$, or Q_ρ, are influenced by the experimental parameters of the system, in particular the series resistance, and relate their values to the stationary distributions of the instantaneous values of the fluctuating electrode potential.

The structure of the article is as follows. First we present an outline of the general results and the tools to quantify the enhancement of the electrochemical kinetics at the nanoscale, introducing the electrochemical master equation and the algorithm employed in the simulations. Then we provide an analytical theory valid in the weak noise situation, which gives insight into the simulation results. Then we discuss how the resistance R_e affects the stochastic dynamics. We consider both a single irreversible reaction and a reversible redox reaction. Finally, we also study the enhancement of the electrochemical kinetics for a single reversible redox reaction under open circuit conditions.

I. ELECTROCHEMICAL MASTER EQUATION AND OUTLINE OF THE ALGORITHM EMPLOYED IN THE SIMULATIONS

Charge transfer in an electrochemical cell under an externally applied potential difference U can be understood in terms of the equivalent circuit depicted in Figure 1. The

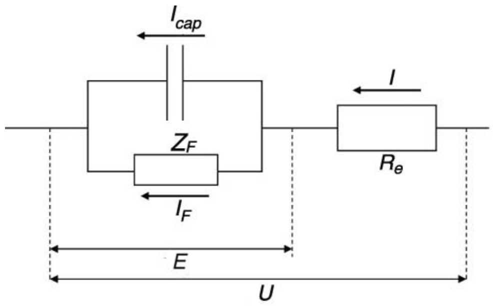

FIG. 1. Equivalent circuit for a macroscopic electrochemical cell. The total current I through the external ohmic resistance R_e splits at the interface in two components: the faradaic I_F and the capacitive I_{cap} currents.

total current flowing through the system I splits into two components, a capacitive one I_{cap} involved in the charging of the double layer and a faradaic one I_F coming from electrochemical reactions involving electron transfer to/from the electrode. At the interface, the electric charge is conserved. Hence, $I_{cap} = I - I_F$, and, therefore,[14]

$$C\frac{dE}{dt} = -i_F(E) + \frac{U-E}{R_e A}, \tag{5}$$

where C is the double layer capacitance per unit area, A is the electrode area, and i_F is the faradaic current density. At high electrolyte concentration the Gouy-Chapman-Stern model predicts a constant value for C, independent of E,[13] as we assume in all the following. This is also a valid approximation for mesoscopic nanoparticle sizes. Any stationary state is characterized by $E =$ constant. Eq. (5) provides the macroscopic evolution law for the electrode potential that behaves then deterministically: when the value of the electrode potential is known at a certain time, it is also known at any future or past time by means of integration of Eq. (5).

In general, the dynamics of the electrode potential is coupled to the one of the chemical species at the interface (given by a vector $\mathbf{c}$) through a (generally nonlinear) vector function $\mathbf{f}(E, \mathbf{c})$ in the following way:

$$C\frac{dE}{dt} = -i_F(E, \mathbf{c}) + \frac{U-E}{R_e A}, \tag{6}$$

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(E, \mathbf{c}), \tag{7}$$

the stationary state is then given by a constant value for all mesoscopic variables, E and $\mathbf{c}$. At the nanoscale, this deterministic description does not longer hold.[8] A reaction event occurs always at random, and this randomness needs to be incorporated in the dynamical description. Each electrochemical reaction in a network labeled with ρ can be represented formally as

$$\sum_{i=1}^{s} \nu^i_{<\rho} N_i + n_{<\rho} e^- \to \sum_{i=1}^{s} \nu^i_{>\rho} N_i + n_{>\rho} e^- . \tag{8}$$

Here the index i runs over the different chemical species involved in a given reaction ρ, and N_i is the number of particles of species i. The stoichiometric numbers $\nu^i_\rho = \nu^i_{>\rho} - \nu^i_{<\rho}$ control the number of molecules of each species formed or consumed each time the reaction takes place. The number of electrons transferred is similarly given by $n_\rho = n_{>\rho} - n_{<\rho}$. If we assume that after a time τ_ρ a reaction ρ involving a transfer of n_ρ electrons takes place, the electrode potential evolves discretely as

$$E_{j+1} = E_j + \frac{U-E_j}{R_e C A}\tau_\rho - \frac{n_\rho e_0}{CA}, \tag{9}$$

where the term proportional to τ_ρ comes from the external potentiostatic control and the one proportional to n_ρ (e_0 denotes here the elementary charge of the electron) from the faradaic current of reaction ρ.[8] The numbers of electrons transferred and the number of molecules of the chemical species are controlled by the electrochemical master equation

$$\frac{dP(\mathbf{N}, t)}{dt} = \sum_\rho [W_\rho(\mathbf{N} - \nu_\rho)P(\mathbf{N} - \nu_\rho) - W_\rho(\mathbf{N})P(\mathbf{N})], \tag{10}$$

where $P(\mathbf{N}, t)$ is the probability of having specific numbers of chemical species $\mathbf{N} = (N_A, N_B \ldots) = \Omega\mathbf{c}$ at a specific time and

$$W_\rho(\mathbf{N}) = W^0_\rho e^{c_\rho E} \tag{11}$$

are the so-called propensities, controlling the transition rates from one state to another where W^0_ρ is given by

$$W^0_\rho = \Omega k^0_\rho e^{-c_\rho E^0} \prod_{i=1}^{s} \prod_{m=1}^{\nu_{\langle\rho}} \frac{N_i - m + 1}{\Omega}. \tag{12}$$

