Numerical and analytical study of bifurcations in a model of electrochemical reactions in fuel cells

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Abstract

The bifurcations in a three-variable ODE model describing the oxygen reduction reaction on platinum surface is studied. The investigation is motivated by the fact that this reaction plays an important role in fuel cells. The goal of this paper is to determine the dynamical behaviour of the ODE system, with emphasis on the number and type of the stationary points, and to find the possible bifurcations. It is shown that a non-trivial steady state can appear through a transcritical bifurcation, or a stable and an unstable steady state arise as a result of saddle-node bifurcation. The saddle-node bifurcation curve is determined by using the Parametric Representation Method, and this enables us to determine numerically the parameter domain where bistability occurs that is important from the chemical point of view.

Keywords: fold, transcritical, Hopf bifurcations, oxygen reduction reaction, bistability

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1 Introduction

During the development of efficient and reliable fuel cells it is crucial to understand the oxygen reduction reaction (ORR) on platinum surface. Several attempts has been made to establish the reaction scheme [2, 5, 6, 7, 8, 11], however, there is no final conclusion. The most widely used scheme that also serves as a common base for others was introduced by Damjanovic and Brusic [5] and this will be the one that we will use in this paper. The detailed mathematical study of the model can also help the experimental researchers to develop more realistic reaction schemes.

In our model the first step is a fast oxygen adsorption followed by an electrochemical reaction forming an adsorbed O_2H molecule, see the first reaction below. The next step is a chemical reaction between the adsorbed O_2H and a water molecule resulting in adsorbed OH species. Finally, the adsorbed OH species are reduced to water in a fast electrochemical step in the last reaction step. So the reaction scheme reads as follows.

$$\begin{aligned} O_2 + H^+ + e^- &\leftrightarrow O_2H(ads) \\ O_2H(ads) + H_2O &\leftrightarrow 3OH(ads) \\ OH(ads) + H^+ + e^- &\leftrightarrow H_2O \end{aligned}$$

Let us introduce the variables θ_1, θ_2 to denote the relative coverage of the surface with OH and O_2H molecules, and let θ_s denote the number of free surface spaces per surface unit, and c denote the water concentration in the system. The reaction rates of the above reactions can be given as

$$\begin{aligned} v_1 &= K_1\theta_s - L_1\theta_2, \\ v_2 &= K_2\theta_2\theta_s^2 c - L_2\theta_1^3, \\ v_3 &= K_3\theta_1 - L_3\theta_s c, \end{aligned}$$

where

$$K_1 = k_1 \exp\left(-\frac{\beta_1(\eta - E_1)F}{RT}\right), \quad K_2 = k_2, \quad K_3 = k_3 \exp\left(-\frac{\beta_2(\eta - E_2)F}{RT}\right)$$

$$L_1 = k_{-1} \exp\left(\frac{(1-\beta_1)(\eta - E_1)F}{RT}\right), \quad L_2 = k_{-2},$$

$$L_3 = k_{-3} \exp\left(\frac{(1-\beta_2)(\eta - E_2)F}{RT}\right),$$

η is the electrode potential, F is Faraday's constant, R is universal gas constant, k_i are rate constants, and β_i, E_i are electro-chemical parameters [1].

Based on the above reactions the kinetic equations take the form

$$\begin{aligned} \dot{\theta}_1 &= 3v_2 - v_3, & (1) \\ \dot{\theta}_2 &= v_1 - v_2, & (2) \\ \dot{c} &= v_3 - v_2 - \alpha c, & (3) \end{aligned}$$

where α is a parameter describing the drainage of water. In our previous model [4] the water concentration c was assumed to be constant, which is a reasonable approximation, leading to the two-dimensional system (1)-(2). The detailed study of that two dimensional dynamical system was given in [4], and now our goal is to understand the role of water in the mathematical model. From the chemical point of view the amount of water is extremely important since it has a strong effect on the performance of the fuel cell.

Substituting the expressions of v_i into system (1)-(3) we get the following non-linear system of ODEs.

$$\begin{aligned} \dot{\theta}_1 &= 3K_2\theta_2\theta_s^2 c - 3L_2\theta_1^3 - K_3\theta_1 + L_3\theta_s c, && (4)\\ \dot{\theta}_2 &= K_1\theta_s - L_1\theta_2 - K_2\theta_2\theta_s^2 c, +L_2\theta_1^3 && (5)\\ \dot{c} &= K_3\theta_1 - L_3\theta_s c - K_2\theta_2\theta_s^2 c + L_2\theta_1^3 - \alpha c, && (6)\end{aligned}$$

where $\theta_s = 1 - \theta_1 - \theta_2$. The goal of this paper is to understand the dynamical behavior of system (4)-(6).

In Section 2 it is shown how can the steady state system be reduced to a single equation. The number of solutions of this equation will yield the number of steady states. To find the number of solutions we will use the Parametric Representation Method [9, 10]. Using this method the discriminant curve (i.e. the saddle-node bifurcation curve or D-curve) can be determined analytically. The shape of the D-curve is studied in Section 3. It will be shown that the D-curve belongs to one of two different classes, leading to two different bifurcation diagrams. In the first case only transcritical bifurcation may occur, while in the second case saddle-node bifurcation can also be found. The exact condition for the transcritical bifurcation is given in Section 4, where the non-existence of Hopf bifurcation is also revealed. The possible phase portraits of the system are summarized in Section 5.

2 Reduction of the steady state system to a single equation

First, let us investigate the steady states of system (4)-(6). The equations defining the stationary points are $\dot{\theta}_1 = 0, \dot{\theta}_2 = 0$ and $\dot{c} = 0$. Our aim in this Section is to reduce this system to a single equation with only one unknown. It turns out that we get the most convenient form if this unknown is θ_s. From (1)-(3) we get $3v_2 - v_3 = 0, v_1 - v_2 = 0$ and $v_3 - v_2 - \alpha c = 0$. The sum of first and third equation gives $v_2 = \frac{\alpha c}{2}$, so we get $v_1 = \frac{\alpha c}{2}$ and $v_3 = \frac{3\alpha c}{2}$. The definitions of v_i yield

$$\begin{aligned} K_1\theta_s - L_1\theta_2 &= \frac{\alpha c}{2}, && (7)\\ K_2\theta_2\theta_s^2 c - L_2\theta_1^3 &= \frac{\alpha c}{2}, && (8)\\ K_3\theta_1 - L_3\theta_s c &= \frac{3\alpha c}{2}. && (9)\end{aligned}$$

Starting from equations (7), (9) and $\theta_s = 1 - \theta_1 - \theta_2$ a simple calculation shows that

$$\theta_1 = P_1(\theta_s), \quad \theta_2 = P_2(\theta_s), \quad c = P_c(\theta_s), \tag{10}$$

where

$$P_1(\theta_s) = \frac{A_1(\theta_s)A_3(\theta_s)}{N(\theta_s)}, \quad P_2(\theta_s) = \frac{A_2(\theta_s)}{N(\theta_s)}, \quad P_c(\theta_s) = 2K_3\frac{A_3(\theta_s)}{N(\theta_s)}$$

and

$$\begin{aligned} A_1(\theta_s) &= 2L_3\theta_s + 3\alpha, \\ A_2(\theta_s) &= 2L_3K_1\theta_s^2 + \alpha(3K_1 + K_3)\theta_s - \alpha K_3, \\ A_3(\theta_s) &= L_1 - (K_1 + L_1)\theta_s, \\ N(\theta_s) &= 2L_1L_3\theta_s + \alpha(3L_1 - K_3). \end{aligned}$$

Thus the unknowns c, θ_1 and θ_2 can be expressed in terms of θ_s. Substituting the above expressions of c, θ_1 and θ_2 into equation (8) the following equation can be derived for the only unknown θ_s.

$$A_3(\theta_s)\left(\alpha K_3N^2(\theta_s) - 2K_2A_2(\theta_s)\theta_s^2K_3N(\theta_s) + L_2A_1^3(\theta_s)A_3^2(\theta_s)\right) = 0$$

Hence the solution of $A_3(\theta_s) = 0$ gives a stationary point. This linear equation can be easily solved for θ_s as $\theta_s = \frac{L_1}{K_1+L_1}$, leading to $\theta_1 = 0, c = 0$ and $\theta_2 = \frac{K_1}{K_1+L_1}$. Since for these values $\theta_1, \theta_2, \theta_s \in [0,1]$ and $c \geq 0$ hold, this gives a chemically realistic steady state $\left(0, \frac{K_1}{K_1+L_1}, 0\right)$ that will be referred to as trivial stationary point.

