# Fluctuation enhanced electrochemical reaction rates at the nanoscale

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**The electrode potential constitutes a dynamical variable whenever an electrode is resistively coupled to the electric circuit. We show that at the nanoscale, the discreteness and stochasticity of an electron transfer event causes fluctuations of the electrode potential that render all elementary electrochemical reactions to be faster on a nanoelectrode than predicted by the macroscopic (Butler–Volmer) electrochemical kinetics. This phenomenon is substantiated by means of a generalized (electro)chemical master equation.**

Butler–Volmer kinetics | chemical master equation | electrochemistry | electrode kinetics | nanoelectrodes

**A** chemical reaction is a priori a stochastic event (1, 2). Yet in a macroscopic system chemical kinetics is accurately described by the chemical concentrations and a reaction constant. In some instances, the latter can be derived from first principles (1), but in most cases it is determined experimentally. When one goes to reaction volumes in the nanoscale, this macroscopic kinetical description breaks down. Rather, the stochasticity of the reactions produces significant deviations in the number of molecules from the macroscopic average concentrations. Hence, the state of the system cannot be given in terms of concentrations but of probability distributions of numbers of particles, and the chemical kinetics of the system is, consequently, described by the time evolution of the probability distributions. This description is provided by the chemical master equation (CME) (3–6). It is well established that the rate constant entering the CME is equal to the macroscopic rate constant.

Now, if we consider an electrochemical system, the rate of an electrochemical reaction depends on the electrode potential. According to the Butler–Volmer electrochemical equation (BVEE), the potential dependence is accounted for in the rate constant, which can be expressed by a preexponential factor (which is analogous to the chemical rate constant), and an exponential dependence on the electrode potential (7). As for a chemical system, at a nanoelectrode, the stochastic nature of electrochemical reactions has to be considered. The problem is, however, more complex, because, in addition to the number of chemical species, the electrode potential can become a fluctuating variable, a problem that has, to the best of our knowledge, never been tackled. In this paper, we formulate the electrochemical master equation (ECME) and show that unlike in the CME, the rate constants in the ECME are not only different for a nanosystem compared to a macroscopic system. In fact, we prove that *for all elementary electrochemical reaction events, the rate constants at the nanoscale are larger than their macroscopic counterparts*. Moreover, *in a network consisting of several electrochemical reaction steps, the rarest ones are the ones that are the most enhanced*. As a consequence, the kinetically controlled faradaic current density of any electrochemical reaction on a nanoelectrode deviates from the one at a macroelectrode. This prediction is even true for ensembles of nanoelectrodes with a total electrode area equal to the one of a macroelectrode. This has profound consequences for the interpretation of experiments in which individual nanoelectrodes or ensembles of them are employed.

A typical electrochemical experiment is controlled by applying an external voltage $U$ between the working and the reference electrode. For nanoscale electrodes an ohmic resistance is often introduced when linking the nanoelectrode to the external control, a frequent realization being a metallic nanoparticle bond to a lipid molecule that is chemically anchored to a conductive macroscopic support. However, any ohmic resistance in series to the working electrode renders the electrode potential $\phi_{dl}$ a dynamic variable of the system (8) (Fig. 1). Clearly, in the presence of a resistance, the electrode potential is influenced by electron transfer processes taking place between the electrode and chemical species dissolved in the electrolyte. The probabilities with which these electrochemical reactions occur depend, in turn, on the electrode potential, and it is exactly for these cases that the electrochemical kinetics cannot be described by the BVEE.

## Results and Discussion

**Electrochemical Kinetics on Nanoelectrodes.** Let us consider the following general form of an electrochemical reaction labeled with $\rho$

$$\sum_{i=1}^{s} \nu^i_{<\rho} N_i + n_{<\rho} e^- \xrightarrow{k_\rho} \sum_{i=1}^{s} \nu^i_{>\rho} N_i + n_{>\rho} e^- \qquad [1]$$
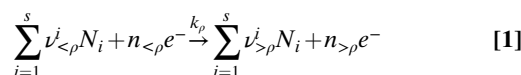
Here $i$ labels the different chemical species, and $N_i$ is the number of particles of each species. The stoichiometric numbers $\nu^i_\rho = \nu^i_{>\rho} - \nu^i_{<\rho}$ control the number of molecules of each species formed or consumed each time the reaction takes place. The number of electrons transferred is similarly given by $n_\rho = n_{>\rho} - n_{<\rho}$. The macroscopic rate of electron transfer $k_\rho$ depends on the electrode potential, $\phi_{dl}$, at which the electron transfer takes place in the following form (the BVEE)