In contrast to chemical systems, in electrochemical systems the propensities in Eq. (11) depend on time, since the electrode potential E changes in time between reaction events as a consequence of the external control. Since the times between reaction events τ_ρ are very small, we can assume that the change in the potential because of the external control is given by $\frac{U-E_j}{R_e C A}\tau_\rho$. After τ_ρ a reaction event takes place involving an electron transfer, which justifies the microscopic evolution law in Eq. (9).

Following the approach suggested in Refs. 1, 2, 15, and 16, we generalized Gillespie's algorithm to reaction steps involving electron transfer processes.[8] The algorithm proceeds as follows. First, an input value is given for the electrode potential and the numbers of chemical species. Then the propensities are calculated for these input values. After that, a random number r_ρ is generated from the uniform distribution for each reaction ρ. Then a waiting time τ_ρ is calculated for each reaction from[8]

$$\tau_\rho = \frac{R_e C A}{c_\rho (U - E_j)} \ln\left[1 + \frac{c_\rho (U - E_j)}{R_e C A W^0_\rho e^{c_\rho E_j}} \ln\left(\frac{1}{r_\rho}\right)\right]. \tag{13}$$

The reaction with the minimal waiting time is then selected to advance. The electrode potential is updated according to Eq. (9) and all particle numbers involved in the selected reaction are updated according to their stoichiometric numbers $N_i \to N_i + \nu^i_\rho$. Then the new propensities are calculated and the algorithm proceeds again as sketched above with the next iteration. Tenths of millions of iterations are usually required to settle at the stationary steady state from an arbitrary initial condition and to perform meaningful time averages on the time series that can be thus obtained. In all simulations performed in this paper the stationary state is unique and stable.

Our algorithm reduces to Gillespie's one when there are no electron transfer processes involved, i.e., if only chemical reaction steps are considered. In the electrochemical master equation, as explained above, the electrode potential is also a stochastic variable coupled to the particle numbers. Because of the external potentiostatic control, deviations of Gaussianity are expected: the constant applied voltage acts as an external drive and a privileged direction appears in the system. In open circuit conditions, however, externally applied voltage and external resistance are absent and the equivalent circuit in Fig. 1 reduces to the capacitor and the faradaic impedance. In this situation, which is totally symmetrical, Eq. (13) reduces to

$$\tau_\rho = \frac{1}{W_\rho^0 e^{c_\rho E_j}} \ln\left(\frac{1}{r_\rho}\right). \tag{14}$$

Although the electrode potential fluctuates in such a case, there is no other source for its change than the stochastic reaction events. Therefore, and because the electrode potential E only changes after reaction events, the stationary distributions are normal as well. A similar expression is obtained in the limit $R_e \to \infty$ by applying L'Hopital's rule to Eq. (13). In the limit $R_e \to 0$, as can be seen from Fig. 1, the electrode potential E is fixed to the externally applied potential U for every step j and Eq. (13) reduces to

$$\tau_\rho = \frac{1}{W_\rho^0 e^{c_\rho U}} \ln\left(\frac{1}{r_\rho}\right), \tag{15}$$

which yields, again, normal distributions for the particle numbers of the chemical species (the electrode potential being no longer a fluctuating stochastic variable). For deviations from Gaussianity then, a potentiostatic control in the system with a finite external resistance R_e, is needed. Below we explore and substantiate this statement.

II. WEAK NOISE THEORY FOR ELEMENTARY REACTION STEPS. SIMULATION RESULTS

A. Irreversible one-electron transfer reaction

Let us first consider an irreversible oxidation reaction

$$A \to B + e^-, \tag{16}$$

where A and B are two chemicals. For this reaction, the (macroscopic) faradaic current density is $i_F = Fk_+e^{cE}$ where $k_+ \equiv \widetilde{k}_+[A]$ is the kinetic rate constant, making explicit its dependence on the concentration of chemical species $[A]$ (we assume in the following a macroscopic reservoir in contact with the nanoelectrode so that the concentrations of chemicals $[A]$ and $[B]$ are kept constant). Considering a nanoelectrode in a macroscopic electrolyte solution thus implies that, as long as no adsorption processes occur, the number of molecules is not a fluctuating variable. We assume for simplicity and without loss of generality that the redox potential is zero. The value of the electrode potential of a macroscopic system at the stationary state E^* can be calculated from Eq. (5) as

