Bifurcation analysis
for a dissolution-depassivation mechanism

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Abstract

A new dissolution-depassivation mechanism showing a non-trivial complex S-shaped polarization curve due to the Frumkin isotherm hypothesis has been studied. A potential domain exists for sufficiently low values of the Frumkin interaction parameter where a negative differential resistance is observed. For this mechanism, the electrode potential acts as an essential system variable due to the double layer capacitance. Harmonic and relaxation oscillations can be observed for the dissolution-depassivation mechanism under galvanostatic control. Hopf bifurcation gives rise to oscillations under galvanostatic control only for sufficiently high values of the double layer capacitance. Bifurcation diagrams are plotted.

Key words
Hopf bifurcation, oscillation, double layer capacitance
1 Introduction

The existence of self-oscillations implies that the minimum phase space di-
mension of the system under study is two. Therefore electrochemical mech-
anisms proposed to explain self oscillating behaviour [1] involve at least two
electroactive species, species adsorbed onto the electrode [2, 3] or soluble
species from the electrolyte [4, 5]. Due to the double layer capacitance, elec-
trode potential is a phase space variable in the case of electrode potential
oscillations occurring under galvanostatic conditions.

This latter case has been studied recently by Strasser et al. [6] in an
article introducing a classification for electrochemical mechanisms giving rise
to oscillations under potentiostatic or galvanostatic conditions. Strasser et
al. define four classes of mechanisms:

- Class I, where the electrode potential is non-essential (i.e. the poten-
tial can be kept constant without altering the system dynamics qual-
itatively), while the essential variable (i.e. the variable for which the
time dependence is indispensable for the overall reaction dynamics) is
purely chemical,

- Class II, where the electrode potential is the essential variable with the
autocatalysis still still governed by chemical characteristics,

- Class III and IV, where the electrode potential is autocatalytic, with a
chemical species forming the slow negative feedback.

The peculiarity of Class II mechanisms is the role of the electrode poten-
tial. The slow negative feedback is provided by the double layer potential,
which makes it an essential system variable. For this reason under strictly potentiostatic conditions, i.e. in the absence of any ohmic potential drop in the electrolyte, all oscillatory behavior ceases. Class II oscillators contain a destabilizing mechanism involving potential-dependent chemical surface phase transitions that lead to deviation from the Langmuir adsorption isotherm due to species interactions in the adsorbate phase. When the electrode potential acts as an essential variable, electrochemical self-oscillating behaviour can be explained by electrochemical mechanisms involving only one electroactive species.

The aim of this paper is to study an example of a Class II mechanism. This mechanism shows a non-trivial complex S-shaped polarization curve. Some of the conclusions made by Strasser et al. are discussed.

2 Dissolution-depassivation mechanism

D. Schuhmann [7] has proposed a metal dissolution-passivation mechanism made of two steps:

\begin{equation}
M,s \rightarrow M^{n_1+} + s + n_1 e^{-}
\end{equation}

\begin{equation}
M,s + A^{n_2-} \leftrightarrow MA,s + n_2 e^{-}
\end{equation}

where s and M,s denote a free site. The first step describes the oxidation of the metal on the bare surface and the second the adsorption of the adsorbate A. The active-to-passive transition shown by this mechanism has been studied by D. D. Macdonald [8] and the concepts of identifiability and distinguishability have been used to study this mechanism [9]. It has been shown that the dissolution-passivation mechanism may present a complex...
N-shaped current vs. electrode potential curve [10, 11], i.e. a curve with mutisteady-states under potentiostatic control (PC) or galvanostatic control (GC), giving rise to a discontinuous electrode impedance under the Frumkin hypotheses [12].

Let us consider the mechanism obtained when the second step (Eq. 2) is replaced by the depassivation reaction:

\[ MA_s \leftrightarrow M_s + A^{n_{2+}} + n_2 e^- \]  \[ (3) \]

As will be shown below (Fig. 1), the electrode is nearly completely covered by the adsorbate A for the most negative potential and the electrode is therefore passive. As the electrode potential increases, the coverage ratio decreases and the electrode is depassivated. This mechanism will therefore be called the DD mechanism (dissolution-depassivation) mechanism hereafter.

The interfacial concentration of \( A^{n_{2+}} \) species is assumed to be constant in the electrolyte and equal to the standard concentration of 1 mol L\(^{-1}\). The dimensionless Faradaic current density \( \Psi_F(\tau) \) is given by:

\[ \Psi_F(\tau) = \frac{j_F(\tau)}{(n_2 F \Gamma \kappa_{02})} = \Psi_1(\tau) + \Psi_2(\tau) \]  \[ (4) \]

where \( \Psi_1 \) and \( \Psi_2 \) are the dimensionless current for the first and second step, with \( \tau = \kappa_{02} t \). \( \kappa_{02} \) is the standard rate constant of the depassivation reaction and \( \Gamma \) the number of electrosorption sites per unit area. The first step of the reaction is assumed to be irreversible and the dimensionless current for this step is given by:

\[ \Psi_1(\tau) = \frac{j_1(\tau)}{(n_2 F \Gamma \kappa_{02})} = \Lambda \ (1 - \theta(\tau)) \ \exp \left( \alpha_{01} n_1 \xi(\tau) \right) \]  \[ (5) \]
where \( \theta \) is the coverage ratio of the adsorbate, \( \xi \) the dimensionless electrode potential given by:

\[
\xi(\tau) = f(E(\tau) - E^\circ_2); \quad f = F/(RT)
\]

and:

\[
\Lambda = n_1 k_{o1} \exp(\alpha_{o1} n_1 fE^\circ_2)/(n_2 k^\circ_2)
\]