$$k_\rho(\phi_{dl}) = k^0_\rho e^{c_\rho \phi_{dl}} \qquad [2]$$

Here the preexponential factor $k^0_\rho$ does not depend on the electrode potential and $c_\rho = \frac{(\beta_\rho - \alpha)|n_\rho|F}{RT}$ with $\beta = 0$ for reduction reactions and 1 for oxidation reactions, $\alpha$ is the transfer coefficient, $F$ the Faraday constant, $R$ the ideal gas constant, and $T$ the temperature. In this paper we will consider $\alpha = 0.5$ and $T = 300$ K and we focus on nonequilibrium stationary situations. In macroscopic systems, the electrode potential is a deterministic variable, its value is well specified at each instant of time, its time evolution is governed by a differential equation, and it does not fluctuate. If we define a probability distribution of such a deterministic variable it is clear that $\phi_{dl}$ coincides with the first moment of the probability distribution $\langle \phi_{dl} \rangle$ with unit probability at the steady state. Thus, the first moment is the time average of $\phi_{dl}$, and
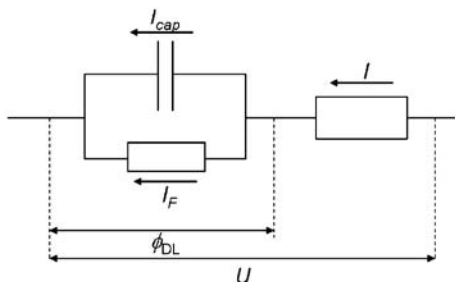
**Fig. 1.** Equivalent circuit for an electrochemical cell. The total current through the ohmic resistor $I$ splits at the interface in two components: the faradaic $I_F$ and the capacitive $I_{cap}$ currents.

we have $<k_\rho^0 e^{c_\rho \phi_{dl}}> = k_\rho^0 e^{c_\rho <\phi_{dl}>} \equiv k_\rho^{(mac)}$. (Note that the cornered brackets always refer to time averages.) The rate constant coincides with the expression provided by the BVEE (Eq. **9**). This equality does not hold at the nanoscale because the instantaneous value of the electrode potential $\phi_{dl}$ does not coincide with the time average of its realizations $\langle \phi_{dl} \rangle$ under the same experimental conditions. Since the fluctuations of the electrode potential are fast, the use of a time averaged kinetic constant is justified (9), and we have $k_\rho^{(nano)} \equiv < k_\rho^0 e^{c_\rho \phi_{dl}} >\geq k_\rho^0 e^{c_\rho <\phi_{dl}>}$. This last relationship comes from the mathematical inequality $\langle e^x \rangle \geq e^{\langle x \rangle}$ (10), which always holds, regardless of the distribution of the stochastic variable $x$. Therefore, the following inequality holds

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

In the following, we are concerned with the exploration of this statement. We would like to stress that both sides of Eq. **3** are related to an experimental measurable quantity, the faradaic current of the reaction, and that it is possible to produce individual electrodes with a few nanometer radius (11). Eq. **3** essentially means that *because of molecular fluctuations, under the same experimental conditions, a reaction will occur faster at the nanoscale than on a macroelectrode*. The stronger the fluctuations, the stronger the inequality holds, the equality being valid in the macroscopic limit $\Omega \to \infty$, where $\Omega$ is the system size of the nanosystem. We then introduce the enhancement factor $Q_\rho$ of reaction $\rho$ as

$$Q_\rho \equiv \frac{k_\rho^{(nano)}}{k_\rho^{(mac)}} = \frac{\langle e^{c_\rho \phi_{dl}} \rangle}{e^{c_\rho \langle \phi_{dl} \rangle}} \geq 1 \qquad [4]$$

The enhancement factor is fully given by the moments of the probability distribution. By expanding it in a Taylor series of the fluctuation strength we have

$$Q_\rho = 1 + \frac{c_\rho^2 \sigma^2}{2} + \frac{c_\rho^3 \xi}{6} + \frac{c_\rho^4 \kappa}{24} + \cdots \qquad [5]$$

where $\sigma^2 \equiv \langle \phi_{dl} - \langle \phi_{dl} \rangle \rangle^2$ is the variance, $\xi \equiv \langle \phi_{dl} - \langle \phi_{dl} \rangle \rangle^3$ is the skewness, and $\kappa \equiv \langle \phi_{dl} - \langle \phi_{dl} \rangle \rangle^4$ the kurtosis of the probability distribution of the electrode potential. For the Gaussian distribution $\xi = \kappa = 0$.