$$Fk_+e^{cE^*} = \frac{U - E^*}{R_e A}, \tag{17}$$

where $c = F/(2RT)$. For the instantaneous electrode potential and the total instantaneous current density flowing through the circuit, the following expression holds:

$$\frac{U - E}{R_e A} = i. \tag{18}$$

If we now assume small fluctuations around the macroscopic steady state (low noise limit), we have on the one hand

$$Fk_+\langle e^{cE}\rangle = \frac{U - \langle E\rangle}{R_e A} = \langle i\rangle = \langle i_F\rangle \tag{19}$$

since $\langle i_{cap}\rangle = 0$ and, on the other hand, from Eq. (5)

$$Fk_+e^{c\langle E\rangle} = \exp\left\langle \ln\left(\frac{U - E}{R_e A} - C\frac{dE}{dt}\right)\right\rangle. \tag{20}$$

The enhancement factor Q satisfies

$$\ln Q = \left\langle \ln \frac{U - \langle E\rangle}{U - \widetilde{E}}\right\rangle \geq 0, \tag{21}$$

where we have defined the fluctuating quantity

$$\widetilde{E} = E + R_e AC\frac{dE}{dt} \tag{22}$$

which, of course, satisfies, $\langle\widetilde{E}\rangle = \langle E\rangle$ as well as

$$\frac{U - \widetilde{E}}{R_e A} = i_F. \tag{23}$$

If we subtract Eq. (23) from Eq. (19) we have

$$\frac{\widetilde{E} - \langle E\rangle}{R_e A} = \langle i_F\rangle - i_F. \tag{24}$$

By using Eq. (19), we can rewrite the enhancement factor as

$$\ln Q = \left\langle \ln \frac{1}{1 - \lambda/R_e}\right\rangle \geq 0, \tag{25}$$

where

$$\lambda = \frac{\widetilde{E} - \langle E\rangle}{FAk_+\langle e^{cE}\rangle} = \frac{\widetilde{E} - \langle E\rangle}{A\langle i_F\rangle} \tag{26}$$

has dimensions of resistance. We denote in the following λ as "fluctuation resistance." By expanding the logarithm in powers of λ/R_e, taking into account that $\langle\lambda\rangle = 0$ and keeping only second order terms in λ/R_e we obtain

$$Q = e^{\langle\lambda^2\rangle/(2R_e^2)} \geq 1. \tag{27}$$

From the latter expression we see that, since λ is bounded, the enhancement factor tends to unity as $R_e \to \infty$. Since in the limit $R_e \to 0$ the electrode potential E no longer fluctuates and is given by the externally applied potential U, we expect that $\lambda = 0$ in such a case and therefore $Q = 1$ as well. The dependence of Q on the resistance is therefore nonmonotonic and is expected to attain its maximum value at some intermediate value of the series resistance when $R_e \ll \sqrt{\langle\lambda^2\rangle/2}$.

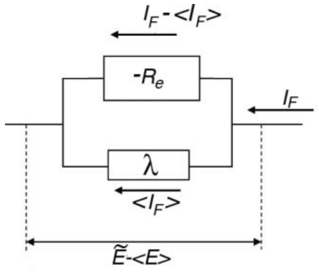

FIG. 2. Electric circuit elements in stochastic electrochemical dynamics (low noise limit) for the faradaic path: a fluctuation resistance λ arises in parallel with the negative ohmic resistance R_e.

Interpreting λ as a resistance allows for a better understanding of the dynamics of fluctuations in electrochemical systems. We note that Eq. (26) can be written, by using Eq. (24) as

$$\lambda = -R_e \frac{i_F - \langle i_F \rangle}{\langle i_F \rangle}. \tag{28}$$

Eqs. (24), (26), and (28) are consistent with the circuit elements in Fig. 2. There we see that we can split the faradaic current into two parallel paths, the average faradaic current and its fluctuating part. The former pathway contains the fluctuation resistance λ, and the latter one the negative series resistance $-R_e$. Thus, the larger λ the larger is the current through the negative ohmic resistance in the parallel branch and, therefore, the larger the fluctuation in the faradaic current both in absolute and relative value. The fluctuation in the electric current enhanced in this way leads to higher Q values in Eq. (27). From Eq. (28), the enhancement factor is just the exponential of half the relative mean square deviation of the faradaic current

$$Q = \exp\left(\frac{\langle i_F^2 \rangle - \langle i_F \rangle^2}{2\langle i_F \rangle^2}\right). \tag{29}$$

In Figure 3, the enhancement factor Q is shown as a function of Ω and for several values of the external resistance $R_e A$. These results are obtained from simulations of the electrochemical master equation employing the extended Gillespie algorithm sketched above. When the system size is small $\Omega \ll$, Q becomes significantly higher than unity, indicating an enhanced electrochemical kinetics and thus proving our general statement Eq. (2). For lower values of R_e this enhancement is higher, according to our prediction given by Eq. (27). In addition, for lower R_e the fluctuations begin to be important in the mesoscopic kinetics at a higher system size Ω, and the associated enhanced kinetics can therefore be noticeable already for disk-shaped electrodes with a diameter of $\approx$ 30-50 nm (the upper bound would be attained by lowering also U as discussed in Ref. 8).