\( \alpha_{o1} \) is the symmetry factor of the first electron transfer step in the oxidation direction and \( E^\circ_2 \) is the formal potential of the depassivation reaction. Assuming the rate constants of the second step change with the coverage ratio of the adsorbate according to the Frumkin hypotheses, the dimensionless current density for the depassivation reaction is given by:

\[
\Psi_2(\tau) = j_2(\tau)/(n_2 FT k^\circ_2) = \theta(\tau) \exp(\alpha_{o2} n_2 \xi(\tau) + g(\theta(\tau) - 1/2)/2) - \\
(1 - \theta(\tau)) \exp (-\alpha_{r2} n_2 \xi(\tau) - g(\theta(\tau) - 1/2)/2)
\]

\( g \) is the Frumkin interaction parameter, \( g > 0 \) (\( g < 0 \)) corresponds to the repulsive (attractive) interaction between the adsorbed species and \( g = 0 \) corresponds to the Langmuir isotherm. The sign of \( g \) is chosen as negative for attractive interaction, the dominant convention in the literature, in opposition with its original definition [13, 14].

The differential equation for the coverage ratio of the adsorbate is given by:

\[
\frac{d\theta}{d\tau} = -\Psi_2(\tau)
\]

and the overall current density \( \Psi(\tau) \) by:

\[
\Psi(\tau) = \Psi_F(\tau) + K_{dc} \frac{d\xi}{d\tau}
\]

5
where $K_{dc}$ is the dimensionless double layer capacitance with:

\[ K_{dc} = \frac{C_{dc}}{(n_1 n_2 f F \Gamma)} \]  

Eqs. (9) and (10) can be compared to Eqs. (13) and (14) in Ref. [6], with $g = -\gamma$, taking into account that the current associated with the electrodeesorption process is not neglected in this article in contrast with Ref. [6].

3 Steady-state

Under steady-state conditions, we have $d\theta/d\tau = 0$, $\Psi_2 = 0$ and $\Psi = \Psi_1 = \Psi_F$. Any steady-state corresponds to equilibrium for the depassivation step (Eq. 3). The classical expression for the dimensionless potential $\xi$ as a function of the fractional coverage $\theta$ is obtained from Eqs. (8) and (9) [15, 16, 17] as:

\[ \xi(\theta) = \frac{1}{n_2} \ln \left( \frac{1 - \theta}{\theta} \right) - \frac{g}{n_2} \left( \theta - \frac{1}{2} \right) \]  

which, combined with Eq. (13):

\[ \Psi_F(\theta) = \Psi_1(\theta) = \Lambda (1 - \theta) \exp (\alpha o_1 n_1 \xi(\theta)) \]  

leads to the parametric equation of the steady-state current density vs. potential relationship.

For $g < g_{c\xi} = -4$, the $\theta$ vs. $\xi$ and $\Psi$ vs. $\xi$ curves show multisteady-states under PC (Fig. 1). The classical values for the bifurcation turning point coverage ratio [15], $\theta_{b\xi_1}$ and $\theta_{b\xi_2}$, are given by (Fig. 2):

\[ \theta_{b\xi_{1,2}} = \frac{1 \pm \sqrt{1 + 4/g}}{2} \]  

6
The bifurcation diagram shown in Fig. 2 has been plotted using Eq. (14).

For sufficiently low values of $g$, the steady-state current density vs. electrode potential curve shows multisteady-states under GC, giving rise to a so-called complex S-shaped steady-state current vs. potential curve [6], as is shown in Fig. 1 plotted for $g = -9$. The values $\theta_{b\Psi_1}$ and $\theta_{b\Psi_2}$ for the galvanostatic turning points are obtained by determining the $\theta$ values which cancel the derivative of Eq. (13) with respect to $\theta$ (Fig. 2). This gives:

$$
\theta_{b\Psi_{1,2}} = \frac{n_2 + gn_1 \alpha_{o1} \pm \sqrt{4g n_1^2 \alpha_{o1}^2 + (n_2 + gn_1 \alpha_{o1})^2}}{2gn_1 \alpha_{o1}} 
$$

(15)

The closed form galvanostatic multisteady-state condition is obtained, writing $\theta_{b\Psi_1} = \theta_{b\Psi_2}$, as

$$
g < g_{c\Psi} = \frac{-n_2 - 2n_1 \alpha_{o1} \pm 2\sqrt{n_1 \sqrt{\alpha_{o1}} \sqrt{n_2 + n_1 \alpha_{o1}}}}{n_1 \alpha_{o1}}
$$

(16)

$g_{c\Psi}$ is equal, for example, to $-7.4641$ for $\alpha_{o1} = 1/2$ and $n_1 = n_2 = 1$ according to the numerical value, $\gamma = 7.5$, given by Strasser et al. [6]. The zone for multisteady-state GC shown in Fig. 2 has been plotted using Eq. (15). The GC bistable region has a classical V-shaped form in the $g$ vs. $\Psi/\Lambda$ plane.

