Frequency of negative differential resistance electrochemical oscillators: theory and experiments

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An approximate formula for the frequency of oscillations is theoretically derived for skeleton models for electrochemical systems exhibiting negative differential resistance (NDR) under conditions close to supercritical Hopf bifurcation points. The theoretically predicted \( \omega \propto (k/R)^{1/2} \) relationship (where \( R \) is the series resistance of the cell and \( k \) is the rate constant of the charge transfer process) was confirmed in experiments with copper and nickel electrodissolution. The experimentally observed Arrhenius-type dependence of frequency on temperature can also be explained with the frequency equation. The experimental validity of the frequency equation indicates that 'apparent' rate constants can be extracted from frequency measurements of electrochemical oscillations; such method can aid future modeling of complex responses of electrochemical cells.

1. Introduction

Electrochemical systems exhibit a variety of non-linear phenomena including bistability, periodic, quasiperiodic, and chaotic oscillations due to the interaction of charge transfer chemical reactions, electric and mass transfer effects.1–3 The dynamical behavior often depends not only on the surface concentration of electrochemically active species but also on the potential drop across the double-layer. When the electrode potential plays an essential role in the origin of current oscillations, the electrochemical system exhibits negative differential resistance (NDR) in a certain region of the overpotential; this NDR can sometimes be hidden (HN-NDR) by a slow charge transfer reaction.1 Because of this general underlying mechanism, the parameter dependence of non-linear behavior is similar for the NDR class of electrochemical systems; this notion serves as a basis for classification of electrochemical oscillations based on dependence of oscillations on external resistance4 and double-layer capacitance.5 For example, the dependence of bifurcation points on resistance can be predicted using impedance spectroscopy methods for bistability and oscillations.6–8 In addition, there exist a few skeleton models,1 which are, although typically not quantitatively accurate, capable of clarifying the essential dynamical features of electrochemical instabilities.

Periodic oscillation in chemical and biological systems is an important far-from-equilibrium process exhibiting self-organization. Oscillations are typically characterized by waveform and frequency; both quantities are expected to have complicated, non-linear dependence of experimental parameters such as concentrations, rate constants, and temperature. Oscillatory reactions often play a role in biological timing processes; therefore, the parameter dependence of frequency is of great importance.9 The effect of temperature on frequency of oscillations has been extensively studied for chemical and biological systems;10–17 in addition to simple Arrhenius dependence, temperature compensation and even ‘over’-compensation18 were observed. The period (P) of the oscillations is often expressed13 with an approximate equation:

\[ P = \tau_0 \prod_{i} k_i^{x_i}, \]

where \( \tau_0 \) and the \( x_i \) values are empirical constants and \( k_i \) values are the rate constants.

Parameter dependence of self-organized, critical behavior is generally expected to be mathematically complicated. However, it was shown that a relatively simple equation can be obtained for the rate of catalytic CO oxidation at the saddle-node bifurcation point.19 A combination of bifurcation theory and singular perturbation simplifies the mathematical description of critical behavior and results in relatively simple rate equations. This notion of 'principle of critical simplification' (PCS) has the advantage of being capable of system description by competing processes without isolation of limiting steps typically used in classical quasi-stationary treatments.

In this paper, we make use of the existing skeleton models1 of electrochemical oscillations and derive a relatively simple equation for the frequency in NDR type electrochemical systems for the onset of oscillations through a Hopf bifurcation. There are a few experimental reports of precise measurements of frequencies of electrochemical oscillations,18,20,21 especially, their temperature dependence; we carry out a systematic study with relatively simple oscillatory electrochemical...
systems to provide a framework for future studies of the parameter dependence of frequency on system parameters. The derived frequency equation is tested in experiments with Cu electrodissolution in phosphoric acid and Ni electrodissolution in sulfuric acid that represent two prototype electrochemical oscillators of N-NDR and HN-NDR types, respectively. The dependence of frequency on external resistance is compared in the two systems. The obtained theoretical formula is used to shed light on the dependence of frequency on temperature; the effect of temperature on oscillation frequency is studied in Ni electrodissolution and compared to the theoretical prediction and to results of temperature dependence obtained in other electrochemical systems.

2. Experimental

2.1 Experiments

The experiments were carried out in a standard three-electrode electrochemical cell. For copper electrodissolution a rotating disk (Pine AFSMRCE) working, Hg/HgSO\textsubscript{4}/saturated K\textsubscript{2}SO\textsubscript{4} reference, and Pt counter electrodes were used. The working electrode was a 5 mm diameter Cu disk (rotated at 1000 rpm) in 85% phosphoric acid at 10 °C. The disk was wet polished with 0.05 μm alumina suspension before the experiments and flushed with deionized water. With Ni electrodissolution, a 1 mm diameter stagnant Ni disk embedded in epoxy was used as a working electrode in 3 mol dm\textsuperscript{-3} sulfuric acid. The electrode was wet polished with a series of sandpapers (P180–P4000) with a Buehler Metaserv 3000 polisher. The temperature of the cell was varied between 10 and 30 °C by a Neslab RTE-7 circulating bath.