Fluctuations are also responsible for a shift in the stationary value of the time averaged electrode potential $\mathcal{E} \equiv \lim_{t\to\infty}\langle E \rangle$ with respect to the macroscopic value $E^* \equiv \lim_{t\to\infty,\Omega\to\infty}\langle E \rangle$. In the low noise limit (Ω large), this shift $\delta = \mathcal{E} - E^*$ has a negative value and is given by

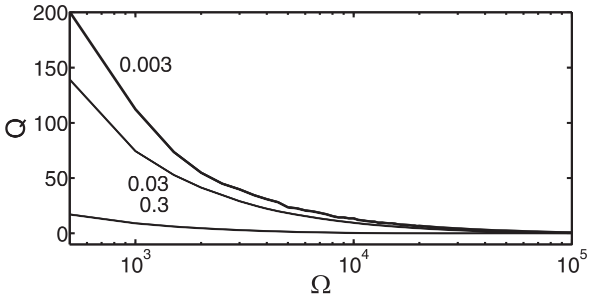

FIG. 3. Enhancement factor Q for an oxidation reaction as a function of the number of sites Ω for the values of $R_e A$ (given in Ω cm^2) indicated in the figure. The electrode area is given by $A = a_0 \Omega$ with $a_0 = 7.55$ Å^2. Other parameter values: $C = 0.05$ F m^{-2}, $k_+ = 10^{-5}$ mol s^{-1} m^{-2}, $U = 0.2$ V.

(see Ref. 8)

$$\delta = -\frac{\sigma^2 c^2}{2} \frac{R_e A F k_+ e^{c\mathcal{E}}}{1 + c R_e A F k_+ e^{c\mathcal{E}}}, \tag{30}$$

where $\sigma^2 \equiv \langle E - \langle E \rangle \rangle^2$ is the variance of the distribution of the instantaneous electrode potential. In Figure 4 δ is shown as a function of the system size Ω for three values of the series resistance $R_e A$. It is observed that for Ω large $\delta < 0$ according to the prediction by Eq. (30). In the limit $R_e \to \infty$, $\delta \to -\frac{\sigma^2 c^2}{2}$, being negative for all system sizes. This is observed in Figure 4: the value $R_e A = 0.3$ Ω cm^2 already approaches this limit, and the minimum of the curve becomes broader compared to larger values of the resistance. For lower system sizes and finite series resistances, however, higher moments of the distribution of the electrode potential become important and Eq. (30) is no longer valid and the displacement can be positive, as shown by the simulations.

B. Reversible one-electron transfer reaction

We consider now a reversible reaction where both forward (oxidation) and backward (reduction) processes are taken into account

$$\mathrm{A} \underset{\tilde{k}_-}{\overset{\tilde{k}_+}{\rightleftharpoons}} \mathrm{B} + e^-. \tag{31}$$

Here A and B are two chemicals. Note that we consider always the kinetically controlled part of the current-voltage characteristic and therefore, diffusion is neglected. We consider, for simplicity, the same values for the kinetic rates

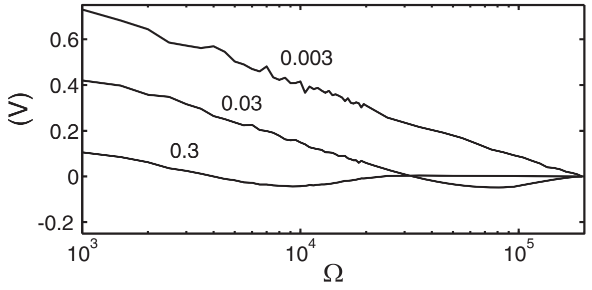

FIG. 4. Displacement of the average stationary electrode potential $\delta = \mathcal{E} - E^*$ for an oxidation reaction as a function of Ω and for the values of $R_e A$ (given in Ω cm^2) indicated in the figure. Other parameter values as in Fig. 3.