The polarisation resistance $R_p^*$, i.e. the reciprocal of the derivative of $\Psi$ with respect to $\xi$, is negative between the two curves defining potentiostatic and galvanostatic multisteady-states (Fig. 2), i.e. there is a region of potential with a negative differential resistance (NDR).

In conclusion, depending on the $g$ value, the steady-state current vs. potential curve may be a single-valued ($g > -4$), S-shaped ($-4 > g > g_{c\Psi}$) or complex S-shaped ($g < g_{c\Psi}$) curve.
4 Stability study

4.1 DD mechanism impedance

The Faradaic dimensionless impedance $Z_F^*(S) = n_2 f F \Gamma k^o_2 Z_F$ calculated using the method proposed by Gerisher [18] and Mehl and developed by Schuhmann [7], Epelboin and Keddam [19], is written:

$$Z_F^*(S) = R_t^* + \frac{R_p^*}{1 + R_p^* C_\theta^* S} = \frac{S + \Psi_{2\theta}}{\Psi_{1\xi} \Psi_{2\theta} - \Psi_{2\xi} \Psi_{1\theta} + S (\Psi_{1\xi} + \Psi_{2\xi})}$$

(17)

with:

$$R_t^* = \frac{1}{\Psi_{1\xi} + \Psi_{2\xi}} ; \quad R_p^* = \frac{\Psi_{2\theta}}{\Psi_{1\xi} \Psi_{2\theta} - \Psi_{1\theta} \Psi_{2\xi}}$$

(18)

$$R_\theta^* = R_p^* - R_t^* ; \quad C_\theta^* = \frac{(\Psi_{1\xi} + \Psi_{2\xi})^2}{\Psi_{2\xi} (\Psi_{1\theta} + \Psi_{2\theta})}$$

(19)

where $\Psi_{ix} = \partial \Psi_i / \partial x$. $S$ is the dimensionless Laplace variable, $S = i \Omega = i \omega / k^o_2$ with $i = \sqrt{-1}$ and $\omega$ denotes the angular frequency. The partial derivatives are obtained from Eqs. (4) and (8):

$$\Psi_{1\xi} = \alpha_{o1} n_1 \Lambda (1 - \theta) \exp (\alpha_{o1} n_1 \xi(\theta))$$

(20)

$$\Psi_{2\xi} = \alpha_{o2} n_2 \theta \exp (\alpha_{o2} n_2 \xi(\theta) + g(\theta - 1/2)/2) + \alpha_{r2} n_2 (1 - \theta) \exp (-\alpha_{r2} n_2 \xi(\theta) - g(\theta - 1/2)/2)$$

(21)

$$\Psi_{1\theta} = -\Lambda \exp (\alpha_{o1} n_1 \xi(\theta))$$

(22)

$$\Psi_{2\theta} = (1 + g (1 - \theta)/2 + (1 + g \theta/2) \exp (n_2 \xi(\theta) + g (\theta - 1/2))) \times \exp (-\alpha_{r2} n_2 \xi(\theta) - g (\theta - 1/2)/2)$$

(23)
The dimensionless electrode impedance $Z^*(S)$, taking into account the double layer capacitance, is given by:

$$Z^*(S) = Z_F^*(S)/(1 + S K_{dc} Z_F^*(S))$$  \hfill (24)$$

and therefore, from Eqs. (17) and (4.1):

$$Z^*(S) = \frac{S + \Psi_2}{\Psi_1 \Psi_2 - \Psi_1 \Psi_2 + (\Psi_1 + \Psi_2 + K_{dc} \Psi_2)S + K_{dc} S^2}$$  \hfill (25)$$

4.2 Poles and zeros of the transfer function, eigenvalues of the Jacobian matrix

The stability of a steady-state under an infinitesimal perturbation is studied classically using the eigenvalues of the Jacobian matrix of the system of equations describing the dynamic behaviour of the electrochemical system around a steady-state point [40, 6]. The number of zeros in the Jacobian matrix indicates the presence of multiple steady-states and the sign indicates steady-state stability.

On the other hand, a system is stable when the real parts of all the poles of its transfer function are negative. The poles of a transfer function are the roots of the denominator. Information on system stability for a potential (current) input is therefore obtained by studying the poles (zeros) of the electrode admittance or the zeros (poles) of the electrode impedance [32, 33]. The different possible shapes of the impedance diagram have been studied for an electrochemical reaction with two adsorbed species analysing the position of impedance poles and zeros in the s (Laplace variable)-plane [31]. On the other hand, Sadkowski [14] proposed a criterion for inductive behaviour in
the low frequency domain based on the respective position of impedance poles and zeros.

Koper proposed a bifurcation criterion based on the Nyquist diagram of the electrode impedance [1, 30]. Under PC, an electrochemical reaction will exhibit a saddle-node bifurcation when \( Z(\omega) = 0 \) for \( \omega = 0 \), or alternatively a Hopf bifurcation when \( Z(\omega) = 0 \) for \( \omega = \omega_H \neq 0 \). Under GC, the same criterion applies with the admittance in place of the impedance. This criterion has been applied to a simple electrocatalytic reaction [1, 4, 30] and a Ni dissolution-passivation reaction [32]. In contrast to the Jacobian matrix, electrochemical impedance correspond to an experimental data, and it is possible to predict the stability of the GC steady-state from impedance measurement under PC as has already been shown for the study of Ni oxidation in an \( \text{H}_2\text{SO}_4 \) medium [32].