The circuit potential was set and the current of the electrode was measured (sampling frequency: 200 Hz) with a potentiostat (ACM Instruments, Gill AC). (The potential values are given with respect to the Hg/HgSO\textsubscript{4}/saturated K\textsubscript{2}SO\textsubscript{4} reference electrode.) The current was digitized with a National Instruments (PCI 6255) data acquisition board. The working electrode was connected to the potentiostat through an external resistance \( R_{\text{ext}} \); the total resistance \( R_{\text{tot}} \) of the cell is the sum of the external resistance and the cell resistance measured with impedance spectroscopy.\(^8\) The cell resistance was found to be 17 Ω for copper, and about 1 Ω for nickel electrodissolution. For nickel dissolution the attached external resistors (600 Ω to 6 kΩ) were much larger than the solution resistance, therefore, the reported total resistance includes only the external resistance. Additional experimental procedures (e.g., electrode pretreatments and polarization curves) are described in previous publications.\(^8,24,25\)

2.2 Numerical tools

The ordinary differential equations were solved numerically with the XPPAUT program package\(^{26}\) applying a fourth-order Runge–Kutta method with variable step size.

The frequencies of the current oscillations were determined with the Hilbert-transform method.\(^{25,27,28}\)

3. Results

3.1 Frequency of electrochemical oscillators: analytical derivation

The skeleton model of a potentiostatic N-NDR type electrochemical oscillator\(^{29}\) is given by the following set of ordinary differential equations:

\[
\frac{da}{dt} = \frac{V - e}{AR} - nFk(e)c
\]

\[
\frac{dc}{dt} = \frac{2}{a}k(e)c + \frac{2D}{a^2}(c_0 - c)
\]

Eqn (2) and (3) describe the charge and mass balances, respectively, for a reduction reaction. The essential variables are the electrode potential \( e \) and near-surface concentration of the electroactive species, \( c \). \( C_a \) is double-layer capacitance, \( A \) is the surface area of electrode, \( F \) is Faradaic constant, \( n \) is the number of electrons in the reaction, \( V \) is circuit potential, \( R \) is series resistance, \( a \) is Nernst diffusion layer thickness, and \( D \) and \( c_0 \) are the diffusion constant and the bulk concentration of the electroactive species, respectively. \( k(e) \) is the potential dependent rate constant; for NDR systems considered in this study \( k(e) \) exhibits N-shaped dependence on \( e \) with a negative differential resistance region.\(^1\) In a typical potentiostatic experiment the current \( i(t) = \frac{(V - e(t))}{R} \) is measured while the circuit potential \( V \) is kept constant. The dynamical behavior of the equations has been analyzed in great detail;\(^1,3\) it was shown that oscillation can develop if \( \frac{dk(e)}{de} < 0 \), i.e., when there is a negative slope on the polarization curve (N-NDR system).

Our goal is to obtain an approximate relationship for the frequency of the oscillations. It was shown that the oscillation develops through a Hopf bifurcation when \( \frac{dk(e)}{de} < 0 \) at appropriate cell resistance \( R \).\(^1,3\) At the bifurcation point the trace of the Jacobian of eqn (2) and (3) is zero and the determinant is larger than zero according to the Andronov–Hopf theorem.\(^{30}\) Since the Jacobian is:

\[
J = \begin{pmatrix}
-\frac{1}{C_a R} & \frac{nFk(e)^2}{ce} & \frac{-nFk(e)c}{c_0} \\
2\frac{e ek(e)c}{a} & \frac{2k(e)c}{a} & \frac{-2k(e)c}{a} - \frac{2D}{a^2}
\end{pmatrix}
\]

where \( e^* \) and \( c^* \) are the steady-state values of the variables obtained by setting the right hand side of eqn (2) and (3) to zero. Therefore, the trace (Eqn (5))

\[
\text{Tr}(J) = \frac{1}{C_a R A} - \frac{nFk^2(e^*)}{C_a} - \frac{2k(e^*)}{a} - \frac{2D}{a^2} = 0
\]

imposes a relationship between the important parameters in the system at the bifurcation point. Provided that this condition is satisfied and \( \det(J) > 0 \) the frequency of the oscillations is the square root of the determinant of \( J \):\(^{30}\)

\[
\text{det}(J) = \frac{2(k(e^*)a + D + RADnFc^*\frac{dk(e^*)}{de})}{C_a R A a^2}
\]

\[
\omega = \sqrt{\text{det}(J)}
\]
By combining eqn (5) with eqn (6a) we obtain a simplified formula for the determinant that does not contain the derivative of the rate constant:

$$\det(J) = \frac{2k(e^*)}{aC_dRA} - \frac{4k(e^*)D}{a^3} - \frac{4D^2}{a^4}$$  

(7)