k_+ and $k_- = \widetilde{k}_-[B]$ of the forward and backward reactions, respectively. We substantiate now an observation made in Ref. 8 that in the overpotential (underpotential) regime one can simply consider separately contributions from the forward and the backward processes, whose main features are described in Sec. II A. Considering again first a macroelectrode, the value of the electrode potential at the stationary state E^* now reads, from Eq. (5)

$$Fk_+e^{cE^*} - Fk_-e^{cE^*} = \frac{U - E^*}{R_e A}. \tag{32}$$

If we now assume small fluctuations around the macroscopic steady state (low noise limit), we have

$$Fk_+\langle e^{cE}\rangle - Fk_-\langle e^{-cE}\rangle = \frac{U - \langle E\rangle}{R_e A} \equiv \langle i_F^{\rightarrow}\rangle + \langle i_F^{\leftarrow}\rangle. \tag{33}$$

We also have

$$Fk_+e^{cE} - Fk_-e^{-cE} = \frac{U - \widetilde{E}}{R_e A} \equiv i_F^{\rightarrow} + i_F^{\leftarrow}. \tag{34}$$

Subtracting both equations leads to

$$\frac{\widetilde{E} - \langle E\rangle}{R_e A} = \langle i_F^{\rightarrow}\rangle - i_F^{\rightarrow} + \langle i_F^{\leftarrow}\rangle - i_F^{\leftarrow}. \tag{35}$$

For the forward and backward processes, we can follow the same approach as in Sec. II A to calculate the enhancement factors $Q_\rightarrow$ and $Q_\leftarrow$. In the low noise limit, we obtain

$$\begin{aligned} Q_\rightarrow &= e^{\langle\lambda_\rightarrow^2\rangle/(2R_e^2)} \geq 1 \\ Q_\leftarrow &= e^{\langle\lambda_\leftarrow^2\rangle/(2R_e^2)} \geq 1, \end{aligned} \tag{36}$$

where

$$\begin{aligned} \lambda_\leftarrow &= R_e\frac{\langle i_F^{\leftarrow}\rangle - i_F^{\leftarrow}}{|\langle i_F^{\leftarrow}\rangle|} \\ &= \frac{\widetilde{E} - \langle E\rangle + R_eAFk_+(e^{cE} - \langle e^{cE}\rangle)}{FAk_-\langle e^{-cE}\rangle} \end{aligned} \tag{37}$$

$$\begin{aligned} \lambda_\rightarrow &= R_e\frac{\langle i_F^{\rightarrow}\rangle - i_F^{\rightarrow}}{|\langle i_F^{\rightarrow}\rangle|} \\ &= \frac{\widetilde{E} - \langle E\rangle - R_eAFk_-(e^{-cE} - \langle e^{-cE}\rangle)}{FAk_+\langle e^{cE}\rangle}. \end{aligned} \tag{38}$$

These expressions are analogous to the ones obtained for one irreversible equation. They show that the stochastic reaction kinetics can be separated for each reaction pathway. In the regime $\langle E\rangle \gg 0$ we have

$$\lambda_\leftarrow \gg \lambda_\rightarrow = \frac{\widetilde{E} - \langle E\rangle}{A|\langle i_F^{\rightarrow}\rangle|}. \tag{39}$$

Conversely, in the regime $\langle E\rangle \ll 0$, we have

$$\lambda_\rightarrow \gg \lambda_\leftarrow = \frac{\widetilde{E} - \langle E\rangle}{A|\langle i_F^{\leftarrow}\rangle|}. \tag{40}$$

The expressions for the macroscopically favored reactions in such limiting cases reduce to Eq. (26) found for the irreversible reaction. Most importantly, Eqs. (39) and (40) imply a statement made in Ref. 8: *rare events are the most enhanced at the nanoscale* since the macroscopically unfavored reactions are, in each case, the ones with higher fluctuation resistance λ and therefore, the ones with a higher enhancement factor. The latter expressions indicate that the more we move to more positive (negative) applied voltage U, the more the backward (forward) process is enhanced and the larger is $Q_\leftarrow$ ($Q_\rightarrow$).

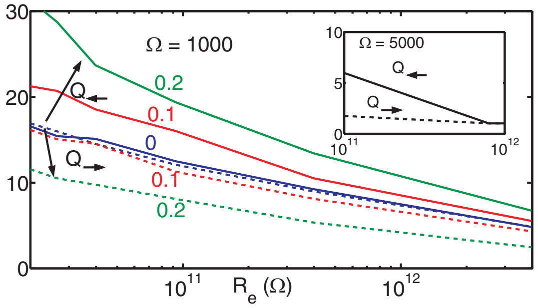

FIG. 5. Enhancement factors $Q_\leftarrow$ (continuous curve) and $Q_\rightarrow$ (dashed curve) for a reversible redox reaction as a function of the external resistance R_e and for $\Omega = 1000$ active sites. Beside the curves values of the externally applied potential U (in V) are indicated. Inset: $\Omega = 5000$ and $U = 0.2V$. For the backward reaction: $k_- = 10^{-5}$ mol s^{-1} m^{-2}. Other parameter values as in Figure 3.

The dependence of the enhancement factors $Q_\leftarrow$ and $Q_\rightarrow$ on the external series resistance is similar to the one explained above for only one irreversible reaction. In the limits $R_e \to \infty$ and $R_e \to 0$ one has for both enhancement factors $Q_\leftarrow \to 1$ and $Q_\rightarrow \to 1$ and their maximum is attained for some intermediate positive value of R_e. We have performed simulations of the electrochemical master equation in the large resistance regime before the limit $R_e \to \infty$ is reached. In Fig. 5 we plot the enhancement factors $Q_\leftarrow$ (continuous curve) and $Q_\rightarrow$ (dashed curve) as a function of the external resistance R_e for several values of the applied potential U. We note that at $U = 0$, the enhancement factors for forward and backward reactions are equal at every set of parameters and that they increase following the same curve as R_e is lowered. This means that the current is always vanishing, or, in other words, that the equilibrium potential is always equal to the macroscopic one. As we move in the overpotential regime, $Q_\leftarrow$ becomes larger than $Q_\rightarrow$ in consistency with our findings above. As $R_e \to \infty$, both $Q_\leftarrow \to 1$ and $Q_\rightarrow \to 1$, in consistency with Eq. (36). When the system size is larger, the infinite resistance limit is attained for lower values of the external resistance, since the fluctuations are smaller, and so are $\lambda_\leftarrow$ and $\lambda_\rightarrow$ in Eq. (36). This is shown in the inset of the figure.

We explore now the nonmonotonic dependence of the enhancement factor on the external resistance. In Fig. 6 we plot $Q_\leftarrow$ for several decades of values of the external resistance R_e. To avoid infinitely large faradaic currents as the resistance is lowered, we varied U so that the total faradaic current through the external resistance corresponding to the infinite size limit remains constant

$$\frac{U - E^*}{R_e A} = \frac{U_1 - E^*}{R_e^1 A} = ct. \tag{41}$$

Here E^* is first calculated separately in the infinite system size limit for values of $U_1 = 10^{-8}V$ and $R_e^1 A = 0.03\ \Omega$ cm^2, i.e., very close to the equilibrium potential. Then the external

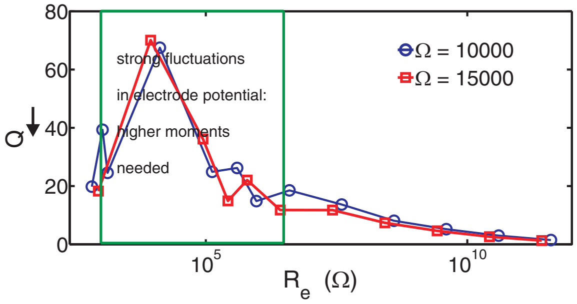

FIG. 6. Enhancement factor $Q_{\leftarrow}$ for a reversible redox reaction as a function of the external resistance R_e and for the values of the system size Ω indicated in the figure. U is varied along the curve according to Eq. (41). Other parameter values as in Figure 5.

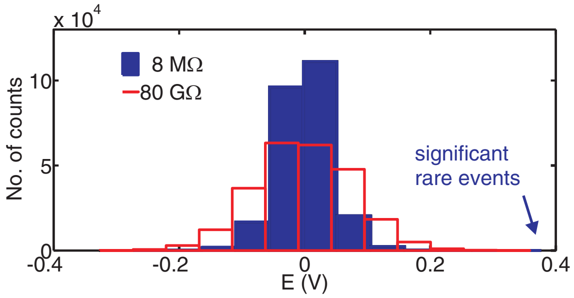

FIG. 8. Histogram of the the values of the electrode potential around the stationary state for $R_e = 8$ MΩ and $R_e = 80$ GΩ. U obtained from Eq. (41). Other parameter values as in Figure 7.

resistance R_e is varied and Eq. (41) is solved for U which is varied also accordingly. In such a way, the curves obtained are universal and valid for every reversible electrochemical reaction and independent of the specific values of the rate constants k_- and k_+ (provided they are equal). Both limits $R_e \to \infty$ and $R_e \to 0$ are reproduced, with $Q_{\leftarrow} \to 1$, although the latter limit is, in practice, unreachable by the simulations since $\tau_\rho \to 0$ as $\sim -R_e \ln R_e$. We observe that values of the resistance of the order of 1 MΩ or higher lead to a significant increase of the reaction kinetics of the individual oxidation or reduction reaction with a well defined average reaction rate $\langle e^{-cE} \rangle \gg e^{-c\langle E \rangle}$ (i.e., $Q_{\leftarrow} \gg 1$). All our results in Ref. 8 were reported in this regime. It corresponds also to the results in Fig. 5. For values of R_e of the order of 1 kΩ the individual reaction steps are strongly enhanced, but the description in terms of enhancement factors Q becomes incomplete and insufficient, since the reaction rate strongly fluctuates as well, and higher moments or cumulants of the distribution of the reaction rate itself are needed, i.e., $\langle e^{-cE} \rangle^2 - e^{-2c\langle E \rangle}$ and so on. In such a situation the faradaic current is no longer well described only by its time average.