The denominator of the electrode impedance for the DD mechanism is a second degree polynomial with respect to \( S \) and the numerator a first degree polynomial with respect to \( S \). The electrode impedance therefore has two poles and a zero. The poles are given by:

\[
S_p = \frac{1}{2K_{dc}} \left( -\Psi_{1\xi} - K_{dc} \Psi_{2\theta} - \Psi_{2\xi} \pm \right.
\frac{\sqrt{(\Psi_{1\xi} + K_{dc} \Psi_{2\theta} + \Psi_{2\xi})^2 - 4K_{dc}(\Psi_{1\xi} \Psi_{2\theta} - \Psi_{2\xi} \Psi_{1\theta})}}{2K_{dc}} \right)
\]  

(26)

The poles depend on the \( K_{dc} \) value and may be real or complex. The zero is given by:

\[
S_z = -\Psi_{2\theta}
\]

(27)

The zero is real and independent of the \( K_{dc} \) value. The change with elec-
trode potential of the zero $S_z$ (linear stability for potentiostatic regulation) and the poles $S_p$ (linear stability for galvanostatic regulation) is presented in Fig. 4, 6 and 9. This representation of the change of poles and zeros with potential has been introduced to carry out bifurcation analysis for the Volmer-Heyrovsky mechanism [23] and can be used when the poles or zeros of the electrode impedance are complex, given that it is always possible to plot the variation in the real part of the impedance poles or zeros with the electrode potential.

5 Bifurcation analysis

5.1 Single-valued steady-state curve

The current density vs. electrode potential curve is a single-valued function for $g > -4$. As shown in Fig. 4, the real part of the poles and the zero of electrode impedance are negative, whatever the value of the dimensionless capacitance $K_{dc}$, and therefore the DD mechanism is stable, under PC or GC. Hence, the steady-state curve may be plotted both under PC and GC.

Impedance diagrams are inductive for a certain range of electrode potential as shown in Figs. 3, 5, 8. Such diagrams show inductive behaviour although the coverage ratio vs. electrode potential curve does not show any maximum. The DD mechanism is therefore a counter-example to the "general rules" given by Conway et al. to explain the inductive behaviour of Faradaic impedance, which are based on the observation of the slope of the steady-state coverage ratio vs. electrode potential curve [20, 21, 22].
5.2 Potentiostatic multisteady-state curve

The current density vs. potential curve is a potentiostatic multisteady-state curve for $g_{c\psi} < g < g_{c\xi} = -4$. The steady-state curve shows a negative differential resistance (NDR), i.e. the polarisation resistance $R^*_p$ is negative, over a range of potential for the steady-state S-shaped current vs. electrode potential curve. The impedance diagram has an unusual shape (Fig. 5 left, diagrams c, d), characteristic of a non-minimum phase-shift system in parallel with a capacitance, which has been predicted by Strasser et al. [6]. The stability of such a system is investigated in Appendix A. It has been shown that the Volmer-Heyrovsky mechanism studied under Frumkin isotherm conditions may exhibit this unusual impedance diagram shape (See Fig. 3, diagram b of [23]). The V-H mechanism exhibits a steady-state loop-shaped current vs. potential curve. This loop-shaped curve is another non-trivial steady-state current vs. electrode potential curve [24]. This loop-shaped steady-state curve has been studied by Wacker et al. [25] but not by Strasser et al. [6].

**Potentiostatic control**  Depending on the $g$ value, an electrode potential domain exists such that steady-states for the DD mechanism become unstable under PC as is shown by the change of the zero of the electrode impedance with the coverage ratio $\theta$ (Fig. 6). Under PC, a pair of steady-state points, one stable and one unstable, come together and disappear as the potential is varied, giving rise to a saddle-node bifurcation [26, 27, 28, 29].
Galvanostatic control  For a low value of the dimensionless double-layer capacitance \( K_{dc} = 10^{-2} \) for example, as in Fig. 5 left and Fig. 6a-c) the real part of the poles of the electrode impedance are negative whatever the \( \theta \) value. Therefore the steady-state curve and the impedance diagrams can be plotted under GC for a sufficiently low value of the double layer capacitance as is shown by the change with \( \theta \) of the real part of the pole of the electrode impedance (Fig. 6a-c).

This is not the same for higher values of the dimensionless capacitance \( K_{dc} > 1 \) for example, as in Fig. 5 right and Fig. 6d-f). For such high \( K_{dc} \) values the real part of the complex poles of the electrode impedance becomes positive giving rise to a Hopf bifurcation. The characteristic equation for a Hopf bifurcation can be deduced from Eq. (26) by cancelling the real part of the poles. This gives:

\[
\Psi_{1\xi} + \Psi_{2\xi} + K_{dc} \Psi_{2\theta} = 0
\]  

(28)

Steady-state conditions correspond to equilibrium conditions for depassivation step Eq. (3). The partial derivative is therefore simplified:

\[
\Psi_{2\theta}/\Psi_{2\xi} = -d\xi/d\theta
\]  