If the stationary point is not trivial, then θ_s is the solution of

$$\alpha K_3N^2(\theta_s) - 2K_2A_2(\theta_s)\theta_s^2K_3N(\theta_s) + L_2A_1^3(\theta_s)A_3^2(\theta_s) = 0. \tag{11}$$

Thus concerning the steady states of system (4)-(6) we have proved the following Lemma.

Lemma 1 *System (4)-(6) has a trivial steady state* $\left(0, \frac{K_1}{K_1+L_1}, 0\right)$. *Besides this state, a point* (θ_1, θ_2, c) *is a steady state if and only if the numbers* $\theta_1, \theta_2 \in [0,1]$, $c \geq 0$ *satisfy (10) with* $\theta_s \in [0,1]$ *being a solution of (11).*

In the rest of this Section we derive a condition on θ_s ensuring that the values obtained from (10) satisfy $\theta_1, \theta_2 \in [0,1]$ and $c \geq 0$.

Proposition 1 *The equation* $N(\theta_s) = A_1(\theta_s)A_3(\theta_s)$ *has a unique positive solution. Denoting this solution by* θ_s^* *we have that* $\theta_1 = P_1(\theta_s) \in [0,1]$ *holds if and only if* θ_s *is between* θ_s^* *and* $\frac{L_1}{K_1+L_1}$.

Proof. The left hand side of the equation is linear and increasing, while the right hand side is a concave parabola. Hence $N(0) = \alpha(3L_1 - K_3) < 3\alpha L_1 = A_1(0)A_3(0)$ implies that the equation has exactly one positive solution.

According to the position of θ_s^* we can distinguish three cases. In the first case $\theta_s^* < \frac{L_1}{K_1+L_1}$. Now we show that $\theta_1 = P_1(\theta_s) \in [0,1]$ if and only if $\theta_s^* \leq \theta_s \leq \frac{L_1}{K_1+L_1}$.

- If $\theta_s < \theta_s^*$, then $0 < N(\theta_s) < A_1(\theta_s)A_3(\theta_s)$ so $\theta_1 > 1$, or $N(\theta_s) < 0 < A_1(\theta_s)A_3(\theta_s)$ so $P_1(\theta_s) < 0$, or $\theta_s < 0$.
- If $\theta_s > \frac{L_1}{K_1+L_1}$, then $N(\theta_s) > 0 > A_1(\theta_s)A_3(\theta_s)$ so $P_1(\theta_s) < 0$.
- If $\theta_s \in \left[\theta_s^*, \frac{L_1}{K_1+L_1}\right]$, then $N(\theta_s) > A_1(\theta_s)A_3(\theta_s) > 0$ so $P_1(\theta_s) \in [0,1]$.

Now we show that the statement holds also in the second case when $\theta_s^* > \frac{L_1}{K_1+L_1}$.

- If $\theta_s > \theta_s^*$, then $N(\theta_s) > 0 > A_1(\theta_s)A_3(\theta_s)$ so $\theta_1 < 0$, or $0 > N(\theta_s) > A_1(\theta_s)A_3(\theta_s)$, but $|N(\theta_s)| < |A_1(\theta_s)A_3(\theta_s)|$ so $P_1(\theta_s) > 1$.
- If $\theta_s < \frac{L_1}{K_1+L_1}$, then $N(\theta_s) < 0 < A_1(\theta_s)A_3(\theta_s)$ so $P_1(\theta_s) < 0$, or $\theta_s < 0$.
- If $\theta_s \in \left[\frac{L_1}{K_1+L_1}, \theta_s^*\right]$, then $N(\theta_s) < A_1(\theta_s)A_3(\theta_s) < 0$ so $P_1(\theta_s) \in [0,1]$.

In the third case $\theta_s^* = \frac{L_1}{K_1+L_1}$ yielding $P_1(\theta_s) < 0$ when $\theta_s \neq \theta_s^*$, and $P_1(\theta_s) = 0$ when $\theta_s = \frac{L_1}{K_1+L_1}$.
□

As an obvious consequence of the definitions of the functions P_1 and P_c below (10) we get the following statement.

Proposition 2 *The functions P_1 and P_c have the same sign, that is $\theta_1 \geq 0$ holds if and only if $c \geq 0$.*

The definition $\theta_s = 1 - \theta_1 - \theta_2$ implies the following.

Proposition 3 *If $\theta_1, \theta_s \in [0,1]$, then $\theta_2 \leq 1$.*

So it remains to derive a condition for $\theta_2 \geq 0$. The function A_2 is a convex parabola, and we have $A_2(0) < 0$ and $A_2(1) > 0$. Hence A_2 has exactly one root in the interval $[0,1]$. Let us denote this root by θ_s'. Let us introduce the closed intervals

$$I_1 = I\left(\theta_s^*, \frac{L_1}{K_1+L_1}\right) \quad I_2 = I\left(\theta_s', \frac{\alpha(K_3-3L_1)}{2L_1L_3}\right), \tag{12}$$

where $I(a,b)$ denotes the closed interval with endpoints a and b. Then the sign of $\theta_2 = P_2(\theta_s)$ can be given as follows.

Proposition 4 *The inequality $\theta_2 > 0$ holds if and only if $\theta_s \notin I_2$.*

Proof. Since $\theta_2 = P_2(\theta_s) = \frac{A_2(\theta_s)}{N(\theta_s)}$, we investigate the signs of A_2 and N. The only root of A_2 is θ_s' and root of N is $\frac{\alpha(K_3-3L_1)}{2L_1L_3}$. We divide the proof into two parts according to the mutual position of these roots.

Let us start with the case $\frac{\alpha(K_3-3L_1)}{2L_1L_3} < \theta_s'$. The two roots divide the real line into three parts. If $\theta_s \in \left(-\infty, \frac{\alpha(K_3-3L_1)}{2L_1L_3}\right)$, then $N(\theta_s) < 0$ and $A_2(\theta_s) < 0$, hence θ_2 is positive. If θ_s is in the interval $\left(\frac{\alpha(K_3-3L_1)}{2L_1L_3}, \theta_s'\right)$, then $N(\theta_s) > 0$ and $A_2(\theta_s) < 0$, therefore $\theta_2 < 0$, and finally, when θ_s is in the interval (θ_s', ∞), then $N(\theta_s) > 0$ and $A_2(\theta_s) > 0$ i.e. $\theta_2 > 0$. Thus we obtained, that $\theta_2 > 0$ holds if and only if $\theta_s \notin I_2$.

Let us turn now to the second case when $\frac{\alpha(K_3-3L_1)}{2L_1L_3} > \theta_s'$. The two roots divide the positive half line into three parts. We can check the signs similarly in each part separately, and we get that $\theta_2 > 0$ holds if and only if $\theta_s \notin I_2$.

It is easy to see that the statement holds also in the border case when $\frac{\alpha(K_3-3L_1)}{2L_1L_3} = \theta_s'$.

□

The next two Propositions will be used to determine the mutual position of the intervals I_1 and I_2.