Therefore, the frequency of the oscillations (in rad s\(^{-1}\)) at the bifurcation point is

$$\omega^* = \sqrt{\frac{2k(e^*)}{aC_dRA} - \frac{4k(e^*)D}{a^3} - \frac{4D^2}{a^4}}$$  

(8)

Note that eqn (8) gives the frequency of the oscillations provided that the Hopf bifurcation exists at \(e^*\); it is not meant to give full conditions for the onset of oscillations. In addition, the frequency is expressed with a steady-state value of electrode potential \(e^*\). \(e^*\) has complicated dependence on system parameters (especially, \(V\) and \(R\)). Therefore, eqn (8) does not describe full dependency of the frequency on system parameters. Instead, it is meant for the approximation of the frequency at the bifurcation point where the \(e^*\) value can be determined in the experiments.

Eqn (8) can be rationalized by noting the fact that there are three major important time-scales (\(\tau\)) in the system. Each time-scale is related to a linear term of the corresponding rate equation (in eqn (2) and (3)); the inverse of the time-scale can be considered a related frequency (\(\omega\)).

(i) The electrical time-scale is related to double-layer charging, therefore:

$$\tau_{el} = C_dRA; \omega_{el} = \frac{1}{C_dRA}$$  

(9)

(ii) The chemical time-scale is related to the inverse of the first order chemical reaction rate constant; because \(k(e^*)\) should relate to the near-surface layers, the Nernst-diffusion layer thickness has to be taken into account:

$$\tau_c = \frac{a}{2k(e^*)}; \omega_c = \frac{2}{a} k(e^*)$$  

(10)

(iii) The diffusional time-scale characterizes the time needed for the electroactive species to diffuse to the surface:

$$\tau_{D} = \frac{a^2}{2D}; \omega_D = \frac{2D}{a^2}$$  

(11)

The frequency of the oscillations in eqn (8) can be expressed with a combination of these frequencies (inverse time-scales):

$$\omega^* = \sqrt{\omega_c \omega_{el} - \omega_c \omega_D - \omega_D^2} = \sqrt{\omega_c \omega_{el} - \omega_D (\omega_c + \omega_D)}$$  

(12)

We can see that the frequency of electrochemical oscillation is obtained from the product of electrical and chemical frequencies diminished by terms related to diffusion.

The full eqn (12) can be further simplified; for NDR oscillators the electrode potential is considered the fast variable, \(\omega_c \gg \omega_{el}, \omega_D\); therefore, the frequency would be dominated by the first term in eqn (12):

$$\omega^* \approx \sqrt{\omega_c \omega_{el}} = \sqrt{\frac{2k(e^*)}{aRC_dA}}$$  

(13)

This simplification is not trivial; as we will show below, for the investigated models and experiments the \(\omega_c \gg \omega_{el}, \omega_D\) condition holds and thus we did not have to use the full eqn (12).

Eqn (13) thus predicts the frequency of the electrochemical oscillations as the geometric mean of the inverse electrical and chemical time-scales. The frequency is expected to increase with increasing rate constant, and decrease with increasing Nernst-diffusion layer thickness, double-layer capacitance, and resistance provided that the \(e^*\) value in eqn (13) does not change to a large extent. (Note that there is no direct dependence on surface area since the resistance of an electrochemical cell should be characterized by the quantity \(RA\)). Moreover, these dependencies should follow a square-root law; therefore, when we keep all other parameters constant the frequency should be proportional to resistance:

$$\omega \propto \sqrt{\frac{1}{R}}$$  

(14)

However, as we shall show below, the experiments are difficult to carry out with keeping the rate constant at the same potential; therefore, it is more useful to consider the dependence of frequency to be proportional to the square root of the rate constant and resistance:

$$\omega \propto \sqrt{\frac{k(e^*)}{R}}$$  

(15)

(Note that in these final equations we use \(\omega\) for frequencies expressed in Hz in place of \(\omega^*\) in rad s\(^{-1}\).)

Next we carry out numerical simulations and experiments to confirm that the full eqn (12) can indeed be simplified to the form of eqn (13) and to explore whether this simple formula is capable of describing the frequency of electrochemical oscillations. The numerical simulations and experiments will also shed light on to what extent the dependency of \(e^*\) on system parameters will affect the square-root relationships.