(29)

and Eq. (28) becomes:

\[
1 + \Psi_{1\xi}/\Psi_{2\xi} = K_{dc} d\xi/d\theta
\]  

(30)

and, from Eqs. (20), (21) and (23) we have for \( n_1 = n_2 = 1 \):

\[
1 + K_{dc} \left( g + \frac{1}{\theta - \theta^2} \right) + \exp \left( \frac{(-1 + 1/\theta)^{1+\alpha_{o1} - \alpha_{o2}} \Lambda \alpha_{o1}}{g (-1 + 2 \theta) (1 + 2 \alpha_{o1} - 2 \alpha_{o2})} \right) = 0
\]  

(31)

13
The equation for the locus of Hopf bifurcation in the $g$ vs. $\theta$ plane can be written in closed form for $n_1 = n_2 = 1$, solving Eq. (31) with respect to $g$ as:

$$
g = -\frac{1}{K_{dc}} - \frac{1}{\theta - \theta^2} - \frac{1}{(1 - 2 \theta) (1 + 2 \alpha_{o1} - 2 \alpha_{o2})}$$

$$
\times 4 W \left( \frac{(-1 + 1/\theta)^{\alpha_{o1} - \alpha_{o2}} (1 - 3 \theta + 2 \theta^2) \Lambda \alpha_{o1} (1 + 2 \alpha_{o1} - 2 \alpha_{o2})}{4 \exp \left( \frac{(-1 + 2 \theta) (K_{dc} + \theta - \theta^2) (1 + 2 \alpha_{o1} - 2 \alpha_{o2})}{4 K_{dc} (-1 + \theta) \theta} \right) K_{dc} \theta} \right)
$$

(32)

where $W(z)$ denotes the product log function giving the solution for $w$ in $z = w \exp(w)$ [35]. The Hopf bifurcation locus plotted in Fig. 2 is calculated for $K_{dc} = 1$ corresponding to Fig. 6d. The Hopf bifurcation locus encircling the oscillatory region loops around the tip of the saddle-node V. On the left side of the V, the Hopf bifurcation locus is very close to the saddle-node V [41, 42].

Koper’s criterion is suitable for the study of DD mechanism stability. A discontinuous impedance diagram exists necessarily between diagrams b and c in Fig. 5. Two points of the impedance diagram tend towards infinity. Therefore, the admittance diagram passes through the origin of the complex plane for a non-zero value of the dimensionless angular frequency $\Omega_H$. The steady-state becomes unstable under GC, the trajectory of the system tends toward a limit cycle in the phase space and the angular frequency of the electrode potential oscillations is equal to $\Omega_H$. $\Omega_H = 0.45$, obtained numerically in the case of Fig. 7. This frequency is such that $\text{Re} \ Z_f = \text{Re} \ Y_f = 0$ (cf. Appendix A).
5.3 Galvanostatic multisteady-state curve

For $\alpha_{o1} = 1/2$, $n_1 = n_2 = 1$ and $g < g_{e\psi} = -7.4641$ the steady-state current vs. electrode potential curve is complex S-shaped. This curve presents multisteady-states both under PC and GC and cannot be entirely plotted under PC or GC.

**Potentiostatic control**  The change of the zero of the electrode impedance with the coverage ratio $\theta$ is analogous to the case studied in paragraph 5.2

**Galvanostatic control**  For steady-state complex S-shaped current vs. electrode potential curves the potential domain such that $R_p^* < 0$ has two different parts, one of them being very narrow (Fig. 2). For increasing current values, the shape of electrode impedance diagram becomes again (Fig. 8 left diagrams b and c), characteristic of a non-minimum phase-shift system in parallel with capacitance as for PC multisteady-state curves. It is therefore possible to find a high value of the double layer capacitance giving rise to Hopf bifurcation.

For a higher current density, a saddle-node bifurcation is observed for a current value very close to the current density corresponding to the Hopf bifurcation. An admittance diagram such that $Y(\omega) = 0$ for $\omega = 0$ exists necessarily between diagrams c and d in Fig. 8. Impedance diagrams plotted after $R_p$ becomes positive again (Fig. 8 diagrams d-f left) correspond to unstable PC and GC. These diagrams have been known for a long time [39]. They have already been simulated for a Volmer-Heyrovsky reaction loop-shaped current vs. potential steady-state curve [23].
An equivalent behaviour with successively Hopf and Saddle-Node bifurcation is encountered when studying by decreasing values of the current.

6 Linear sweep voltammetry simulation

In order to check the stability study using the above method it is possible to simulate the response of the DD mechanism to a perturbation superimposed on steady-state conditions [5, 40]. It is also possible to simulate the voltammetric response of the electrochemical reaction under PC or GC.

Considering linear potential sweep voltammetry, the electrode potential changes at a constant rate and the coverage ratio vs. potential relationship is derived from the differential equation:

$$\nu_\xi \frac{d\theta(\xi)}{d\xi} = -\Psi_2(\xi)$$  \hspace{1cm} (33)

and:

$$\Psi(\xi) = \Psi_F(\xi) + \nu_\xi K_{dc} = \Psi_1(\xi) + \Psi_2(\xi) + \nu_\xi K_{dc}$$  \hspace{1cm} (34)

where \( \xi = \xi_i + \nu_\xi \tau \). \( \nu_\xi \) is the reduced scan rate given by \( \nu_\xi = \nu_b f/k^o \) and \( \xi_i \) the initial value of the electrode potential.