Proposition 5 *For any values of the parameters we have $\theta_s^* \in I_2$.*

PROOF. A simple calculation shows that

$$N(\theta_s) - A_1(\theta_s)A_3(\theta_s) = A_2(\theta_s) + \theta_s N(\theta_s). \tag{13}$$

Since θ_s^* is the root of the left hand side, therefore it is also a root of the right hand side. Thus $A_2(\theta_s^*)$ and $N(\theta_s^*)$ have opposite signs. This means that $P_2(\theta_s^*) = \frac{A_2(\theta_s^*)}{N(\theta_s^*)} < 0$, hence according to Proposition 4 we have $\theta_s^* \in I_2$.

□

Proposition 6 *The root θ_s' is between $\frac{\alpha(K_3-3L_1)}{2L_1L_3}$ and $\frac{L_1}{K_1+L_1}$.*

PROOF. Rearranging (13) we get $A_2(\theta_s) = N(\theta_s)(1-\theta_s) - A_1(\theta_s)A_3(\theta_s)$. The number θ_s' is the root of A_2, i.e. $A_2(\theta_s') = 0$ yielding $N(\theta_s')(1-\theta_s') = A_1(\theta_s')A_3(\theta_s')$. Since $\theta_s' \in [0,1]$ and $A_1(\theta_s) > 0$ holds for any $\theta_s \in [0,1]$, we obtain that the signs of $A_3(\theta_s')$ and $N(\theta_s')$ are same. Thus θ_s' is between the roots of N and A_3.

□

From the previous two Propositions we obtain the following relation for the intervals I_1 and I_2. (We recall that the notation $I(a,b)$ was introduced below (12).)

Proposition 7 *The set $I_1 \setminus I_2$ is a semi-closed interval, namely*

$$I_1 \setminus I_2 = I\left(\theta_s', \frac{L_1}{K_1+L_1}\right] =: I_3,$$

where this notation means that the interval is closed at the end point $\frac{L_1}{K_1+L_1}$, and open at the other end point.

PROOF. We divide the proof into two parts according to the mutual position of $\frac{\alpha(K_3-3L_1)}{2L_1L_3}$ and $\frac{L_1}{K_1+L_1}$.

If $\frac{\alpha(K_3-3L_1)}{2L_1L_3} < \frac{L_1}{K_1+L_1}$, then according to Proposition 6 we have $\frac{\alpha(K_3-3L_1)}{2L_1L_3} < \theta_s'$, hence $I_2 = \left[\frac{\alpha(K_3-3L_1)}{2L_1L_3}, \theta_s'\right]$. Then $\theta_s^* \in \left(\frac{\alpha(K_3-3L_1)}{2L_1L_3}, \theta_s'\right)$ according to Proposition 5. Thus the ordering of the endpoints of the intervals is

$$\frac{\alpha(K_3-3L_1)}{2L_1L_3} < \theta_s^* < \theta_s' < \frac{L_1}{K_1+L_1}, \tag{14}$$

hence $I_1 \setminus I_2 = \left(\theta_s', \frac{L_1}{K_1+L_1}\right]$.

If $\frac{L_1}{K_1+L_1} < \frac{\alpha(K_3-3L_1)}{2L_1L_3}$, then similarly we get $\theta_s^* \in \left(\theta_s', \frac{\alpha(K_3-3L_1)}{2L_1L_3}\right)$, thus the ordering of the endpoints is

$$\frac{L_1}{K_1+L_1} < \theta_s' < \theta_s^* < \frac{\alpha(K_3-3L_1)}{2L_1L_3}, \tag{15}$$

hence $I_1 \setminus I_2 = \left[\frac{L_1}{K_1+L_1}, \theta_s'\right)$.

□

The above considerations lead us to the following Lemma.

Lemma 2 *The inequalities $P_1(\theta_s), P_2(\theta_s) \in [0,1]$ and $P_c(\theta_s) \geq 0$ hold if and only if $\theta_s \in I_3$.*

This Lemma together with Lemma 1 yields that the non-trivial steady states can be obtained as follows.

Theorem 1 *A point (θ_1, θ_2, c) is a non-trivial steady state if and only if these numbers are given by (10) and $\theta_s \in I_3$ is a solution of (11).*

In the next Section we will apply the Parametric Representation Method [9] to determine the number of solutions of (11) in the interval I_3.

3 The possible shapes of the discriminant curve and the exact number of steady states

In order to apply the parametric representation method we need to choose two control parameters that are involved linearly in the equation that is to be solved. We have to solve the equation $p(\theta_s) = 0$, where according to (11)

$$p(\theta_s) = \alpha K_3 N^2(\theta_s) - 2K_2A_2(\theta_s)\theta_s^2 K_3 N(\theta_s) + L_2 A_1^3(\theta_s) A_3^2(\theta_s).$$

We will use K_2 and L_2 as control parameters that are involved linearly. Then our equation takes the form

$$f_0(\theta_s) + K_2 f_1(\theta_s) + L_2 f_2(\theta_s) = 0, \tag{16}$$

where

$$f_0(\theta_s) = \alpha K_3 N^2(\theta_s), \qquad f_1(\theta_s) = -2A_2(\theta_s)\theta_s^2 K_3 N(\theta_s),$$
$$f_2(\theta_s) = A_1^3(\theta_s)A_3^2(\theta_s).$$

The number of solutions of the equation $p(\theta_s) = 0$ can change when $p'(\theta_s) = 0$ also holds. Hence the bifurcation value of the parameters K_2 and L_2 is given by (16) and by

$$f_0'(\theta_s) + K_2 f_1'(\theta_s) + L_2 f_2'(\theta_s) = 0. \tag{17}$$

These two equations together determine the discriminant curve in the (K_2, L_2) parameter plane. One of the main advantages of the parametric representation method is that this curve is expressed in explicit form parametrized by θ_s [9, 10]. Solving system (16)-(17) for K_2 and L_2 we get the following parametric representation of the discriminant curve.

$$K_2 = D_1(\theta_s) := \frac{f_0' f_2 - f_0 f_2'}{f_1 f_2' - f_1' f_2} \qquad L_2 = D_2(\theta_s) := \frac{f_0 f_1' - f_0' f_1}{f_2' f_1 - f_2 f_1'} \tag{18}$$

We will refer to this curve as D-curve.

The reason for using the parametric representation method is that the number of solutions of the equation can be easily determined by the so called tangential property. This means that the number of solutions of (16) belonging to a given parameter pair (K_2, L_2) is equal to number of tangents drawn to the D-curve from the point (K_2, L_2), see [9, 10] or the brief summary of the parametric representation method in [4]. We note that similarly to the parametric representation method the so-called envelope method, developed by Cheng and Lin [3], can also be applied to determine the bifurcation curve. To apply the tangential property we need to know the shape of the D-curve that will be investigated in the next subsections.

3.1 Numerical classification of the possible shapes of the D-curve

In this section our goal is the investigation of the D-curve. For this we need the following formulas for the derivatives of the functions f_0, f_1 and f_2.

$$f_0'(\theta_s) = 2\alpha K_3 N(\theta_s) N'(\theta_s)$$
$$f_1'(\theta_s) = -2A_2'(\theta_s)\theta_s^2 K_3 N(\theta_s) - 2A_2(\theta_s)\theta_s^2 K_3 N'(\theta_s) - 4A_2(\theta_s)\theta_s K_3 N(\theta_s)$$
$$f_2'(\theta_s) = 3A_1^2(\theta_s)A_3^2(\theta_s)A_1'(\theta_s) + 2A_1^3(\theta_s)A_3(\theta_s)A_3'(\theta_s)$$

Since the D-curve depends on many parameters we made first a systematic numerical study of the curve by simply plotting $(D_1(\theta_s), D_2(\theta_s))$ for $\theta_s \in I_3$ for different values of the parameters K_1, L_1, K_3, L_3 and α. It turned out that the D-curve has a vertical asymptote belonging to the end point $\theta_s = \frac{L_1}{K_1+L_1}$. At this asymptote the second coordinate can tend to $+\infty$ or to $-\infty$, hence the shape of the curve can basically belong to two different types.