**Electrochemical Master Equation and Extended Gillespie Algorithm.** In Fig. 1 the equivalent circuit of an electrochemical cell under potentiostatic conditions (where an external potential difference $U$ is applied to the system) is depicted. The 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. Charge conservation at the interface implies $I_{cap} = -I_F + I$ or equivalently

$$C \frac{d\phi_{dl}}{dt} = -i_F(\phi_{dl}) + \frac{U - \phi_{dl}}{R_e A} \qquad [6]$$

where $R_e$ is the ohmic resistance, $C$ is the capacitance per unit area, $A$ is the electrode area, and $i_F$ is the faradaic current density. Clearly, any stationary state is characterized by $\phi_{dl} = $ constant. Eq. **6** provides the macroscopic evolution law for the electrode potential that then behaves deterministically. At the nanoscale, the contribution from the faradaic current comes from the reaction events that take place at random. Let us assume that after a time $\tau_\rho$ a reaction $\rho$ involving a transfer of $n_\rho$ electrons takes place. The electrode potential evolves then discretely as

$$\phi_{dl,j+1} = \phi_{dl,j} + \frac{U - \phi_{dl,j}}{R_e CA} \tau_\rho - \frac{n_\rho e}{CA} \qquad [7]$$

where the term proportional to $\tau_\rho$ comes from the potentiostatic control and the one proportional to $n_\rho$ from the faradaic current of reaction $\rho$. The numbers of the electrons transferred and of the molecules of the chemical species are controlled by the CME

$$\frac{dP(\mathbf{N},t)}{dt} = \sum_\rho [W_\rho(\mathbf{N}-\nu_\rho)P(\mathbf{N}-\nu_\rho,t) - W_\rho(\mathbf{N})P(\mathbf{N},\mathbf{t})] \qquad [8]$$

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

$$W_\rho(\mathbf{N}) = W_\rho^0 e^{c_\rho \phi_{dl}} \qquad [9]$$

are the so-called propensities, controlling the transition rates from one state to another. $W_\rho^0$ is given by

$$W_\rho^0 = \Omega k_\rho^0 \prod_{i=1}^s \prod_{m=1}^{\nu_{i\rho}} \frac{N_i - m + 1}{\Omega} \qquad [10]$$

Contrasting to chemical systems, the propensities in Eq. **9** depend on time, because the electrode potential $\phi_{dl}$ changes in time between reaction events as a consequence of the external control. Because the times between reaction events $\tau_\rho$ are very small, we can assume that the change in the potential because of the external control is given by $\frac{U - \phi_{dl,j}}{R_e CA} \tau_\rho$. After $\tau_\rho$ a reaction event takes place involving an electron transfer, which justifies the microscopic evolution law in Eq. **7**. With Eqs. **7**, **9**, and **10**, Eq. **8** can be interpreted as an ECME.

Following the approach suggested in refs. 12 and 13, we can generalize Gillespie's algorithm, calculating the appropriate expresions for the waiting times of each reaction $\rho$ to occur (see *SI Text*)

$$\tau_\rho = \frac{R_e CA}{c_\rho(U - \phi_{dl,j})} \ln \left[ 1 + \frac{c_\rho(U - \phi_{dl,j})}{R_e CA W_\rho^0 e^{c_\rho \phi_{dl,j}}} \ln \left( \frac{1}{r_\rho} \right) \right] \qquad [11]$$

where $r_\rho$ is a number drawn from the uniform probability distribution. When there are no electron transfer reactions involved, $c_\rho = 0$ and by applying L'Hopital's rule to (Eq. **11**) we find

$$\tau_\rho = \frac{1}{W_\rho^0} \ln \left( \frac{1}{r_\rho} \right) \qquad [12]$$

which is the waiting time for a reaction to occur in the original Gillespie's algorithm (1, 2). The generalized First Reaction Method proceeds as follows. A random number is generated from the uniform distribution for each reaction. Then, the corresponding waiting time is calculated from Eq. **11**. The reaction with the minimal waiting time is then selected to advance. All particle numbers in that reaction are updated according to their stoichiometric numbers $N_i \to N_i + \nu_\rho^i$, the electrode potential is updated according to Eq. **7**, the propensities are recalculated from Eqs. **9** and **10**, and a new iteration begins. Performing several tens of millions of iterations of the algorithm, the stochastic time series of the electrode potential and the particle numbers of chemical species coupled through redox processes are obtained.