### 3.2 The effect of resistance on frequency of an N-NDR electrochemical oscillator: copper electrodissolution

The capability of the obtained theoretical formulae (eqn (12)–(15)) to describe the frequency of electrochemical oscillations is tested in numerical simulations and experiments of copper electrodissolution.

**Numerical simulations.** The Koper–Gaspard dimensionless model\(^{31}\) was used to simulate Cu dissolution in phosphoric acid solution:

\[
\frac{de}{dt} = \frac{v - e}{r} - 120k(e)u \quad \text{(16a)}
\]

\[
\frac{du}{dt} = -1.25e^{1/2}k(e)u + 2d(w - u) \quad \text{(16b)}
\]

\[
\frac{dw}{dt} = 1.6d(2 - 3w + u) \quad \text{(16c)}
\]
eqn (16)–(18) have been studied in detail by Koper and the current is obtained as
\[ i = w(e) \]
where the constant value \( w \) we complete frequency formula (eqn (12)) gives a frequency of
do appear in the experiments. For conditions of Fig. 1a, the oscillations that are not possible in the skeleton model but the oscillation in the \( e \) variable has small amplitude oscillations around \( w \) by the electroactive species:
\[ y = k(e) \]
where \( k(e) = 2.5\theta^2 + 0.01\exp[0.5(e - 30)] \]
(17)
where \( \theta \) is related to the potential dependent surface coverage by the electroactive species:
\[ \theta = \begin{cases} 1 & \text{for } e \leq 35 \\ \exp[-0.5(e - 35)^2] & \text{for } e > 35 \end{cases} \]
(18)
the current is obtained as \( i = (v - e)/r \). The dynamics of model eqn (16)–(18) have been studied in detail by Koper and Gaspard.31

For an appropriate range of parameters the three variable model simulates well the essential dynamical features of Cu dissolution in phosphoric acid observed in our potentiostatic experiments.8,24 In this study we set \( d = 0.115 \) and the frequency of the oscillations is studied as a function of the resistance \( r \).

Fig. 1a shows a typical oscillatory current with a frequency of \( \omega = 0.8726 \) at a relatively low resistance of \( r = 0.023 \); the applied circuit potential \( v = 36.547 \) was determined in such a way that it is just above (by 0.001 increment) the Hopf bifurcation point. The obtained frequency value can be interpreted using the frequency formulae eqn (12) and (13). Note that these formulae were derived from the two variable skeleton model (eqn (2) and (3)). The third variable \( w \) was introduced31 in eqn (16a–c) to account for aperiodic oscillations that are not possible in the skeleton model but do appear in the experiments. For conditions of Fig. 1a, the \( w \) variable has small amplitude oscillations around \( w^* = 0.7267 \); the oscillation in the \( e \) variable has a mean value of \( e^* = 35.7288 \). By replacing the \( w \) variable in eqn (16b) with the constant value \( w^* \), we can identify \( \omega_c = 1/r = 0.4338 \), \( \omega_c = k(e^*)1.25\sqrt{d} = 0.6973 \), and \( \omega_D = 2d = 0.230 \). The complete frequency formula (eqn (12)) gives a frequency of \( \omega^*/(2\pi) = 0.873 \) while the approximate (eqn (13)) formula gives \( \omega^*/(2\pi) = 0.876 \). These values agree well with the numerical \( \omega = 0.8726 \) value. These results imply that (i) the results of the skeleton model are transferable to more realistic models (at least for systems described by eqn (16a–c)) and (ii) the approximation of \( \omega_c \gg \omega_c \), \( \omega_D \) holds for the oscillatory conditions and thus the simplified formula is capable of describing the frequency within 0.4% accuracy.

When the resistance is increased to \( r = 0.04 \) the oscillations slow down; a frequency of \( \omega = 0.7698 \) was obtained at \( v = 36.891 \). Therefore, the qualitative prediction of eqn (14) and (15) is correct; the oscillations do slow down at larger resistances.

The frequencies of the oscillations were determined as a function of resistance for \( 0.023 \leq r \leq 0.04 \); in these simulations for each resistance the circuit potential was just above the Hopf bifurcation point. The results are shown in Fig. 2a; for better comparison, the frequencies are referenced to the frequency at \( r = 0.023 \); therefore, the relative frequencies \( [\omega/\omega(r = 0.023)] \) are shown. There is a decreasing trend at high resistances; however, the frequencies seem to level off and even decrease for low resistances. The figure also shows the expected frequency values assuming the \( \omega \propto \sqrt{1/R} \) relationship; it is clear that this relationship greatly underestimates the frequencies. For example, for a change of resistance from \( r = 0.023 \) to 0.04 about 25% decrease is expected in the frequency value; however, the model exhibits only 12% decrease.