The first type, for which the second coordinate tends to $-\infty$, does not enter the positive quadrant of the (K_2, L_2) parameter plane. It may be a concave arc or it can have a cusp depending on the values of the parameters K_1, L_1, K_3, L_3 and α, see Figure 1.

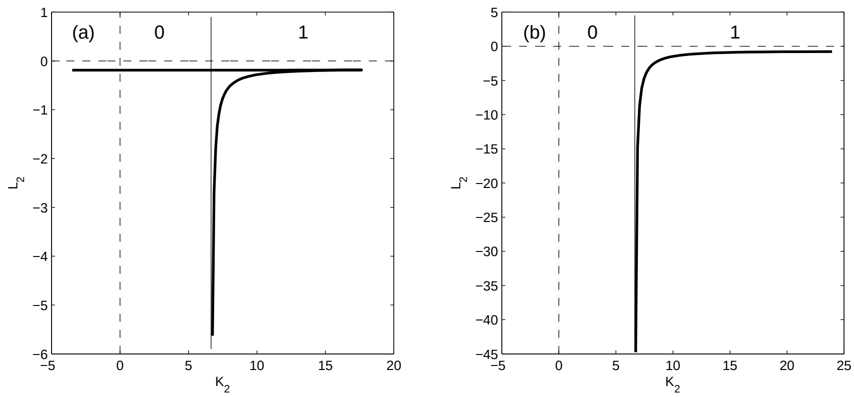

Figure 1: The two possible shapes of the D-curve when it belongs to the first type. The parameters in the concave case (a) are $K_1 = 10$, $L_1 = 1$, $K_3 = 6.5$, $L_3 = 90$, $\alpha = 0.1$, and in the cusp case (b) $K_1 = 10$, $L_1 = 1$, $K_3 = 6.5$, $L_3 = 5$, $\alpha = 0.1$.

The number of solutions of (16) in the different regions is also shown in Figure 1. If we choose a point from the right hand side of the vertical asymptote in the positive quadrant, then we can draw exactly one tangent from this point to the D-curve, so in this case the number of stationary points is two (the trivial stationary point is always a solution). If the point (K_2, L_2) is in the left hand side of the vertical asymptote, then we cannot draw any tangent from this point to the D-curve, so in this case the number of stationary points is one, it is the trivial stationary point.

The second type, for which the second coordinate tends to $+\infty$, enters the positive quadrant of the (K_2, L_2) parameter plane. It may be a convex arc or it can have a cusp depending on the values of the parameters K_1, L_1, K_3, L_3 and α, see Figure 2.

The number of solutions of (16) in the different regions is also shown in Figure 2. If we choose a point from the right hand side of the vertical asymptote in the positive quadrant, then we can draw exactly one tangent from this point to the D-curve, so in this case the number of stationary points is two (the trivial stationary point is always a solution). If the point (K_2, L_2) is between the vertical asymptote and the D-curve, then we can draw two tangents from this point to the D-curve, so in this case the number of stationary points is three. If the point (K_2, L_2) is in the left hand side of the D-curve, then we cannot draw any tangent from this point to the D-curve, so in this case the number of stationary points is one, it is the trivial stationary point.

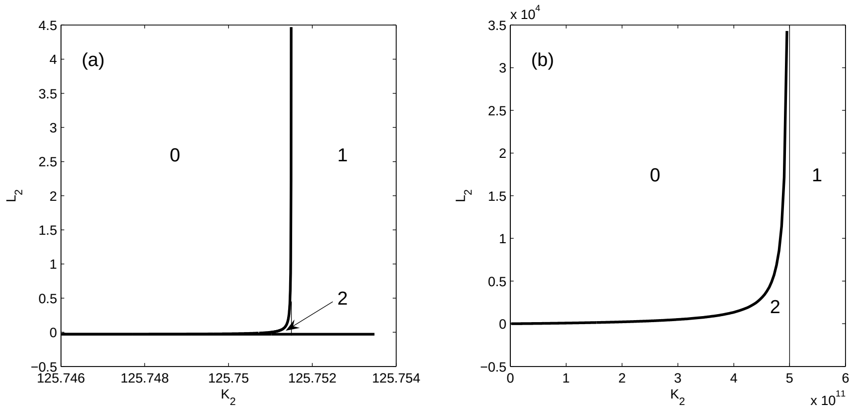

Figure 2: The two possible shapes of the D-curve when it belongs to the second type. The parameters in the convex case (a) are $K_1 = 5$, $L_1 = 0.01$, $K_3 = 5$, $L_3 = 82.5$, $\alpha = 0.001$ and in the cusp case (b) $K_1 = 10000$, $L_1 = 0.01$, $K_3 = 1$, $L_3 = 1$, $\alpha = 1$.

3.2 Analytic classification of the possible shapes of the D-curve

In this subsection we determine the shape and position of the curve

$$\{(D_1(\theta_s), D_2(\theta_s)) \ : \ \theta_s \in I_3\},$$

where D_1, D_2 are given in (18) and I_3 is given in Proposition 7. The sign of the numerator of D_2 will play an important role during our investigation. After some algebra we get that it can be expressed as

$$f_0(\theta_s)f_1'(\theta_s) - f_0'(\theta_s)f_1(\theta_s) = -2\alpha K_3^2 N^2(\theta_s)\theta_s H(\theta_s), \tag{19}$$

where

$$H(\theta_s) = A_2'(\theta_s)\theta_s N(\theta_s) - A_2(\theta_s)\theta_s N'(\theta_s) + 2A_2(\theta_s)N(\theta_s). \tag{20}$$

We will see that the shape of the D-curve is partly determined by the sign of H.

Proposition 8 *The function D_2 has a singularity in the point $\frac{L_1}{K_1+L_1} := \overline{\theta_s}$.*

- *If $\theta_s' < \overline{\theta_s}$, then we have*

$$\lim_{\theta_s \to \overline{\theta_s}} D_2(\theta_s) = -\infty.$$

- *If $\theta_s' > \overline{\theta_s}$ and $H(\overline{\theta_s}) < 0$, then*

$$\lim_{\theta_s \to \overline{\theta_s}} D_2(\theta_s) = -\infty.$$

- *If $\theta_s' > \overline{\theta_s}$ and $H(\overline{\theta_s}) > 0$, then*

$$\lim_{\theta_s \to \overline{\theta_s}} D_2(\theta_s) = \infty.$$

We note that here the limit $\theta_s \to \overline{\theta_s}$ is understood in the sense that θ_s is between θ_s' and $\overline{\theta_s}$.

Proof. The root of A_3 is $\overline{\theta_s} = \frac{L_1}{K_1+L_1}$, hence the denominator of $D_2(\overline{\theta_s})$ is zero, while the numerator is non-zero. Therefore $|D_2|$ converges to infinity as θ_s tends to $\overline{\theta_s}$. This means that the D-curve has a vertical asymptote.

In the case $\theta_s' < \overline{\theta_s}$ a more general statement will be proved in Proposition 12, hence we omit the proof here.

Let us consider now the case $\theta_s' > \overline{\theta_s}$. According to (19) the sign of the numerator of $D_2(\theta_s)$ as $\theta_s \to \overline{\theta_s}$ is given by the sign of $H(\overline{\theta_s})$. Hence it is enough to prove that the denominator of $D_2(\theta_s)$ is negative as $\theta_s \to \overline{\theta_s}$. Since $\overline{\theta_s}$ is the root of A_3, f_2 contains a factor A_3^2 and $f_2' = 3A_1^2A_3^2A_1' + 2A_1^3A_3A_3'$, the sign of the denominator $f_2'f_1 - f_2f_1'$ when θ_s is close to $\overline{\theta_s}$ is equal to the sign of

$$2A_1^3(\theta_s)A_3(\theta_s)A_3'(\theta_s)f_1(\theta_s) = -4A_1^3(\theta_s)A_3(\theta_s)A_3'(\theta_s)A_2(\theta_s)\theta_s^2K_3N(\theta_s).$$

The signs of these functions can be easily determined, their graphs are shown schematically in Figure 3. Using this Figure one can easily check that the denominator is really negative.

□

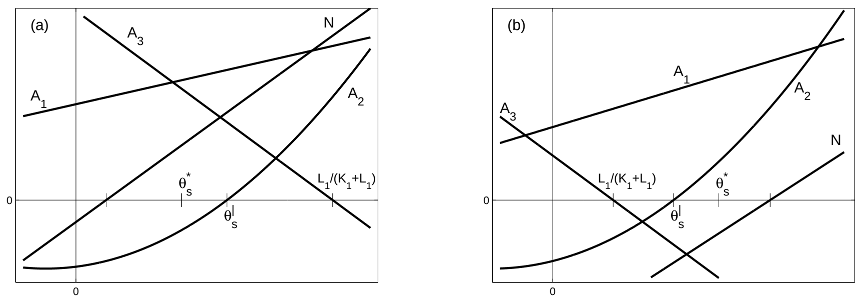

Figure 3: The schematic graphs of the functions A_1, A_2, A_3 and N in the case $\theta_s' < \overline{\theta_s}$ (a), and in the case $\theta_s' > \overline{\theta_s}$ (b). The order of the roots of the functions is given in (14) and (15).

Proposition 9 *The vertical asymptote of the D-curve is at a positive position, more exactly*

$$\lim_{\theta_s \to \overline{\theta_s}} D_1(\theta_s) = \frac{\alpha(K_1+L_1)^3}{2K_1L_1^2} > 0.$$

Proof. Using the formulas for f_0, f_1, f_2 and for f_0', f_1', f_2', and exploiting the fact that the root of A_3 is $\overline{\theta_s}$ one can easily get that

$$\lim_{\theta_s \to \overline{\theta_s}} D_1(\theta_s) = -\frac{f_0(\overline{\theta_s})}{f_1(\overline{\theta_s})}.$$

Then the definitions of f_0 and f_1 yield

$$-\frac{f_0(\overline{\theta_s})}{f_1(\overline{\theta_s})} = \frac{\alpha}{2\overline{\theta_s}^2} \frac{N(\overline{\theta_s})}{A_2(\overline{\theta_s})}.$$

It can be easily seen that the identity

$$L_1 A_2(\theta_s) - K_1 \theta_s N(\theta_s) = \alpha K_3(\theta_s(K_1 + L_1) - L_1)$$

holds for any θ_s. Substituting $\theta_s = \overline{\theta_s}$ the right hand side becomes zero, hence $\frac{N(\overline{\theta_s})}{A_2(\overline{\theta_s})}$ can be easily expressed as $\frac{L_1}{K_1 \overline{\theta_s}}$. Substituting this into the above equation we get the desired formula.

□

Now the behaviour of the D-curve at the endpoint $\overline{\theta_s}$ of the interval I_3 has been determined. Let us turn to the study of the behaviour at the other endpoint θ_s'.

Proposition 10 *We have $D_2(\theta_s') < 0$.*

Proof. The number θ_s' was defined as the root of the function A_2, hence $f_1(\theta_s') = 0$. Therefore

$$D_2(\theta_s') = -\frac{f_0(\theta_s')}{f_2(\theta_s')} < 0$$

because f_0 and f_2 are positive functions. The positivity of the first one is obvious from its definition, and the positivity of the second follows from the fact that $A_1(0) > 0$ and A_1 is an increasing function.

□

This Proposition implies that one endpoint of the D-curve is in the negative half plane. Now we prove that it reaches this negative value with a horizontal tangent. The tangent vector of the D-curve is (D_1', D_2') and this is horizontal if and only if $D_2' = 0$.

Proposition 11 *We have $D_2'(\theta_s') = 0$.*

Proof. The derivative of D_2 can be expressed as

$$D_2' = \frac{(f_0 f_1' - f_0' f_1)'(f_2' f_1 - f_2 f_1') - (f_2' f_1 - f_2 f_1')'(f_0 f_1' - f_0' f_1)}{(f_2' f_1 - f_2 f_1')^2}.$$

We have $f_1(\theta_s') = 0$, hence the numerator can be considerably simplified as follows. (The functions in the next expressions are taken at θ_s'.)

$$(f_0 f_1' - f_0' f_1)'(f_2' f_1 - f_2 f_1') - (f_2' f_1 - f_2 f_1')'(f_0 f_1' - f_0' f_1) =$$

$$= (f_0'f_1' + f_0f_1'' - f_0''f_1 - f_0'f_1')(f_2'f_1 - f_2f_1') -$$
$$(f_2''f_1 + f_2'f_1' - f_2'f_1' - f_2f_1'')(f_0f_1' - f_0'f_1) =$$
$$= (f_0'f_1' + f_0f_1'' - f_0'f_1')(-f_2f_1') - (f_2'f_1' - f_2'f_1' - f_2f_1'')f_0f_1' =$$
$$= f_0f_1''(-f_2f_1') - (-f_2f_1'')f_0f_1' = 0.$$

□

Our numerical investigations showed that in the case when the D-curve tends to $-\infty$ at the vertical asymptote, it is below the horizontal line $L_2 = 0$. This is what we will prove now separately in the cases $\overline{\theta_s} > \theta_s'$ and $\overline{\theta_s} < \theta_s'$.

Proposition 12 *If $\overline{\theta_s} > \theta_s'$, then for any $\theta_s \in I_3$ the inequality $D_2(\theta_s) < 0$ holds.*

Proof. We prove that the numerator of D_2 is negative and its denominator is positive. First, let us consider the numerator as it is given in (19). We will prove that $H(\theta_s) > 0$ holds for any $\theta_s \in I_3 = (\theta_s', \overline{\theta_s})$. Observe first, that $H(\theta_s') > 0$, since $A_2(\theta_s') = 0$ (by definition), $A_2'(\theta_s') > 0$, because A_2 is a convex parabola and θ_s' is its larger root, and N is positive, see Figure 3. Moreover, H is an increasing function in I_3 since

$$H'(\theta_s) = A_2''(\theta_s)\theta_s N(\theta_s) + 3A_2'(\theta_s)N(\theta_s) + A_2(\theta_s)N'(\theta_s) > 0,$$

by using again the properties of the functions A_2 and N.

Let us consider now the denominator of D_2. We will use that in the interval I_3 we have the following signs (see Figure 3):

$$A_1 > 0,\ A_1' > 0,\ A_2 > 0,\ A_2' > 0,\ A_3 > 0,\ A_3' < 0,\ N > 0,\ N' > 0. \qquad (21)$$

A straightforward but tiresome calculation shows that

$$f_2'f_1 - f_2f_1' = J[G_1 + G_2 + G_3 + G_4 - 3F], \qquad (22)$$

where

$$J(\theta_s) = 2K_3A_1^2(\theta_s)A_3(\theta_s)\theta_s, \qquad F(\theta_s) = A_3(\theta_s)A_1'(\theta_s)A_2(\theta_s)\theta_s N(\theta_s),$$
$$G_1(\theta_s) = A_1(\theta_s)A_3(\theta_s)A_2'(\theta_s)\theta_s N(\theta_s),$$
$$G_2(\theta_s) = A_1(\theta_s)A_3(\theta_s)A_2(\theta_s)\theta_s N'(\theta_s),$$
$$G_3(\theta_s) = 2A_1(\theta_s)A_3(\theta_s)A_2(\theta_s)N(\theta_s),$$
$$G_4(\theta_s) = -2A_1(\theta_s)A_3'(\theta_s)A_2(\theta_s)\theta_s N(\theta_s).$$

Using the signs in (21) we have that J and G_4 are positive functions. In order to prove the positivity of the denominator it is enough to prove that $G_i - F > 0$ for $i = 1, 2, 3$. Let us introduce the notations $A_2(\theta_s) = a_2\theta_s^2 + a_1\theta_s + a_0$, $A_1(\theta_s) = b_1\theta_s + b_0$ and $N(\theta_s) = n_1\theta_s + n_0$. It is easy to see from the definitions of these functions that $a_2 > 0, a_1 > 0, b_0 > 0, a_0 < 0, b_1 > 0$.

Then

$$G_1(\theta_s) - F(\theta_s) = A_3(\theta_s)\theta_s N(\theta_s)\left[A_1(\theta_s)A_2'(\theta_s) - A_1'(\theta_s)A_2(\theta_s)\right].$$

This is positive because $A_3(\theta_s)\theta_s N(\theta_s) > 0$ and

$$A_1(\theta_s)A_2'(\theta_s) - A_1'(\theta_s)A_2(\theta_s) = (b_1\theta_s + b_0)(2a_2\theta_s + a_1) - b_1(a_2\theta_s^2 + a_1\theta_s + a_0) =$$
$$= b_1a_2\theta_s^2 + 2b_0a_2\theta_s + (b_0a_1 - b_1a_0) > 0.$$

The second part is

$$G_2(\theta_s) - F(\theta_s) = A_3(\theta_s)A_2(\theta_s)\theta_s\left[A_1(\theta_s)N'(\theta_s) - A_1'(\theta_s)N(\theta_s)\right].$$

This is positive because $A_3(\theta_s)A_2(\theta_s)\theta_s > 0$ and

$$A_1(\theta_s)N'(\theta_s) - A_1'(\theta_s)N(\theta_s) = (b_1\theta_s + b_0)n_1 - b_1(n_1\theta_s + n_0) =$$
$$b_0n_1 - b_1n_0 = 3\alpha 2L_1L_3 - 2L_3\alpha(3L_1 - K_3) = 2\alpha L_3K_3 > 0.$$

The third part is

$$G_2(\theta_s) - F(\theta_s) = A_2(\theta_s)A_3(\theta_s)N(\theta_s)\left[2A_1(\theta_s) - A_1'(\theta_s)\theta_s\right].$$

This is positive bacause $A_2(\theta_s)A_3(\theta_s)N(\theta_s) > 0$ and

$$2A_1(\theta_s) - A_1'(\theta_s)\theta_s = 2b_1\theta_s + 2b_0 - b_1\theta_s = b_1\theta_s + 2b_0 > 0.$$

Thus we have proved that the denominator is positive.

□

Proposition 13 *If $\overline{\theta_s} < \theta_s'$ and $H(\overline{\theta_s}) < 0$, then for any $\theta_s \in I_3$ the inequality $D_2(\theta_s) < 0$ holds. (We recall that H is defined in (20).)*

Proof. Similarly to the proof of the previous Proposition we will determine the signs of the numerator and the denominator of D_2. In this case the numerator is positive and the denominator is negative. First, let us consider the numerator as it is given in (19). We will prove that $H(\theta_s) < 0$ holds for any $\theta_s \in I_3 = (\overline{\theta_s}, \theta_s')$. At the left end point of the interval we have $H(\overline{\theta_s}) < 0$. Moreover, H is a decreasing function in I_3 since

$$H'(\theta_s) = A_2''(\theta_s)\theta_s N(\theta_s) + 3A_2'(\theta_s)N(\theta_s) + A_2(\theta_s)N'(\theta_s) < 0,$$

by using again the properties of the functions A_2 and N, see Figure 3.

Let us consider the sign of the denominator of D_2. Using (22) the denominator can be expressed as

$$f_2'f_1 - f_2f_1' = J[G_1 + G_2 - 3F] + J[G_3 + G_4].$$

Now it is easy to see from Figure 3 that $J[G_1 + G_2 - 3F] < 0$. Furthermore, one can observe that $G_3 + G_4 = 2A_1A_2NL_1 > 0$. Hence using that $J < 0$ we get that the denominator is negative.

□

Using the above Propositions the possible shapes of the D-curve can be classified, then based on the simple rules of the PRM [9] for counting the number of tangents we get the following Theorem.

Theorem 2 *The D-curve has a vertical asymptote at*

$$K_2 = \frac{\alpha(K_1 + L_1)^3}{2K_1 L_1^2}.$$

- *If $\theta_s' < \overline{\theta_s}$, then the D-curve tends to $-\infty$ at this asymptote and does not enter the positive quadrant. The number of tangents that can be drawn to the D-curve from a given point of the positive quadrant is one if the point is in the right hand side of the asymptote, and it is zero if it is in the left hand side.*
- *If $\theta_s' > \overline{\theta_s}$ and $H(\overline{\theta_s}) < 0$, then we have the same conclusion.*
- *If $\theta_s' > \overline{\theta_s}$ and $H(\overline{\theta_s}) > 0$, then the D-curve tends to $+\infty$ at the asymptote and enters the positive quadrant. The number of tangents that can be drawn to the D-curve from a given point of the positive quadrant is one if the point is in the right hand side of the asymptote, it is two if the point is between the D-curve and the asymptote, and it is zero if it is in the left hand side of the D-curve.*

4 Bifurcations of the steady states

4.1 Bifurcations of the trivial steady state

In this subsection we investigate the transcritical and Hopf bifurcations. Hopf bifurcation may occur in the system if the Jacobian has a complex eigenvalue with zero real part. The characteristic polynomial of the Jacobian is a cubic, hence we will need the following two Lemmas.

Lemma 3 *The characteristic polynomial of a matrix $A \in \mathbb{R}^{3\times 3}$ is $\lambda^3 - \lambda^2 \mathrm{Tr A} + \lambda(\mathrm{A}_{11} + \mathrm{A}_{22} + \mathrm{A}_{33}) - \det \mathrm{A} = 0$, where A_{ii} is the 2-by-2 determinant obtained from the matrix A after omitting the i-th row and column.*

Lemma 4 *The polynomial $\lambda^3 - b_2\lambda^2 + b_1\lambda - b_0$ with real coefficients has a complex root with zero real part if and only if $b_0 = b_1 b_2$ and $b_1 > 0$.*

Proof. If there is a complex root with zero real part, then we have $\lambda_{1,2} = \pm i\omega \neq 0$ because the polynomial is real. Let us denote the third root by $\lambda_3 = a$. Then we have $\lambda^3 - b_2\lambda^2 + b_1\lambda - b_0 = (\lambda^2 + \omega^2)(\lambda - a) = \lambda^3 - a\lambda^2 + \omega^2\lambda - a\omega^2$, yielding $b_2 = a, b_1 = \omega^2$ and $b_0 = a\omega^2$. If the coefficients b_0, b_1, b_2 are given, then one can find a and ω if and only if $b_0 = b_1 b_2$ and $b_1 > 0$ hold, namely $a = b_2$ and $\omega = \sqrt{b_1}$.

□

Let us express the Jacobian of the system in terms of the v_i's as follows

$$\begin{pmatrix} 3\partial_1 v_2 - \partial_1 v_3 & 3\partial_2 v_2 - \partial_2 v_3 & 3\partial_3 v_2 - \partial_3 v_3 \\ \partial_1 v_1 - \partial_1 v_2 & \partial_2 v_1 - \partial_2 v_2 & \partial_3 v_1 - \partial_3 v_2 \\ \partial_1 v_3 - \partial_1 v_2 & \partial_2 v_3 - \partial_2 v_2 & \partial_3 v_3 - \partial_3 v_2 - \alpha \end{pmatrix} \quad (23)$$

where ∂_1, ∂_2 and ∂_3 denote differentiation with respect to θ_1, θ_2 and c, respectively and

$$\partial_1 v_1 = -K_1, \qquad \partial_2 v_1 = -K_1 - L_1, \qquad \partial_3 v_1 = 0,$$

$$\partial_1 v_2 = -2K_2\theta_2\theta_s c - 3L_2\theta_1^2, \qquad \partial_2 v_2 = K_2\theta_s^2 c - 2K_2\theta_2\theta_s c, \qquad \partial_3 v_2 = K_2\theta_2\theta_s^2,$$

$$\partial_1 v_3 = K_3 + L_3 c, \qquad \partial_2 v_3 = L_3 c, \qquad \partial_3 v_3 = -L_3\theta_s.$$

Let us investigate first the trivial steady state where $\theta_s = \frac{L_1}{K_1+L_1}, \theta_1 = 0, \theta_2 = \frac{K_1}{K_1+L_1}$, and $c = 0$. The Jacobian in this stationary point takes the following form:

$$A := \begin{pmatrix} -K_3 & 0 & 3K_2\theta_2\theta_s^2 + L_3\theta_s \\ -K_1 & -K_1 - L_1 & -K_2\theta_2\theta_s^2 \\ K_3 & 0 & -L_3\theta_s - K_2\theta_2\theta_s^2 - \alpha \end{pmatrix}.$$

According to Lemma 3 the coefficients of its characteristic polynomial are

$$b_0 = \det A, \quad b_1 = A_{11} + A_{22} + A_{33}, \quad b_2 = \mathrm{TrA}.$$

It can be easily seen that $\det A = -(K_1+L_1)A_{22}$. Hence the condition $b_0 = b_1 b_2$ in Lemma 4 takes the form $\det A = (A_{11} + A_{22} + A_{33})\mathrm{TrA}$ that is equivalent to

$$(K_1+L_1)A_{22} = (A_{11}+A_{22}+A_{33})(K_3-a_{33})+(A_{11}+A_{33})(K_1+L_1)+(K_1+L_1)A_{22}.$$

If this is true, then $b_1 > 0$ cannot hold, because $b_1 = A_{11} + A_{22} + A_{33}$ and if this is positive, then the left hand side is less then the right hand side. Hence according to Lemma 4 we have proved the following.

Proposition 14 *Hopf bifurcation cannot occur at the trivial steady state.*

In order to find the transcritical bifurcation we examine the stability of the trivial stationary point by using the Routh-Hurwitz criterion.

Proposition 15 *The trivial stationary point is stable if and only if*

$$-\mathrm{TrA} > 0, \tag{24}$$

$$-\mathrm{TrA}(\mathrm{A}_{11} + \mathrm{A}_{22} + \mathrm{A}_{33}) + \det \mathrm{A} > 0, \tag{25}$$

$$\det A[\det A - \mathrm{TrA}(\mathrm{A}_{11} + \mathrm{A}_{22} + \mathrm{A}_{33})] > 0. \tag{26}$$

Condition (24) is obviously always true, because the variables and parameters are positive. We have seen above that there is no Hopf bifurcation, hence in the case $-\det A > 0$ condition (25) also holds. Hence the condition of stability is $-\det A > 0$. This enables us to prove the following.

Proposition 16 *The trivial stationary point is stable if and only if the inequality $K_2 < \frac{\alpha(K_1+L_1)^3}{2K_1L_1^2}$ holds.*

Proof. The inequality $-\det A > 0$ holds if and only if $A_{22} > 0$ that is equivalent to the given inequality.

□

Thus we have the following Theorem concerning the bifurcations at the trivial steady state.

Theorem 3 *There cannot be Hopf bifurcation at the trivial stationary point, and for* $K_2 = \frac{\alpha(K_1+L_1)^3}{2K_1L_1^2}$ *transcritical bifurcation occurs.*

We note that the condition of the transcritical bifurcation gives the first coordinate of the vertical asymptote of the D-curve.

4.2 Numerical study of the Hopf bifurcation at the non-trivial steady state

The investigation of the stability of the non-trivial stationary points becomes too complicated analytically, hence we will show numerical evidence that there is no Hopf bifurcation at a non-trivial steady state. Based on Lemma 3 and Lemma 4 it is enough to show that $b_0 = b_1b_2$ and $b_1 > 0$ cannot hold at the same time. Now we explain how an exhaustive parameter search was carried out to show numerical evidence that there is no Hopf bifurcation at a non-trivial steady state.

First a mesh in the five dimensional parameter space of the parameters K_1, L_1, K_3, L_3 and α was given. At every mesh point, i.e. for a given value of these parameters, the following procedure was carried out. First, the interval $I_3 = I(\theta_s', \overline{\theta_s})$ is determined, then the points of the D-curve can be obtained from (18). Taking a mesh in this interval, the value of θ_s is varied along the mesh points. We have seen that once θ_s is given, then the coordinates of the steady state are determined by (10). Moreover, according to the Tangential property (see [9, 10]), if θ_s is given, then the parameter pair (K_2, L_2) lies on the tangent line of the D-curve drawn at the point $D(\theta_s)$. Therefore the Hopf bifurcation points could be found in the following way. For a given θ_s we introduce a distance parameter d along the tangent line of the D-curve at $D(\theta_s)$. From the value of d we determine the K_2 and L_2 value along the tangent, which determines a point being in distance d from the tangent point $D(\theta_s)$. The values of θ_1, θ_2 and c are given by (10). Hence in the Jacobian (23) every term is expressed in terms of θ_s and d. Hence for a given θ_s the coefficients b_i of the characteristic polynomial are functions of d. Then choosing a sufficiently large number R the value of d is varied in the interval $(-R, R)$ and the values of $b_1b_2 - b_0$ and b_1 are determined. We found that for all values of d for which $b_1 > 0$ holds the expression $b_1b_2 - b_0$ gives a positive number which means that Hopf bifurcation cannot occur. This has been tested for all values of θ_s in the given mesh, and for all values of the parameters K_1, L_1, K_3, L_3 and α given by the mesh in the five dimensional parameter space.

5 Dynamical behaviour

Let us consider first the phase space of the system. Since the variables θ_1, θ_2 denote the relative coverage of the surface with OH and O_2H molecules, and θ_s denotes the number of free surface spaces per surface unit, therefore the values of these variables are between zero and one. The third variable c is obviously non-negative by chemical reasons, however, according to the next Proposition there is a bounded positively invariant set.

Proposition 17 *The* $(0,0,0),(1,0,0),(0,1,0)$ *triangular prism in the phase plane with height* $\frac{K_3+L_2}{\alpha}+\epsilon$ *is positively invariant for system (4)–(6) (for any positive value of* ϵ*).*

Proof. From equation (4) one can see that $\theta_1 = 0$ and $\theta_2 \in [0,1]$ imply $\dot{\theta}_1 > 0$. Similarly, if $\theta_2 = 0$, and $\theta_1 \in [0,1]$, then $\dot{\theta}_2 > 0$. If $\theta_1+\theta_2 = 1$ (so $\theta_s = 0$), and $\theta_1, \theta_2 \in [0,1]$, then $\dot{\theta}_1 + \dot{\theta}_2 < 0$. From equation (6) if $c = 0$ and $\theta_1, \theta_2 \in [0,1]$ then $\dot{c} > 0$.

We need to show that $\dot{c} < 0$ holds if c is large. Since $\dot{c} = K_3\theta_1 - L_3\theta_s c - K_2\theta_2\theta_s^2 c + L_2\theta_1^3 - \alpha c$ therefore $\dot{c} < 0$ follows from $\dfrac{K_3\theta_1 + L_2\theta_1^3}{\alpha + K_2\theta_2\theta_s^2 + L_3\theta_s} < c$. Now using $\dfrac{K_3\theta_1 + L_2\theta_1^3}{\alpha + K_2\theta_2\theta_s^2 + L_3\theta_s} \leq \dfrac{K_3+L_2}{\alpha}$ the statement follows.

Hence the trajectories cross the boundaries of the prism in the direction of the interior of the prism, therefore the prism is positively invariant.

□

Let us consider now the number of stationary points. As it was mentioned above, the number of solutions of the equation can be easily determined by the so called tangential property. This means that the number of solutions of (16) belonging to a given parameter pair (K_2, L_2) is equal to number of tangents drawn to the D-curve from the point (K_2, L_2). Moreover, according to Theorem 1 the number of non-trivial steady states is equal to the number of solutions of (16) in the interval I_3. Furthermore, there is a trivial steady state given in Lemma 1. Thus the exact number of stationary points for different values of K_2 and L_2 can be given as follows based on Theorem 2.

Theorem 4 *Transcritical bifurcation may occur along the vertical asymptote of the D-curve at*

$$K_2 = \frac{\alpha(K_1+L_1)^3}{2K_1L_1^2}.$$

- *If* $\theta_s' < \overline{\theta_s}$ *or* $\theta_s' > \overline{\theta_s}$ *and* $H(\overline{\theta_s}) < 0$*, then this asymptote, dividing the positive quadrant into two parts, is the only bifurcation curve. The number of steady states is two if the point* (K_2, L_2) *is in the right hand side of the asymptote, and it is one if it is in the left hand side, see Figure 4 (a).*
- *If* $\theta_s' > \overline{\theta_s}$ *and* $H(\overline{\theta_s}) > 0$*, then the D-curve and the asymptote divide the positive quadrant into three parts. The number of steady states is two if the point* (K_2, L_2) *is in the right hand side of the asymptote, it is three if the point is between the D-curve and the asymptote, and it is one if it is in the left hand side of the D-curve, see Figure 4 (b).*

Our results about the possible phase portraits are based on those about the steady states. According to the previous theorem there are two different cases.

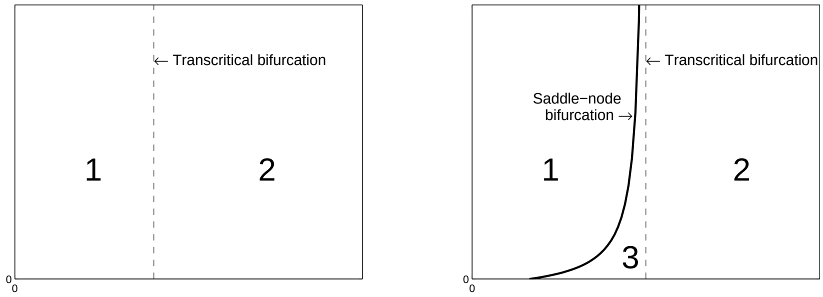

Figure 4: The two different bifurcation diagrams described in Theorem 4. In the first case (a) only transcritical bifurcation may occur, while in the second case (b) there can be also saddle-node bifurcation. The number of steady states belonging to the different parameter regions is also shown.

In the first case only transcritical bifurcation may occur along the vertical asymptote of the D-curve. If the point (K_2, L_2) is in the right hand side of the asymptote, then the trivial steady state is unstable and there is a non-trivial steady state (with positive coordinates). If the point (K_2, L_2) is in the left hand side of the asymptote, then there is a unique stationary point, the trivial steady state and it is stable.

In the second case described in the above Theorem two bifurcations may occur, see Figure 5. Along the vertical asymptote there is transcritical bifurcation, similarly to the previous case, and in addition saddle-node bifurcation may occur along the D-curve. These two bifurcation curves divide the positive quadrant of the (K_2, L_2) parameter plane into three parts yielding three different phase portraits shown in Figure 5. If the point (K_2, L_2) is in the right hand side of the asymptote, then the trivial steady state is unstable and there is a stable non-trivial steady state. If the point (K_2, L_2) is between the D-curve and the asymptote then the trivial steady state is stable and there are two non-trivial steady states, one of them is stable, the other one is unstable, i.e. bistability occurs in this region of the parameter space. Finally, if the point (K_2, L_2) is in the left hand side of the D-curve, then the two non-trivial steady states disappear and there is a unique stationary point, the trivial steady state that is stable.

6 Discussion

We studied the dynamical behaviour of the ODE system (4)-(6) describing the oxygen reduction reaction (ORR) on platinum surface in nafion. Our mathematical model is the generalization of a simpler, two-variable model that describes the same ORR reaction on platinum in electrolyte, i.e. in water containing sulfuric acid. In this later case the water concentration can be considered to be constant, hence only two equations, (4) and (5) are needed. We investigated this

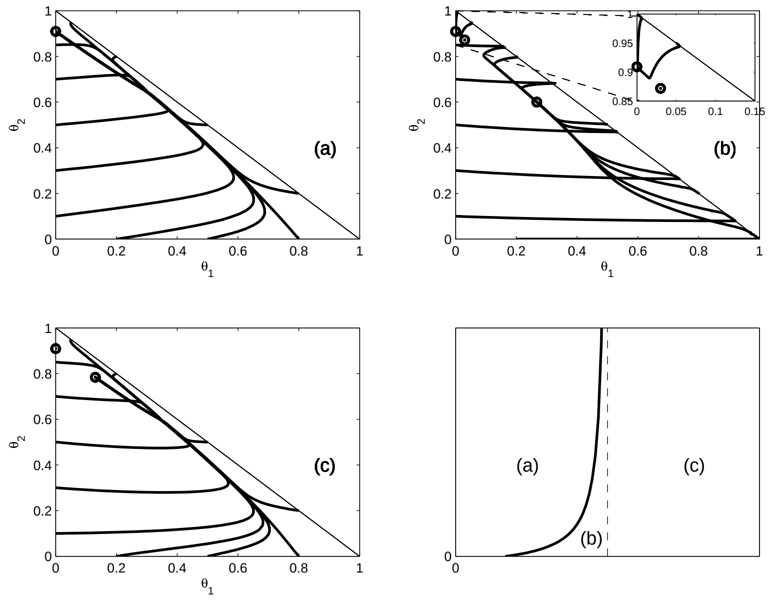

Figure 5: The three different phase portraits belonging to the three parameter regions determined by the saddle-node and transcritical bifurcation curves. The bifurcation diagram is shown in part (d) and the phase portraits belonging to the three regions are shown in parts (a), (b) and (c).

simpler system in [4] and found that the unusual surface mass changes in the course of the oxygen reduction reaction can be explained by using that simple kinetic model. Chronopotentiometry and simultaneous electrochemical quartz crystal nanobalance measurements showed that surface mass can increase during the reduction [1], that can be interpreted in terms of the presence of bistability, i.e. the coexistence of two stable steady states. If the reaction takes place in nafion, instead of the water containing electrolyte, then the water produced during the reaction should be drained, this process is described by the parameter α. In this case the mathematical model is the ODE system (4)-(6) where the third equation is for water concentration.

The detailed mathematical study of the simpler, two-variable model was carried out in [4]. In that paper it was revealed that the D-curve (saddle-node bifurcation curve) can have two different shapes. Under certain conditions on the parameters the D-curve enters the positive quadrant and has a cusp point there. Hence for those parameter pairs lying inside the cusp domain there are three equilibria, and for those lying outside there is one. If these conditions do not hold, then the D-curve does not enter the positive quadrant, hence for all parameter pairs there there is one equilibrium point. It was also proved that Hopf bifurcation cannot occur in the system and periodic orbits do not exist for any values of the parameters.

In this paper we studied the three-variable model (4)-(6) in detail. Compared to the two-dimensional case, it is a new feature that there is a trivial steady state with zero water concentration. This steady state may undergo transcritical bifurcation when it looses its stability and a new stable non-trivial steady state (with non-zero surface mass and water concentrations) appears. It is also a new phenomenon in this three-dimensional system that bistability occurs between the saddle-node and transcritical bifurcation curves (the cusp of the D-curve cannot enter the positive quadrant of the parameter plane). We showed numerical evidence that Hopf bifurcation cannot occur in this system, however it is proved only for the trivial steady state. The non-existence of periodic orbits is conjectured based on our systematic numerical experiments, however its rigorous proof could be the subject of future work.

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