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**Irreversible One-Electron Transfer Reaction.** In Fig. 2 we show simulations of the ECME using the extended Gillespie algorithm sketched above for an irreversible oxidation reaction

$$A \xrightarrow{k_+} B + e^-$$ [13]

where $A$ and $B$ are two chemicals. For this reaction, the (macroscopic) faradaic current density is $i_F = F[A]k_+^0 e^{c_\rho \phi_{dl}}$ where $[A]$ is the concentration of species $A$. The value of the electrode potential at the stationary state $\phi_{dl}^*$ can be calculated from (Eq. 6) as

$$Fk_+^0 e^{c_\rho \phi_{dl}^*} = \frac{U - \phi_{dl}^*}{R_e A}$$ [14]

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

$$Fk_+^0 \langle e^{c_\rho \phi_{dl}} \rangle = \frac{U - \langle \phi_{dl} \rangle}{R_e A}$$ [15]

and, on the other hand

$$Fk_+^0 e^{c_\rho \langle \phi_{dl} \rangle} = \exp \left\langle \ln \frac{U - \phi_{dl}}{R_e A} \right\rangle.$$ [16]

Therefore, the enhancement factor $Q$ satisfies

$$\ln Q = \left\langle \ln \frac{U - \langle \phi_{dl} \rangle}{U - \phi_{dl}} \right\rangle \geq 0$$ [17]

Because for large positive $U$ $\langle \phi_{dl} \rangle$ grows as $\ln U$, it is clear from this equation that in the limit $U$ large, $Q \to 1$. The same applies to the limit $U \to -\infty$ because $\langle \phi_{dl} \rangle \sim -e^{|U|}$. The enhancement is higher for lower $|U|$, where also the difference $U - \langle \phi_{dl} \rangle$ is smaller. This is a consequence of the fact that the inequality $\langle \ln x \rangle \leq \ln \langle x \rangle$ is stronger when $\langle x \rangle$ is smaller. In Fig. 2A and B the average faradaic current at the stationary state is shown as a function of the average stationary electrode potential $\Phi_{dl} \equiv \langle \phi_{dl} \rangle$ and of the applied voltage $U$, respectively, for several values of the extensivity parameter $\Omega$ (which is related to the electrode area as $A = a_0^2 \Omega$ with $a_0$ being a typical lattice constant). We observe that the smaller the system size $\Omega$, the stronger the molecular fluctuations and *the higher the faradaic current density*, thus proving our general statement, Eq. 3. Fluctuations are also responsible for a shift in the stationary value of $\Phi_{dl}$ with respect to the macroscopic value. In the low-noise limit ($\Omega$ large), this shift $\delta = \Phi_{dl} - \phi_{dl}^*$ (see *SI Text*) has a negative value and is given by

$$\delta = -\frac{\sigma^2 c_\rho^2}{2} \frac{R_e A F k_+^0 e^{c_\rho \Phi_{dl}}}{1 + c_\rho R_e A F k_+^0 e^{c_\rho \Phi_{dl}}}$$ [18]

In Fig. 2C, $\delta$ is shown as a function of the system size $\Omega$ for three values of the applied voltage $U$. It is observed that for a large $\Omega$, $\delta < 0$ according to the prediction by Eq. 18. For lower system sizes, higher moments of the distribution of the electrode potential become important and Eq. 18 is no longer valid. In Fig. 2D the enhancement factor $Q$ is shown as a function of $\Omega$ and for several values of $U$. When the system size $\Omega$ is small, $Q$ becomes significantly higher than unity, indicating an enhanced electrochemical kinetics in consistency with Eq. 4. For lower values of $U$ this enhancement is higher, according to our prediction given by Eq. 17. It is to be noted that for lower $U$ the fluctuations begin to be important in the mesoscopic kinetics at a higher system size $\Omega$, and the associated enhanced kinetics can therefore be noticeable already for disk-shaped electrodes with a diameter of 30 nm.

The huge value of the enhancement at low $U$ and $\Omega$, as well as the fact that $\delta > 0$, is reflected in the probability distribution of the electrode potential. In Fig. 3A, this distribution is shown for $U = 0.075$ V and $\Omega = 1000$. The distribution is skewed to positive values $\xi > 0$ in Eq. 5, indicating that the average value has a higher positive value than the most probable value. This is associated to the enhancement of the kinetics through noise and to the positive shift $\delta$ at low $U$ and small system sizes (see also Fig. 2C). These effects are absent in chemical systems. Besides this significant positive skewness, controlled by the third moment of the probability distribution, the latter is highly leptokurtic $\kappa >> 0$, 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. The asymmetry in the distribution of the fluctuations around the stationary state is also noticed in the time series of the electrode potential (see Fig. 3B).