The \( \omega \propto \sqrt{1/R} \) relationship is valid when the electrode potential and thus \( k(e^*) \) in eqn (13) remains constant. The mean electrode potentials and the Hopf potentials (\( e_H \)) for the oscillations at the different resistances are shown in Fig. 2b. (The Hopf potentials are the electrode potentials at which the
oscillations occur; the mean electrode potentials are good approximations ($\pm 0.001$ of $e^*$. ) Because the Hopf potentials vary to a large extent with resistance, the potential dependence of the rate constant should be considered, thus $\omega \propto \sqrt{k(e^*)/R}$.

In the numerical simulation we do know the potential dependence of the rate constant. However, in the experiments it is not straightforward to obtain the dependency. Therefore, we utilize a simple potential step experiment for the determination of $k(e^*)$. Assuming that we apply a low resistance in the cell such that oscillations do not occur, at a circuit potential of $v_1$ we obtain electrode potential $e_1$ and current $i_1 = nFk(e_1)e_1)$. When the circuit potential is abruptly changed to $v_2$ (see Fig. 2c), after a quick transient (double-layer charging) the electrode potential changes to $e_2$ and the current is $i_2 = nFk(e_2)e_1)$. Because diffusion is a slow process, the surface concentration does not have enough time to relax to the equilibrium value of $e_2)$. Therefore, the ratio of rate constants $k(e_2)/k(e_1)$ can be approximated by the ratio of the current before the potential step $(i_1)$ and the peak current $(i_2)$:

$$\frac{k(e_2)}{k(e_1)} = \frac{i_2}{i_1}$$  \hspace{1cm} (19)

We note that this chronoamperometric procedure can only be applied if the time-scale of double-layer charging is much smaller than that of the Faradaic and mass transfer processes involving the chemical species. This approximate method for determining the potential dependence of rate constants was tested in numerical simulations.

We have applied a low resistance of $r = 0.001$ in the model, determined the circuit potentials that correspond to the Hopf potentials, and carried out the potential step experiments to determine the relative rate constants $k/r = 0.023)$, where $k(r = 0.023)$ is the rate constant at the Hopf potential for $r = 0.023$. The relative rate constants at potentials that correspond to the oscillations at various resistances are shown in Fig. 2d. With increasing resistance the rate constants increase; the increase is larger for lower resistances than the increase observed for higher resistances.

The prediction for relative oscillation frequencies with the $\omega \propto \sqrt{k(e^*)/R}$ equation is shown in Fig. 2a (triangles). The numerically obtained values are very well reproduced; the strongly decreasing trend due to increasing resistance is counterbalanced by the increase in rate constant at low resistance values. At high resistance values, the frequency decreases due to the resistance decrease; however, this decrease is still diminished by the increase in rate constant.

The numerical simulations thus imply that for accurate estimation of the effect of resistance on oscillation frequencies eqn (15) can be used and the variation of rate constant with potential should be considered.

**Experiments.** A series of experiments were carried out to confirm the resistance dependence of frequency with copper electrodissolution in phosphoric acid solution. Fig. 3a shows a typical oscillatory current just above (by about 5 mV) a Hopf bifurcation with $R_{tot} = 37 \Omega$ at $V = 55$ mV; the frequency of the oscillations is $\omega = 3.070$ Hz. When the resistance is increased to $R_{tot} = 77 \Omega$ the oscillations slow down to a frequency of $\omega = 2.545$ Hz just above the bifurcation point at $V = 201$ mV (see Fig. 3b). We note that the investigated resistance range (37–77 $\Omega$) is the experimentally available range where simple periodic oscillations can be observed: for resistance lower than 37 $\Omega$ the robust oscillations cannot be observed while for resistance values larger than 77 $\Omega$ mixed-mode oscillations occur in accordance with the model behavior and previous experimental investigations.
The relative frequency as a function of the resistance at potentials just above the bifurcation point is shown in Fig. 4a; similar to that of the numerical finding the frequency has a decreasing trend at large resistance that levels off at low resistance values. Apparently, the \( \omega \propto \sqrt{1/R} \) relationship (dashed line) overestimates the slowing down of the oscillations due to resistance. Therefore, we estimated the variation of the rate constant with the Hopf potential (Fig. 4b) with potential step experiments. Without added resistance \( R_{\text{tot}} = 17 \Omega \) the circuit potential was increased from values that correspond to the Hopf potential at \( R = 37 \Omega \) to circuit potentials that correspond to the target Hopf potentials. A potential step experiment is shown in Fig. 4c; the ratio of the rate constants is obtained as the ratio of the current peak and the base current similar to the numerical simulations. The determined relative rate constants at Hopf potentials that correspond to the resistance values are shown in Fig. 4d. Similar to the numerical simulation the rate constant increases with resistance and there is a larger increase at low resistances than at large resistances.