Considering alternatively linear current sweep voltammetry, the current density changes at a constant rate \( \Psi = \Psi_i + \nu_\Psi \tau \) and the coverage ratio vs. current relationship is obtained from:

$$\nu_\Psi \frac{d\theta(\Psi)}{d\Psi} = -\Psi_2(\Psi)$$  \hspace{1cm} (35)

where \( \nu_\Psi = \nu_b/(n_1 f \Gamma k^o \tau) \) with:

$$\Psi = \nu_\Psi \tau = \Psi_F + \nu_\Psi K_{dc} \frac{d\xi(\Psi)}{d\Psi}$$  \hspace{1cm} (36)
LSV simulations are carried out below, using the NDSolve function of Mathematica software [35], for the parameter values corresponding respectively to potentiostatic and galvanostatic multisteady-state curves.

6.1 Potentiostatic multisteady-state curve

6.1.1 Potentiostatic control

The voltammograms shown in Fig. 10 are calculated for different values of the potential scan rate and a value of \( g < g_{c\xi} \). The jump observed for the smallest value of the scan rate is transformed into a current spike as the scan rate increases. This result is encountered for all the PC multisteady-state curves. It has been studied for loop-shaped current vs. potential curve [23].

6.1.2 Galvanostatic control

For low values of \( K_{dc} \), i.e. values such that the real part of the pole is negative whatever \( \theta \), steady-state points are stable under GC. The steady-state current vs. electrode potential curve is correctly plotted for sufficiently low values of the scan rate. Nevertheless it is possible to observe oscillations around the steady-state current vs. potential curve for high current sweep rates as shown in Fig. 11 for the dimensionless sweep rate \( v_\Psi = 2 \times 10^{-2} \).

For higher values of \( K_{dc} \), the sign of the real part of the complex poles changes, then the impedance poles of the electrode impedance become real again. The observation of oscillations and their shapes depends on the current
sweep rate [36, 37, 38]. Oscillation is harmonic in the case of Fig. 12 and
the enlargement shows that the Hopf bifurcation is supercritical.

6.2 Galvanostatic multisteady-state curve

6.2.1 Potentiostatic control

Potentiostatic behaviour is similar to that observed for an S-shaped current
vs. electrode potential. (Fig. 10). Therefore complex S-shaped curves can-
not be studied under PC.

6.2.2 Galvanostatic control

The coverage ratios $\theta$ of Hopf and saddle-node bifurcations are very close,
therefore either a saddle-node bifurcation or a Hopf bifurcation is observed
depending on the $K_{dc}$ value.

For sufficiently low values of $K_{dc}$, the real part of the impedance poles
changes sign for real poles (Fig 9a-c) and a saddle-node bifurcation is observed.
The potential jump observed for the smallest value of the scan rate
is transformed into a potential spike as the scan rate increases. (Fig. 13).

For high values of $K_{dc}$, the real part of the impedance poles changes
sign for complex poles (Fig. 14) and a Hopf bifurcation is observed, giving
rise to electrode potential oscillations. Poles are complex only for a very
narrow range of coverage ratios (Fig. 9d) and the oscillations are relaxation
oscillations. It is not possible to observe harmonic oscillation even for very
low values of $\nu_b$. Such a behaviour has already been encountered for the
Koper-Sluyters electrocatalytic reaction [4, 5].

7 Discussion

In this article, an example of a Class II mechanism, according to Strasser’s classification [6], has been studied. This dissolution-depassivation mechanism shows a non-trivial complex S-shaped polarization curve due to Frumkin isotherm hypothesis. A potential domain exists for sufficiently low values of the Frumkin interaction parameter where a negative differential resistance is observed. For this mechanism, the electrode potential acts as an essential system variable under GC, due to the double layer capacitance. It has been shown that it is possible to observe harmonic and relaxation oscillations for the mechanism.

It has also been shown that Hopf bifurcations only give rise to oscillations under GC for sufficiently high values of the double layer capacitance. The $K_{dc}$ values giving rise to self oscillating behaviour appear to be somewhat unrealistic. As noted by Strasser et al [34], usually the relative time scale of the electrode potential and $\theta$ is very small, which makes the electrode potential a fast variable. The value of the dimensionless capacitance is given by Eq. (11) above. For typical values of the parameters: $C_{dc} = 50 \, \mu F \, cm^{-2}$, $n_1 = n_2 = 1$, $f = 40 \, V^{-1}$ and $\Gamma = 10^{-9} \, mol \, cm^{-2}$, we obtain $K_{dc} \approx 10^{-2}$. As shown in Fig. 6 and 9, the values of $K_{dc}$ giving rise to Hopf bifurcation are $K_{dc} > 0.56$ for $g = -6$ and $K_{dc} > 0.17$ for $g = -9$, therefore the typical value $K_{dc} \approx 10^{-2}$ is less than the value giving rise to electrode potential oscillations. Therefore electrode potential oscillations observed experimentally for the DD
reaction can be envisaged only for very low values of the Frumkin parameter, *i.e.* for a very strong attractive interaction in the adsorbate layer.