It is to be noted that we could have considered an irreversible reduction reaction as well and then all of the above results equally apply, but then the electrode potential, applied voltages, and current all have opposite signs. This proves our general statement above that all elementary electrochemical reactions are *faster* on a nanoelectrode than predicted by the macroscopic BVEE. This phenomenon seems to be related to a constructive role of noise called stochastic focusing that was recently reported in biochemistry (14) with studies concerning the Michaelis–Menten kinetics with a noisy input according to different predefined probability distributions. It was found that, because of the nonlinear form of this kinetics, an enhanced signal can be obtained in some biochemical processes having measurable consequences. This
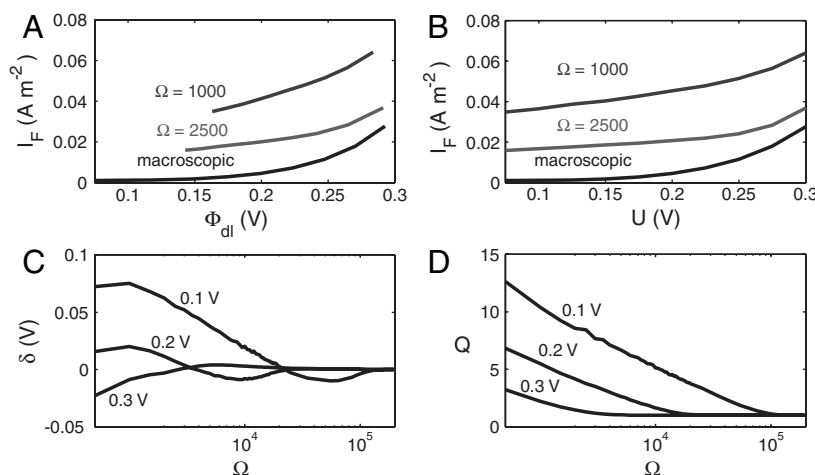


**Fig. 2.** (A) Stationary (time average) faradaic current density as a function of the averaged stationary electrode potential $\Phi_{dl} \equiv <\phi_{dl}>$ for three values of the extensivity parameter $\Omega$ as indicated in the figure. The external applied potential $U$ runs in each curve from 0.075 V to 0.3 V. (B) Stationary (average) faradaic current as a function of $U$ and for the values of $\Omega$ indicated in the figure. (C) Displacement of the average stationary electrode potential $\delta = \Phi_{dl} - \phi_{dl}^*$ as a function of $\Omega$ and for the values of $U$ indicated in the figure. (D) Enhancement factor $Q$ as a function of $\Omega$ for the values of $U$ indicated in the figure. Other parameter values: $C = 0.05$ F m$^{-2}$, $k_+^0[A] = 10^{-5}$ mol s$^{-1}$ m$^{-2}$, $R_e A = 0.3$ $\Omega$ cm$^{-2}$, $a_0^2 = 7.55$ Å$^2$.

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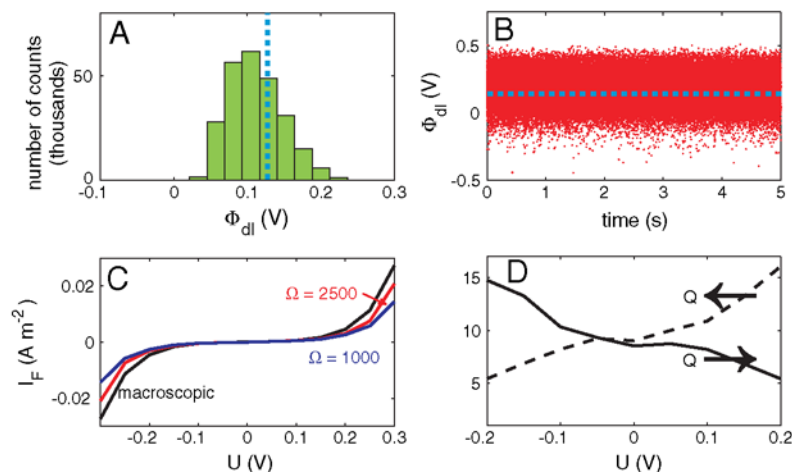
**Fig. 3.** (A) Histogram of the the averaged stationary electrode potential $\Phi_{dl} \equiv \langle \phi_{dl} \rangle$ for a time window of 5 s, $U = 0.075$ V and $\Omega = 1000$ for an irreversible reaction. Other parameter values as in Fig. 2. (B) Time series for $\Phi_{dl}$ corresponding to A. (C) Stationary (average) faradaic current density for a reversible redox reaction as a function of $U$ and for the values of $\Omega$ indicated in the figure. (D) Enhancement factors $Q_{\leftarrow}$ and $Q_{\rightarrow}$ for the backward and forward reactions, respectively as a function of $U$ and $\Omega = 1000$. In C and D $k_-^0[B] = 10^{-5}$ mol s$^{-1}$ m$^{-2}$. Other parameter values as in Fig. 2