When the potential dependence of the rate constant is considered the \( \omega \propto \sqrt{k(e)/R} \) relationship describes the nearly linear dependence of the frequency on resistance for \( R_{\text{tot}} \geq 47 \Omega \) (Fig. 4a dashed line). For \( R_{\text{tot}} = 37 \Omega \) the relationship improves the \( \omega \propto \sqrt{1/R} \) by about 50%; however, the frequency plateau is not reproducible. It should be noted that at the low resistance \( R_{\text{tot}} = 37 \Omega \) the variations of Hopf potential and rate constant are the strongest with resistance; therefore, the predictions are very sensitive to small drifts of bifurcation point, which is common in electrochemical systems. Overall, eqn (15) satisfactorily describes the frequency dependence of copper electrodissolution in phosphoric acid for 75% of the resistance parameter region where simple oscillations occur.

### 3.3 The effect of resistance and temperature on frequency of an HN-NDR oscillator: nickel electrodissolution in sulfuric acid

For the electrodissolution of nickel in sulfuric acid the negative differential resistance character of the polarization curve is hindered by a slow process, and thus the negative resistance can be observed only on the time-scale of the oscillations.\(^{1,3,32}\) Such systems are known to produce oscillations under galvanostatic conditions (equivalent to \( R_{\text{tot}} \rightarrow \infty \) in potentiostatic mode); therefore, there is no upper limit for resistance at which oscillations can develop.

To investigate the validity of eqn (15) for an HN-NDR oscillator we consider a general skeleton model:\(^1\)

\[
\frac{C_d}{dt} \frac{de}{dt} = \frac{v - e}{AR} - nFk^*(e)(1 - \Theta) \quad (20a)
\]

\[
\frac{d\Theta}{dt} = k_p[\Theta_0(e) - \Theta] \quad (20b)
\]

where \( \Theta \) and \( \Theta_0(e) \) are the coverage of some inhibiting species and its potential dependent equilibrium value, respectively, \( k^*(e) \) is the rate constant for the slow hindering reaction, \( k_p \) is the rate constant for the relaxation of \( \Theta \) to its equilibrium value. The frequency of the oscillations at the Hopf bifurcation point can again be derived as the square root of the determinant of Jacobian by using the zero trace condition. The obtained frequency is:

\[
\omega^* = \sqrt{\frac{k_p}{RC_dA} \left( \frac{1}{C_d} \frac{di(e^*)}{de} \right)} \quad (21)
\]

where \( i(e^*) = nFk^*(e^*)(1 - \Theta^*) \) is the Faradaic current density at the bifurcation point. This equation exhibits some similarities and differences to the frequency formula of an N-NDR oscillation (eqn (13)). It is seen that for low resistance values the first term of the right-hand side of eqn (21) could dominate, and thus resistance dependence \( \left( \omega^* \propto \sqrt{k_p/(RC_dA)} \right) \) similar to eqn (13) is obtained. However, for large resistance values \( (R \rightarrow \infty) \), the frequency of oscillations reaches a limiting value of \( \omega^* = \sqrt{\frac{1}{C_d} \frac{di(e^*)}{de}} \).

**Effect of resistance.** We have carried out a series of experiments with nickel electrodissolution to test the validity of the frequency formulae. Fig. 5a shows a typical oscillatory current just above a Hopf bifurcation with \( R_{\text{tot}} = 600 \Omega \) at \( V = 1075 \) mV; the frequency of the oscillations is \( \omega = 0.505 \) Hz. When the resistance is increased to \( R_{\text{tot}} = 1000 \Omega \) the oscillations slow down to a frequency of \( \omega = 0.403 \) Hz just above the bifurcation point at \( V = 1080 \) mV (see Fig. 3b). Therefore, we observe a slowing down of oscillations due to resistance increase. With nickel electrodissolution it is possible to study the effect of resistance in a large frequency range since oscillations can be observed even for \( R_{\text{tot}} \rightarrow \infty \); Fig. 5d shows the relative frequencies as a function of the resistance at circuit potentials just above the bifurcation points for \( 600 \Omega \leq R_{\text{tot}} \leq 6 \) k\( \Omega \). There is decreasing trend, however, when the resistance was increased from 3 k\( \Omega \) to 6 k\( \Omega \) there was only a small decrease of the

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**Fig. 5 Experiments:** frequency dependence on resistance in an HN-NDR system of nickel electrodissolution. (a) Time series of current oscillations at \( R = 600 \Omega \), \( V = 1075 \) mV, \( \omega = 0.505 \) Hz. (b) Time series of current oscillations at \( R = 1000 \Omega \), \( V = 1080 \) mV, \( \omega = 0.403 \) Hz. (c) Relative rate constants \( [k/k(R = 47 \Omega)] \) at potentials corresponding to the onset of oscillations at different resistances. (d) Measured and approximated frequencies as a function of resistance. Relative frequency \( \omega/\omega(R = 600 \Omega) \) vs. resistance. Circles: experimentally measured frequencies. Squares: \( \omega \propto \sqrt{k/R} \) approximation. \( T = 10^\circ \) C.
Arrhenius-type temperature dependence. Fig. 6a and b show that as the temperature is increased from 10 °C to 30 °C the frequency of the oscillations increases from 0.505 to 1.960 Hz. This increase is similar to that typically observed for rate constants. Fig. 6c and d show the frequency dependence of the oscillations at constant $R_{\text{tot}} = 600 \, \Omega$ at circuit potentials just above the bifurcation points for 10 °C ≤ $T$ ≤ 30 °C. The frequencies exhibit Arrhenius-type temperature dependence with an apparent activation energy of $E_{\text{app}} = 49 \, \text{kJ mol}^{-1}$. For comparison, the temperature dependence of the mean current of the oscillations was also determined (see Fig. 6e and f). The mean current increases with temperature following the Arrhenius equation as well with an apparent activation energy of $E_{\text{app}} = 46 \, \text{kJ mol}^{-1}$.

4. Discussion

We have derived an approximation (eqn (12) and (13)) for the frequency of electrochemical oscillations (close to a Hopf bifurcation point) based on general mechanisms in which negative differential resistance plays an important role. The formula combines the important parameters in the electrochemical system including the electrochemical rate constant, double-layer capacitance, external resistance, Nernst-diffusion layer thickness, and electrode surface area. Although in general the frequency of the oscillation in a non-linear system should depend on system parameters in a complicated way, we have shown that close to a Hopf bifurcation the dependency is quite simple. Close to bifurcation point the mathematical structure describing the oscillations is greatly simplified, therefore, relatively simple equations could be obtained for the oscillations. The notion of ‘principle of critical simplification (PCS)’, i.e., relatively simple reaction rates close to bifurcation points, was previously observed with catalytic CO oxidation. The relatively simple equation for the frequency of oscillations thus could be considered another example of PCS.19

Features of the validity of the theoretical formula (eqn (13)) were confirmed in experiments with copper and nickel electrode-dissolution. In accordance with the theoretical formula, the experimental frequencies were found to be proportional to the square root of the ratio of the rate constant and the resistance, i.e., $\omega \propto \sqrt{k(e^*)/R}$. Because the bifurcation points occur at different electrode potentials at resistances, the rate constants were determined in independent experiments with potential steps. An important consequence of the equation is the possibility of approximating rate constants from frequency measurements at different resistances. Therefore, frequency measurements could provide indirect information about variation of rate constants in parameter regions where direct information with classical electrochemical techniques would be difficult to apply because of cell instabilities. The obtained rate constants are based on a simple skeleton model (eqn (2) and (3)); therefore, the constants in an actual example are likely not rate constant of elementary steps but some apparent rate constants that combine rate constants of several reactions and might include concentrations/coverages of chemical species. This limitation becomes obvious when electro-oxidation of small organic molecules (e.g., formic acid, methanol) is considered where there could be a large number of charge transfer and chemical reaction steps.1 Nonetheless, the
presented approach gives a possibility for the primary kinetic description; based on obtained dependencies of frequency on system parameters useful kinetic information can be extracted for model development and validation.

The hidden negative differential resistance oscillator with Ni electrode dissolution has a more complex mechanism than that of the negative differential resistance oscillator of Cu electrode dissolution. In HN-NDR systems there is a slow Faradaic process that masks the fast NDR chemical reaction. With analysis of a skeleton model of HNDR oscillators, we determined that in the square-root formula \( \omega \propto \sqrt{k(e^*/R)} \) the \( k \) value corresponds to the rate constant of the relaxation process of the inhibiting species. Moreover, the formula shall be corrected at large resistance values (eqn (21)) to account for the non-vanishing frequency. Nonetheless, for relatively small resistances the square-root formula can be used for the description of the frequencies of the oscillations.

The simple \( \omega \propto \sqrt{k(e^*)/R} \) square-root formula can be used to interpret the Arrhenius-type dependency of frequency on temperature observed with Ni electrode dissolution. We note that the prediction is approximate since performing the experiments at different temperatures in such a way that the Hopf bifurcation points would occur at the same electrode potential could be quite difficult. We also observed that the mean current of the oscillations (which is approximately equal to the mean current at the bifurcation points) also follows Arrhenius-type dependency on temperature. The apparent activation energy from frequency (46 kJ mol\(^{-1}\)) was very close to the activation energy from the mean current (49 kJ mol\(^{-1}\)). If we neglect the potential dependence in the \( \omega \propto \sqrt{k(e^*)/R} \) formula, it is expected that the apparent activation energy of the frequency is about half of the activation energy of the rate constant. The apparent activation energy of the current \( i_F = nFk(e)c \) comes from that of the rate constant and the near-surface concentration (or coverage). For example, at low overpotentials (kinetically controlled reaction) it would be expected that the activation energy of the current is about twice that of the activation energy of the frequency. In contrast, in the mass transfer limited region the activation energy is expected to be quite small (e.g., <20 kJ mol\(^{-1}\)) and related to the increased value of the diffusion coefficient. The experimentally observed similar apparent activation energy values from currents and frequency imply that activation energy of the current could stem from a mixed kinetic-mass transfer region. Therefore, the closeness of the activation energies from current and frequencies are likely to be coincidental. It is noted, however, that for methanol electro-oxidation\(^{20}\) and in a fuel cell\(^{21}\) similar experimental observations were made with activation energies about 50–70 kJ mol\(^{-1}\) for both frequency and current.

The Arrhenius-type dependence of frequency on temperature thus a direct consequence of the \( \omega \propto \sqrt{k(e^*)/R} \) relationship. For electro-oxidation of formic acid, temperature compensation and overcompensation were observed under galvanostatic control although the apparent activation energy of current was determined to be in the 50–80 kJ mol\(^{-1}\) range.\(^{18}\) The frequency of galvanostatic oscillations in our theory is approximated by \( \omega^* \propto \sqrt{1/d(e^*)} \), i.e., the slope of the polarization curve \( (d(e^*)/de) \) determines the frequency. Because in general the Faradaic current is not temperature compensated in an electrochemical system, this equation alone cannot interpret temperature (over)compensation of frequencies. It would be useful to test the temperature dependence of the slope of the polarization curve at the Hopf potentials in formic acid oxidation. If the slope exhibits temperature compensation, then the source of temperature compensation of frequency lies in the complicated reaction mechanism. However, if the slope does not exhibit temperature compensation, then the simple theory presented here cannot explain the experimentally observed variation of frequencies. Other explanations for temperature compensation could include the presence of a more complex reaction mechanism including additional positive or negative feedback loops and the deformation of oscillations due to global phase space/global bifurcation effects that are not considered in our approach based on local bifurcations. In particular, our treatment does not describe the extremely large period of oscillations close to homoclinic bifurcation point that can occur in H-NDR systems.

The formula obtained for the frequency of electrochemical oscillations (eqn (13)) could be interpreted in a simple way: the period of the oscillation is the geometric mean of the dominant chemical and electric time-scales present in the system. Here, the geometric mean, in contrast to, for example, arithmetic mean, is derived from the fact that close to Hopf bifurcation the frequency is the square root of the determinant of the Jacobian elements that contain the important system parameters. It is important to point out that for catalytic CO oxidation the oscillation frequency can also be approximated as the geometric mean of two important (chemical) time-scales in the system.\(^{33,34}\) The presence of geometric means in general formulae for periods/frequencies of oscillations thus appears as the geometric mean of two important (chemical) time-scales in the system.\(^{33,34}\) The presence of geometric means in general formulae for periods/frequencies of oscillations thus appears as the geometric mean of different nature; further investigations are required to explore whether there is a fundamental mathematical explanation for the geometric means of time-scales in the frequency of oscillations.

5. Conclusion

We have found that the frequencies of N-NDR and HN-NDR type of electrochemical oscillations can be approximated with relatively simple equations using bifurcation theories and the principle of critical simplification. Although the frequency equation was derived with skeleton models at the onset of oscillations, it was found to be useful for quantitative description of experimental oscillatory systems that has complicated reaction mechanisms. We expect that the presented theory can be extended to other types of electrochemical, chemical, and biological oscillations. For example, the description of frequency of S-NDR/truly potentiostatic electrochemical oscillations\(^1\) could help validate the proposed reaction mechanisms; oscillatory chemical systems could be designed\(^35\) with precise periods for potential applications in drug delivery\(^36,37\) and chemo-mechanical gel systems;\(^38,39\) mathematical equations for the frequency of rhythms in biological systems\(^9\) such as circadian oscillations, neuronal firing, and cell cycle could provide means for controlling the timing of physiological processes.
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