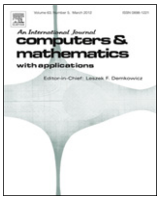
Computers and Mathematics with Applications 65 (2013) 325–337

Contents lists available at SciVerse ScienceDirect

Computers and Mathematics with Applications

journal homepage: www.elsevier.com/locate/camwa



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

Gábor Csörgő*, Péter L. Simon

Department of Applied Analysis and Computational Mathematics, Institute of Mathematics, Eötvös Loránd University, Budapest, Hungary

ARTICLE INFO

Keywords:
Fold
Transcritical
Hopf bifurcations
Oxygen reduction reaction
Bistability

ABSTRACT

The bifurcations in a three-variable ODE model describing the oxygen reduction reaction on a 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 can 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, which is important from the chemical point of view.

1. Introduction

During the development of efficient and reliable fuel cells it is crucial to understand the oxygen reduction reaction (ORR) on a platinum surface. Several attempts has been made to establish the reaction scheme [1–6]; however, no final conclusion has been reached. The most widely used scheme that also serves as a common base for others was introduced by Damjanovic and Brusic [2] and this will be the one that we will use in this paper. The detailed mathematical study of the model can also help 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 and θ_2 to denote the relative coverages 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

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

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* Corresponding author. Tel.: +36 304547141.
E-mail address: csgoaat@inf.elte.hu (G. Csörgő).

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doi:10.1016/j.camwa.2012.04.020

where

$$K_1 = k_1 \exp\left(-\frac{\beta_1(\eta - E_1)F}{RT}\right), \qquad K_2 = k_2, \qquad K_3 = k_3 \exp\left(-\frac{\beta_2(\eta - E_2)F}{RT}\right)$$
$$L_1 = k_{-1} \exp\left(\frac{(1-\beta_1)(\eta - E_1)F}{RT}\right), \qquad L_2 = k_{-2},$$
$$L_3 = k_{-3} \exp\left(\frac{(1-\beta_2)(\eta - E_2)F}{RT}\right),$$

η is the electrode potential, F is Faraday's constant, R is the universal gas constant, the k_i are rate constants, and the β_i and E_i are electrochemical parameters [7].

On the basis of the above reactions, the kinetic equations take the form

$$\dot{\theta}_1 = 3v_2 - v_3, \tag{1}$$
$$\dot{\theta}_2 = v_1 - v_2, \tag{2}$$
$$\dot{c} = v_3 - v_2 - \alpha c, \tag{3}$$

where α is a parameter describing the drainage of water. In our previous model [8] the water concentration c was assumed to be constant, which is a reasonable approximation, leading to the two-dimensional system (1) and (2). The detailed study of that two-dimensional dynamical system was given in [8], 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 for the v_i into system (1)–(3), we get the following nonlinear system of ODEs:

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

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

In Section 2 it is shown how the steady state system can 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 the first and the 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 the v_i yield

$$K_1\theta_s - L_1\theta_2 = \frac{\alpha c}{2}, \tag{7}$$
$$K_2\theta_2\theta_s^2 c - L_2\theta_1^3 = \frac{\alpha c}{2}, \tag{8}$$
$$K_3\theta_1 - L_3\theta_s c = \frac{3\alpha c}{2}. \tag{9}$$

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

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

where

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