Double layer capacitance can play the same role for mechanisms that behave as systems with non-minimum phase shift. Therefore oscillations due to double layer capacitance should be expected for the Volmer-Heyrovsky mechanism taking into account Frumkin hypothesis.

**A Stability of a non-minimum phase-shift system in parallel with a capacitance**

Let us consider the Faradaic impedance:

\[
Z_F(s) = \frac{R(\tau_1 s - 1)}{\tau_2 s + 1}
\]

with \(R, \tau_1, \tau_2 > 0\), characteristic of a non-minimum phase-shift system, *i.e.* a stable system with one zero and a positive real part. The impedance \(Z\) of \(Z_F\) in parallel with a capacitance \(C\) is given by:

\[
Z(s) = \frac{R(\tau_1 s - 1)}{1 + (\tau_2 - \tau) s + \tau \tau_1 s^2}
\]

with \(\tau = RC\). The poles \(s_p\) of \(Z\) are given by:

\[
s_p = \frac{\tau - \tau_2 \pm \sqrt{\tau_1 (\tau + \tau_2)^2}}{2 \tau_1}
\]

The real part of the complex poles cancels, *i.e.* the poles are imaginary, for \(\tau = \tau_2\) (Eq. (39)). Fig. 15 shows the change of the impedance diagram with \(\tau\), that is with the capacitance \(C\). For low values of \(\tau\), the impedance diagram passes successively through quadrants III, IV and I for increasing
frequencies. For high values of $\tau$ ($\tau > \tau_2$) the impedance diagram visits successively quadrants III, II and I by increasing frequencies. The system with impedance $Z$ is therefore unstable as shown in Fig. 16 by the change of the real part of the pole with $\tau$.

As shown in Fig. 15, the impedance diagram plotted for the bifurcation value of $\tau$ ($\tau = \tau_2$) is discontinuous. The point corresponding to $\omega = \omega_H$ tends towards infinity. The admittance ($Y = 1/Z$) diagram therefore passes through the origin of the complex plane for a non-zero angular frequency value and, according to Koper’s criterion [1, 30], gives rise to a Hopf bifurcation. The Hopf angular frequency $\omega_H$ is such that $Y = 0$. The real and imaginary part of the admittance are given by:

$$\text{Re} \ Y = \frac{-1 + \omega^2 \tau_1 \tau_2}{R \left(1 + \omega^2 \tau_1^2\right)} \quad (40)$$

$$\text{Im} \ Y = \frac{\omega \left(\tau + \tau_1 \left(-1 + \tau \omega^2 \tau_1 - \tau_2\right) \right)}{R \left(1 + \omega^2 \tau_1^2\right)} \quad (41)$$

and the admittance diagram passes through the complex plane origin ($\text{Re} \ Y = \text{Im} \ Y = 0$) for $\tau = \tau_2$ and $\omega_H = 1/\sqrt{\tau_1 \tau_2}$. Eqs. (42) and (43):

$$\text{Re} \ Z_F = \frac{R \left(-1 + \omega^2 \tau_1 \tau_2\right)}{1 + \omega^2 \tau_2^2} \quad (42)$$

$$\text{Re} \ Y_F = \frac{-1 + \omega^2 \tau_1 \tau_2}{R \left(1 + \omega^2 \tau_1^2\right)} \quad (43)$$

showing that $\text{Re} \ Z_F = 0$ and $\text{Re} \ Y_F = 0$ for $\omega = \omega_H$.

**References**


Figure captions

Figure 1: Change in coverage ratio of the adsorbate with $\xi$ (left) and steady-state current vs. potential curves (right) for $g = 0, -4, -6, -9$ (curve thickness increases with decreasing $g$), $\alpha_{o1} = 1/2$ and $n_1 = n_2 = 1$.

Figure 2: Bifurcation diagram in the $g$ vs. $\xi$ plane (left) and in the $g$ vs. $\Psi/\Lambda$ plane (right). b: galvanostatic multisteady-state domain, a $\cup$ b: potentiostatic multisteady-state. $\Lambda = 1$, $\alpha_{o1} = \alpha_{o2} = 1/2$, $n_1 = n_2 = 1$. Thick solid lines: potentiostatic saddle-node bifurcation, thin solid lines: galvanostatic saddle-node bifurcation, dashed lines: Hopf bifurcation ($K_{dc} = 1$).

Figure 3: Dimensionless representation of the steady-state current density vs. potential curve (left). Electrode impedance (thick line) and Faradaic impedance (thin line) diagrams (right) plotted using the Nyquist representation. $g = -3$, $K_{dc} = 10^{-1}$, $\alpha_{o1} = \alpha_{o2} = 1/2$, $n_1 = n_2 = 1$.