A better understanding of the transition from stochastic dynamics at high R_e to deterministic dynamics on the electrode potential for low $R_e \to 0$ is provided by the distributions of instantaneous values of the electrode potential. In Fig. 7 we plot the time series for E for a series resistance $R_e = 8$ MΩ (left) and $R_e = 80$ GΩ (right) with U obtained from Eq. (41), i.e., equal current densities in the deterministic limit. We see that at lower values of the external resistance, the fluctuations are much broader although they are more sharply distributed around the average electrode potential. The value $R_e = 8$ MΩ is close to the lowest bound where one can still talk of a well defined average reaction rate in Fig. 6 within the high resistance regime. The value $R_e = 80$ GΩ approaches the infinite resistance limit. The shaded regions in the figure indicate the bounds where the 95% of the instantaneous values of the electrode potential concentrate. The interval within these bounds is thinner at lower resistances. This is more compellingly seen in the histograms of the distribution of instantaneous values of the electrode potential, shown in Fig. 8 for each case in Fig. 7. While the distribution at $R_e = 80$ GΩ is almost Gaussian the one at $R_e = 8$ MΩ is highly leptokurtic, indicating that it is much more peaked around the mean value than a Gaussian, while at the same time, having much longer tails favoring rare events compared to the Gaussian. This non-Gaussianity of the distribution is responsible for the strongly enhanced kinetics and it is caused by the external potentiostatic control.

In the limit $R_e \to 0$ the distribution becomes more and more peaked and below a certain threshold, rare events begin to become insignificant signalling the transition to deterministic behavior $E = U$ for the electrode potential at $R_e = 0$. Note that both distributions are symmetrical because of the value of the external applied voltage, which was chosen $U \approx 0$. A situation far from equilibrium yields also asymmetric skewed distributions with long tails toward the macroscopically unfavored, rare events.

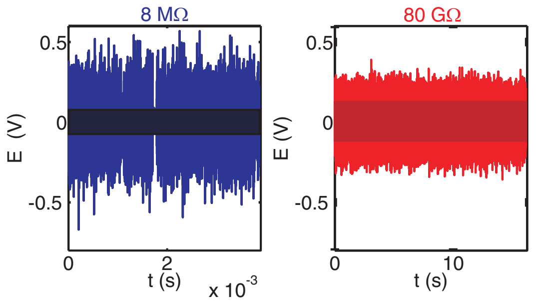

FIG. 7. Time series for E for a series resistance $R_e = 8$ MΩ (left) and $R_e = 80$ GΩ (right). U obtained from Eq. (41). Shaded regions indicate the bounds where the 95% of the instantaneous values of the electrode potential concentrate within. Other parameter values as in Figure 6 ($\Omega = 10\,000$).

C. Reversible one-electron transfer reaction in open circuit conditions

We consider now a situation in which we have a reversible redox process under open circuit conditions. The source of external voltage and the external resistance are absent and the circuit in Figs. 1 and 2 simplify to the capacitor and the faradaic impedance and the parallel fluctuation resistances. The faradaic current coincides with the capacitive current and therefore, at the stationary state $|\langle i_F^{\rightarrow} \rangle| = |\langle i_F^{\leftarrow} \rangle|$. Eq. (33) becomes in this case

$$F k_+ \langle e^{cE} \rangle = F k_- \langle e^{-cE} \rangle. \tag{42}$$

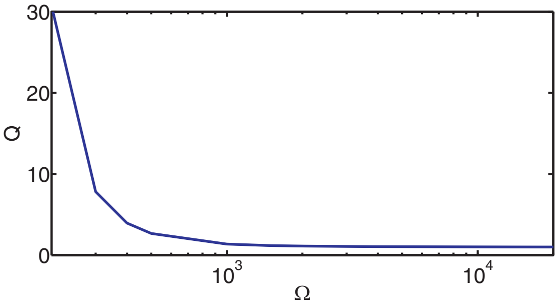

FIG. 9. Enhancement factor Q for a reversible redox reaction in open circuit conditions as a function of the system size. Parameter values: $C = 0.05$ F m^{-2}, $k_+ = k_- = 10^{-5}$ mol s^{-1} m^{-2}. The electrode area is given by $A = a_0\Omega$ with $a_0 = 7.55$ Å^2.

We also have

$$Fk_+e^{c\langle E\rangle} = Fk_-e^{-c\langle E\rangle}. \tag{43}$$

And therefore

$$Q_\leftarrow = Q_\rightarrow \approx 1 + c^2\sigma^2. \tag{44}$$

In this situation the stationary probability distribution of the electrode potential is Gaussian and therefore, contributions from the skewness and kurtosis to Q vanish. The standard deviation σ specifies completely the enhancement of the kinetics in the weak noise limit. In Fig. 9 we plot the enhancement factor as a function of the system size. We observe that the enhancement is only significant for electrode areas in the subnanometer scale (for $\Omega = 200$ active sites we have $Q \approx 30$). The curve in Fig. 9 is universal, i.e., valid for all reversible redox processes independently of the value of the kinetic constants. This enhancement is much lower than with external control. The latter enhances the importance of the fluctuations since it causes non-normal behavior of the stationary probability distributions, as discussed above.

III. CONCLUSIONS

In this article we elucidated that the enhancement of electrochemical kinetics at the nanoscale originates from peaked and long-tailed distributions of the fluctuating electrode potential which, in turn, can be tuned by a system parameter, namely, the series resistance. If we consider a given current density in the infinite resistance limit, where the electrode potential has the maximal freedom to fluctuate, but the fluctuations are irrelevant for the measured current, the normal distribution is recovered and the enhancement vanishes. Therefore, in this limit, there is no qualitative difference between the statistics of the electrochemical system and a purely chemical system. In the vanishing resistance limit, when the electrode potential is not free to vary anymore, we arrive at the deterministic kinetics and the enhancement vanishes as well. To obtain an increased current density, the intermediate situation is imperative, where the fluctuations of the electrode potential due to electron transfer events are constrained by the external control.

We have also quantified the enhancement of the electrochemical kinetics for a single reversible redox reaction under open circuit conditions and found that here the effect is smaller than under potentiostatic control. Only with few hundreds of active sites, the reaction kinetics is significantly enhanced and fluctuations of the electrode potential are purely Gaussian.

The introduction of a resistance implies dissipation of energy. Therefore it is important to look at the ratio between power loss through dissipation and the smaller power consumption because of the reaction enhancement (smaller overpotential). For the irreversible redox reaction, the voltage one has to apply externally in order to draw a certain current density may be − for intermediate values of the resistance and small overvoltage − smaller than in the macroscopic case. This means that the Joule heat dissipated in the ohmic resistor is overcompensated by the enhanced current and the reaction indeed can be driven with a smaller power input.[8] In the case of several elementary electron transfer steps the relative rates will be changed, the slowest one being the most enhanced one. The exploitation of the enhancement might prove to be favorable in certain cases, for example, when one operates in a regime with a negative differential resistance.

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[1] D. T. Gillespie, J. Phys. Chem. **81**, 2340 (1977).
[2] D. T. Gillespie, J. Comput. Phys. **22**, 403 (1976).
[3] G. Nicolis, J. Stat. Phys. **6**, 195 (1972).
[4] G. Nicolis and I. Prigogine, *Self-organization in Nonequilibrium Systems* (Wiley, New York, 1977).
[5] P. Gaspard, J. Chem. Phys. **117**, 8905 (2002).
[6] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (Elsevier, Amsterdam, 2007).
[7] C. Gardiner, *Stochastic Methods* (Springer, Berlin, 2009).
[8] V. Garcia-Morales and K. Krischer, Proc. Natl. Acad. Sci. U.S.A. **107**, 4528 (2010).
[9] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, and C. D. Frisbie, Adv. Mater. **15**, 1881 (2003).
[10] T. Baunach, V. Ivanova, D. M. Kolb, H. G. Boyen, P. Ziemann, M. Buttner and P. Oelhafen, Adv. Mater. **16**, 2024 (2004).
[11] M. Manolova, V. Ivanova, D. M. Kolb, H. G. Boyen, P. Ziemann, M. Buttner, A. Romanyuk and P. Oelhafen, Surf. Sci. **590**, 146 (2005).
[12] D. V. Averin and K. K. Likharev, in *Mesoscopic Phenomena in Solids*, edited by B. L. Altshuler, P. A. Lee, and R. A. Webb (North Holland, Amsterdam, 1991).
[13] A. J. Bard and L. R. Faulkner, *Electrochemical Methods* (Wiley, New York, 2004).
[14] K. Krischer, in *Advances in Electrochemical Sciences and Engineering*, edited by D. M. Kolb and R. C. Alkire, (Wiley-VCH, Weinheim, 2003), Vol. 8, pp. 89–208.
[15] A. P. J. Jansen, Comput. Phys. Commun. **86**, 1 (1995).
[16] M. T. M. Koper, A. P. J. Jansen, R. A. van Santen, J. J. Lukkien, and P. A. J. Hilbers, J. Chem. Phys. **109**, 6051 (1998).