effect was related to a displacement of the stationary state of the biochemical system due to fluctuations as we find it here. It is to be noted that in electrochemical systems, this phenomenon is inescapable at the nanoscale, because it comes from intrinsic molecular noise that is absent in macroelectrodes, i.e., the noiseless situation.
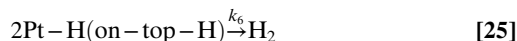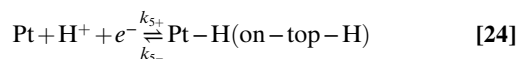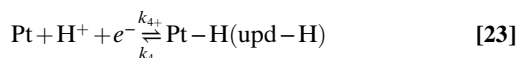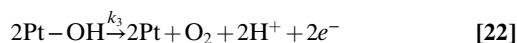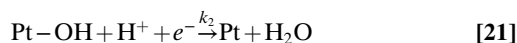
**Reversible One-Electron Transfer Reaction.** In Fig. 3C and D we have simulated the electrochemical master equation, considering the forward and backward reactions

$$A \underset{k_-}{\overset{k_+}{\rightleftharpoons}} B + e^- \qquad [19]$$

where $A$ and $B$ are two chemicals. We consider for simplicity the same values for the kinetic constants $k_+^0$ and $k_-^0$ for the forward and backward reactions, respectively, and the same concentrations of $A$ and $B$. The current/voltage characteristic can be understood as the sum of the separate contributions of each of the reactions, according to the findings presented in the previous example. At more positive $U$ in the overpotential regime, the forward reaction has a lower enhancement, as understood from the previous example, while the backward reaction is enhanced because it is in the opposite branch, where fluctuations have an important impact on its kinetics. As a consequence, the sum of both contributions lead to a *lower* value of the faradaic current compared to the macroscopic value, because the reaction that is most favored by the fluctuations is always the one that is macroscopically disfavored. It is to be noted that the equilibrium potential is not altered by the fluctuations, showing the consistency of the approach and the algorithm. All these findings are also more clearly illustrated in Fig. 3D, where the enhancement factors of the forward $Q_{\rightarrow}$ and backward $Q_{\leftarrow}$ reactions are shown.

**Network of Electrochemical Reactions.** The understanding provided by both examples above makes clear that in systems with several reversible redox reactions, a lower value of the total faradaic current is normally expected as a consequence of the increased rates of all the individual electron transfer reactions. Although this can be counterintuitive, it is to be kept in mind that the electrochemical reactions that are most favored by the molecular fluctuations are the ones that occur most rarely in the predictions of the macroscopic kinetics. This situation changes, however, when, as a consequence of at least two competing mechanisms a negative differential resistance branch arises in the current–voltage characteristic. This gives rise to electrochemical instabilities (15) and occurs in many electrochemical systems and nearly all electrochemical oscillators (8). Then, we would expect the opposite situation, a *higher* faradaic current as a consequence of the fluctuations. To explore this situation we have simulated

the ECME employing a system that is known to have a negative differential resistance branch: the reduction of $H_2O_2$ on a Pt electrode (16). The propensities are given in the *SI Text*. The following are the microscopic processes taking place at the electrode

$$2Pt + H_2O_2 \overset{k_1}{\rightarrow} 2Pt - OH \qquad [20]$$

$$Pt - OH + H^+ + e^- \overset{k_2}{\rightarrow} Pt + H_2O \qquad [21]$$

$$2Pt - OH \overset{k_3}{\rightarrow} 2Pt + O_2 + 2H^+ + 2e^- \qquad [22]$$

$$Pt + H^+ + e^- \underset{k_{4-}}{\overset{k_{4+}}{\rightleftharpoons}} Pt - H(upd - H) \qquad [23]$$

$$Pt + H^+ + e^- \underset{k_{5-}}{\overset{k_{5+}}{\rightleftharpoons}} Pt - H(on - top - H) \qquad [24]$$

$$2Pt - H(on - top - H) \overset{k_6}{\rightarrow} H_2 \qquad [25]$$

The first two reactions correspond to the reduction of $H_2O_2$. This mechanism competes with the underpotential deposition of hydrogen (the fourth reaction) that blocks active sites on the electrode. On macroelectrodes, the competition of these two mechanisms is responsible for the appearance of a negative differential resistance branch at negative applied voltages in the current–voltage characteristics (see Fig. 4). The simulations
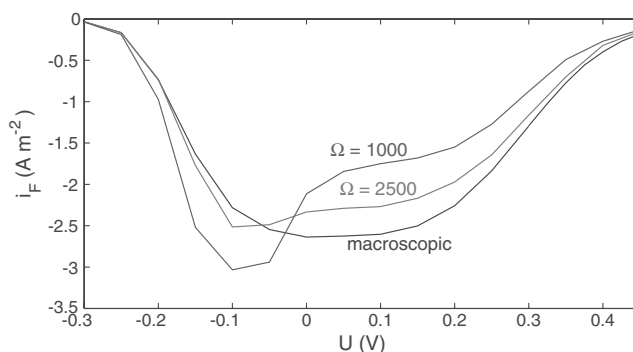


**Fig. 4.** Stationary (average) faradaic current density as a function of $U$ and for the values of $\Omega$ as indicated in the figure. Parameter values: $N = 2.2 \times 10^{-5}$ mol m$^{-2}$, $C_{H_2O_2}^b = 0.7 \times 10^3$ mol m$^{-3}$, $C_{H^+}^b = 0.3 \times 10^3$ mol m$^{-3}$, $C = 0.2$ F m$^{-2}$, $k_1 = 4 \times 10^{-4}$ m s$^{-1}$, $k_2 = 10^{-7}$ m s$^{-1}$, $k_3 = 10^{-4}$ mol m$^{-2}$ s$^{-1}$, $k_{4+} = 10^{-4}$ m s$^{-1}$, $k_{4-} = 10^{-1}$ mol m$^{-2}$ s$^{-1}$, $k_{5+} = 5 \times 10^{-5}$ m s$^{-1}$, $k_{5-} = 5 \times 10^{-2}$ mol m$^{-2}$ s$^{-1}$, $k_6 = 5 \times 10^{-2}$ mol m$^{-2}$ s$^{-1}$, $R_e A = 0.003$ $\Omega$ cm$^{-2}$, $\phi_2^0 = 0.8$ V; $\phi_3^0 = 0.4$ V; $\phi_{4+}^0 = \phi_{4-}^0 = -0.15$ V; $\phi_{5+}^0 = \phi_{5-}^0 = -0.32$ V.

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show that in this branch (around −0.1 V), the faradaic current density is *higher*, having a more negative value for a nanoelectrode when compared to a macroscopic system. As soon as the positive branch is entered at more positive applied voltages, the situation is inverted, and the trend described in Fig. 3*C* and *D* above is again observed.

## Conclusions

In this paper we have shown that individual electron transfer reactions always occur faster on nanoelectrodes compared to the predictions of the mean-field BVEE valid on macroelectrodes, and we have elucidated the dependence of this effect on the main control parameters, $U$ and $\Omega$. We have substantiated this result with numerical simulations based on the ECME, which accounts for the electrode potential as additional dynamic stochastic variable compared to purely chemical systems. There are a number of theories on fluctuations in electrochemical systems (17, 18) based on Langevin equations that work well in the low-noise limit. Here, we have tackled the problem in the most general way, because the ECME is valid for any system size. In order to carry out these simulations, the Gillespie algorithm (First Reaction Method) (1, 2, 12) has been rigorously generalized to take into account electron transfer reactions. The electrode potential can be a stochastic variable, and the constraint of charge balance at the interface allows us to handle its evolution together with the concentrations of chemical species by means of the appropriate master equation. The faradaic current density of each single reaction, independent of its reduction/oxidation character, can be much higher on nanoelectrodes compared to macroelectrodes. It is to be noted that this effect is absent in purely chemical systems (6); rather, it is a direct consequence of electron transfer processes. It can dramatically influence measurable quantities and, thus, special care must be taken when introducing mean-field concepts discussing phenomena involving electron transfer at the nanoscale. The effect acts mainly in the kinetically controlled domain of the characteristic current–voltage curves, and it vanishes for large applied voltages $|U|$. Therefore, diffusion can be safely neglected, as we did also in our approach.

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# Supporting Information

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### SI Text

**1 Proof of Eq. 11 of the manuscript.** The probability that a reaction $\rho$ has not yet occurred after a time $t$, $p_\rho(\mathbf{N},t)$, satisfies the following differential equation:

$$\frac{dp_\rho(\mathbf{N},t)}{dt} = -W_\rho(\mathbf{N}+\nu_\rho|\mathbf{N})p_\rho(\mathbf{N},t) \qquad \textbf{[S1]}$$

Between small time intervals $\Delta t$, in which no reaction occurs at the interface, the electrode potential changes as

$$\phi(t+\Delta t)-\phi_{dl}(t)=\frac{U-\phi_{dl}(t)}{R_e A}\Delta t. \qquad \textbf{[S2]}$$

We can thus integrate **S1**

$$p_\rho(\tau_\rho)=\exp\left(-\int_{t_n}^{t_n+\tau_\rho}W_\rho(\mathbf{N}+\nu_\rho|\mathbf{N})dt\right)$$

$$=\exp\left(-W_\rho^0\int_{t_n}^{t_n+\tau_\rho}\exp(c_\rho\phi_{dl})dt\right)$$

$$=\exp\left(-W_\rho^0\int_{t_n}^{t_n+\tau_\rho}\exp\left[c_\rho\phi_{dl}(t_n)+\frac{c_\rho[U-\phi_{dl}(t_n)]}{R_e A}(t-t_n)\right]dt\right)$$

$$=\exp\left\{-\frac{W_\rho^0 R_e A\exp[c_\rho\phi_{dl,j}]}{c_\rho(U-\phi_{dl,j})}\left(\exp\left[\frac{c_\rho(U-\phi_{dl,j})}{R_e A}\tau_\rho\right]-1\right)\right\} \qquad \textbf{[S3]}$$

where in the last equality we have made the notation change $\phi_{dl}(t_n)\to\phi_{dl,j}$. If $r_\rho$ is a random number drawn from the uniform distribution in the unit interval, by solving the following equation for $\tau_\rho$,

$$p_\rho(\tau_\rho)=r_\rho$$

we obtain

$$\tau_\rho=\frac{R_e CA}{c_\rho(U-\phi_{dl,j})}\ln\left[1+\frac{c_\rho(U-\phi_{dl,j})}{W_\rho^0 R_e CA\exp(c_\rho\phi_{dl,j})}\ln\left(\frac{1}{r_\rho}\right)\right] \qquad \textbf{[S4]}$$

The reaction for which $\tau_\rho$ is the smallest one in a certain iteration of the algorithm, is the one chosen to advance.

**2 Proof of Eq. 18 of the manuscript.** Macroscopically, at the steady state, we have Eq. 14

1. Jansen APJ (1995) Monte Carlo simulations of chemical reactions on a surface with time-dependent reaction rate constants. *Comput Phys Commun* 86:1–12.

$$\frac{U-\phi_{dl}^*}{R_e A}=Fk_+^0\exp(c_\rho\phi_{dl}^*) \qquad \textbf{[S5]}$$

When fluctuations are allowed (smaller system size in the low-noise limit) we have, instead

$$\frac{U-<\phi_{dl}>}{R_e A}=Fk_+^0<\exp(c_\rho\phi_{dl})>$$

$$=Fk_+^0\exp(c_\rho<\phi_{dl}>)Q_\rho$$

$$\approx Fk_+^0\exp(c_\rho<\phi_{dl}>)\left[1+\frac{\sigma^2 c_\rho^2}{2}\right] \qquad \textbf{[S6]}$$

where the expansion of $Q_\rho$ (Eq. 5) up to second order has been employed. By substracting the latter expression from the former one, we have

$$\frac{<\phi_{dl}>-\phi_{dl}^*}{R_e A}=\frac{\delta}{R_e A}$$

$$=Fk_+^0\left(\exp(c_\rho\phi_{dl}^*)-\exp(c_\rho<\phi_{dl}>)\left[1+\frac{\sigma^2 c_\rho^2}{2}\right]\right)$$

$$=Fk_+^0\exp(c_\rho<\phi_{dl}>)\left(\exp(-c_\rho\delta)-1-\frac{\sigma^2 c_\rho^2}{2}\right) \qquad \textbf{[S7]}$$

Since fluctuations are small, so is also $\delta$ and we can expand the exponential on the r.h.s. to linear order in $\delta$.

$$\frac{\delta}{R_e A}=Fk_+^0\exp(c_\rho<\phi_{dl}>)\left(-c_\rho\delta-\frac{\sigma^2 c_\rho^2}{2}\right) \qquad \textbf{[S8]}$$

which can be now solved for $\delta$. We obtain

$$\delta=-\frac{\sigma^2 c_\rho^2}{2}\frac{Fk_+^0\exp(c_\rho<\phi_{dl}>)}{\frac{1}{R_e A}+Fk_+^0\exp(c_\rho<\phi_{dl}>)} \qquad \textbf{[S9]}$$

which is Eq. 18 of the manuscript.

**Table S1. Preexponential factors of the propensities for the $H_2O_2$ reduction on a Pt electrode**

| REACTION NO | PROPENSITY ($W_\rho^0$) |
|---|---|
| 1 | $k_1 C_{HO}^b(\Omega-N_H-N_{OH}-N_X)(\Omega-N_H-N_{OH}-N_X-1)/\Omega$ |
| 2 | $k_2 C_H^b N_{OH}$ |
| 3 | $k_3 N_{OH}(N_{OH}-1)/\Omega$ |
| 4+ | $k_{4+}C_H^b(\Omega-N_H-N_{OH}-N_X)$ |
| 4- | $k_{4-}N_H$ |
| 5+ | $k_{5+}C_H^b(\Omega-N_H')$ |
| 5- | $k_{5-}N_H'$ |
| 6 | $k_6 N_H'(N_H'-1)/\Omega$ |