Figure 4: Change of the real part of the poles (thick lines) and the zero (thin line) of the electrode impedance with $\xi$ for $g = -3$, $\alpha_{o1} = \alpha_{o2} = 1/2$,
\[ n_1 = n_2 = 1 \text{ and } K_{dc} = 0.032 \text{ (a), 0.1 (b), 0.32 (c), 1. (d), 3.2 (e), 10. (f).} \]

Figure 5: Dimensionless representation of the steady-state current density vs. potential curve (left). Electrode impedance (thick line) and Faradaic impedance (thin line) diagrams (right) plotted using the Nyquist representation for a low value of \( K_{dc} (K_{dc} = 10^{-2}, \text{ left}) \) and a high value of \( K_{dc} (K_{dc} = 1, \text{ right )}. \) \( g = -6, \alpha_{o1} = \alpha_{o2} = 1/2, n_1 = n_2 = 1. \)

Figure 6: Change of the real part of the poles (thick lines) and the zero (thin line) of the electrode impedance with \( \xi \) for \( g = -6, \alpha_{o1} = \alpha_{o2} = 1/2, n_1 = n_2 = 1 \text{ and } K_{dc} = 0.032 \text{ (a), 0.1 (b), 0.32 (c), 1. (d), 3.2 (e), 10. (f).} \)

Figure 7: Immittance diagrams for the Hopf bifurcation electrode potential. Electrode impedance (thick line), Faradaic impedance (thin line) (left), electrode admittance (thick line) and Faradaic admittance (thin line) diagrams (right) plotted for a high value of \( K_{dc} (K_{dc} = 1) \) and \( g = -6, \alpha_{o1} = \alpha_{o2} = 0.5, n_1 = n_2 = 1. \) \( \Omega_H = 0.45. \) The arrows indicate the direction of increasing frequency.

Figure 8: Dimensionless representation of the steady-state current density vs. potential curve (left). Electrode impedance (thick line) and Faradaic impedance (thin line) diagrams (right) plotted using the Nyquist representation for a low value of \( K_{dc} (K_{dc} = 10^{-2}, \text{ left}) \) and a high value of \( K_{dc} (K_{dc} = 1 \text{ right)}. \) \( g = -9, \alpha_{o1} = \alpha_{o2} = 1/2, n_1 = n_2 = 1 \)

Figure 9: Change of the real part of the poles (thick lines) and the zero (thin line) of the electrode impedance with \( \xi \) for \( g = -9, \alpha_{o1} = \alpha_{o2} = 1/2, \)
\[ n_1 = n_2 = 1 \text{ and } K_{dc} = 0.032 \text{ (a), 0.1 (b), 0.32 (c), 1. (d), 3.2 (e), 10. (f)}. \]

Figure 10: Potentiodynamic linear sweep voltammograms for an S-shaped steady-state \( \psi/\Lambda \) vs. \( \xi \) curve and different values of the potential scan rate. 
\[ \alpha_{o1} = \alpha_{o2} = 1/2, \ n_1 = n_2 = 1, \ g = -6 \text{ and } \nu_\xi = 10^{-2}, 3 \times 10^{-1}, 1 \text{ (curve thickness increases with increasing } \nu_\xi \text{), dashed lines: steady-state curve}. \]

Figure 11: Galvanodynamic linear sweep voltammograms for an S-shaped steady-state \( \psi/\Lambda \) vs. \( \xi \) curve and different values of the current scan rate for a low value of \( K_{dc} \) and \( g = -6, \ K_{dc} = 0.745, \ \alpha_{o1} = \alpha_{o2} = 1/2, \ n_1 = n_2 = 1, \ \nu_\psi = 10^{-3}, 10^{-2}, 2 \times 10^{-2} \text{ (curve thickness increases with increasing } \nu_\psi \text{), dashed lines: steady-state curve}. \]

Figure 12: Galvanodynamic linear sweep voltammograms for an S-shaped steady-state \( \psi/\Lambda \) vs. \( \xi \) curve, a high value of \( K_{dc} \) and \( \alpha_{o1} = \alpha_{o2} = 0.5, \ n_1 = n_2 = 1, \ g = -6, \ K_{dc} = 1, \ \nu_\psi = 10^{-4}. \) Enlargement of the oscillation beginning in the insert.

Figure 13: Galvanodynamic linear sweep voltammograms for a complex S-shaped steady-state \( \psi/\Lambda \) vs. \( \xi \) curve and different values of the current scan rate. Low value of \( K_{dc} \) (\( K_{dc} = 10^{-2} \)) and \( g = -9, \ \alpha_{o1} = \alpha_{o1} = 1/2, \ n_1 = n_2 = 1, \ \nu_\psi = 10^{-4}, 10^{-2}, 10^{-1} \text{ (curve thickness increases with increasing } \nu_\psi \text{), dashed lines: steady-state curve}. \]

Figure 14: Galvanodynamic linear sweep voltammograms for a complex S-shaped steady-state \( \psi/\Lambda \) vs. \( \xi \) curve. High value of \( K_{dc} \) (\( K_{dc} = 1 \)) and \( \alpha_{o1} = \alpha_{o1} = 1/2, \ n_1 = n_2 = 1, \ \nu_\psi = 10^{-4}. \) Enlargement of the beginning of
the oscillation in the insert.

Figure 15: Change of the the $Z_f$ (thick line) and $Z$ (thin lines) impedance diagrams and of the $Y_f$ (thick line) and $Y$ (thin lines) admittance diagram with $\tau$. The arrows indicate the direction of increasing frequency. Dots: $\omega = \omega_H$.

Figure 16: Change of the real part of the poles with $\tau$. $\tau_1 = \tau_2 = 1$ s.
Figure 1:

Figure 2:

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Figure 3:

Figure 4:
Figure 5:
Figure 6:

Figure 7:
Figure 8:
Figure 9:

Figure 10:
Figure 11:

Figure 12:

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Figure 13:

Figure 14:

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Figure 15:

Figure 16: