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Mechanism and model of the oscillatory electro-oxidation of methanol

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A mechanism for the kinetic instabilities observed in the galvanostatic electro-oxidation of methanol is suggested and a model developed. The model is investigated using stoichiometric network analysis as well as concepts from algebraic geometry (polynomial rings and ideal theory) revealing the occurrence of a Hopf and a saddle-node bifurcation. These analytical solutions are confirmed by numerical integration of the system of differential equations. © 2010 American Institute of Physics. [doi:10.1063/1.3368790]

I. INTRODUCTION

The electro-oxidation of small organic molecules has attracted considerable interest in the past decades, in particular in the context of applications in fuel cells (see Ref. 1 for a recent survey of the literature). A promising candidate as energy source is methanol for so-called direct methanol fuel cells7 on which numerous mechanistic and kinetic studies have been carried out.3–10 The oxidation of MeOH on noble metal electrodes (Pt or Pt/Ru) is known to exhibit kinetic instabilities, e.g., under galvanostatic conditions the process exhibits kinetic oscillations as well as a hard transition to high potential.4 Such dynamic instabilities can be exploited for model development as will be shown in the present study where we identify the core mechanism explaining the experimentally observed bifurcation sequence.

The paper is organized as follows: First we describe the mechanism and develop a parsimonious model (Sec. II), which is subsequently analyzed using stoichiometric network analysis (SNA) (Sec. III). While SNA allows existence proofs of local bifurcations, quantitative solutions require more sophisticated methods from algebraic geometry described in Sec. IV. These are corroborated by numerical studies (Sec. V), followed by a discussion focused on the relevance of analytical mathematical tools for model development and analysis.

II. MECHANISM AND MODEL

Methanol oxidation on Pt occurs via a Langmuir–Hinshelwood mechanism by reversible adsorption on the electrode, followed by (presumably) stepwise dehydrogenation.3–10 An important intermediate is HCO which has been shown to occupy three adjacent sites. It can be further dehydrogenated to CO, which subsequently reacts with adsorbed oxygen species (OH or O) to form CO2. Also the intermediate species can react with oxygen leading to side products such as formaldehyde and formic acid.

In order to keep the model simple, we neglect the side reactions and assume that the whole process runs through HCO and CO

\[ k_1, \Phi \]

\[ [\text{MeOH}] + 3 \rightarrow \text{HCO} + [3\text{H}^+] + 3e^- \quad |v_1 \sim \ast^2, \]

\[ k_2 \]

\[ \text{HCO} \rightarrow \text{CO} + 2 \ast + [\text{H}^+] + (e^-). \] (2)

Here MeOH, denotes methanol in the electrolyte, \( \ast \), a vacant adsorption site on the electrode. Reaction (1) is composed of all steps leading to HCO through methoxide and aldehyde species

\[ \text{MeOH} + \ast \rightarrow \text{MeOH}, \]

\[ \text{MeOH} + \ast \rightarrow \text{CH}_3\text{O} + \text{H}^+ + e^-; \]

\[ \text{CH}_3\text{O} \rightarrow \text{HCO} + \text{H}^+ + e^-; \]

\[ \text{CH}_2\text{O} + \ast \rightarrow \text{HCO} + \text{H}^+ + e^-; \]

Note that although a total of three vacant sites are consumed in process (1), the overall kinetics is assumed to be of second order \( (v_1 \sim \ast^2) \), which arises from the initial adsorption/desorption equilibrium and the rate-determining step of the subsequent chain.

For the complete oxidation of MeOH to CO2 the adsorption and desorption of H2O is considered

\[ k_3, \Phi \]

\[ [\text{H}_2\text{O}] + \ast \rightarrow \text{O} + [2\text{H}^+] + (2e^-), \]

\[ k_4 \]

\[ \text{CO} + \text{O} \rightarrow 2 \ast + [\text{CO}_2], \]

\[ k_5, -\Phi \]

\[ [2\text{H}^+] + (2e^-) + \text{O} \rightarrow \ast + [\text{H}_2\text{O}]. \] (5)

The relevant species are adsorbed oxygen O, adsorbed formyl HCO, adsorbed carbon monoxide CO, the double layer potential \( \Phi \), and the free adsorption sites \( \ast \). Species in squared brackets are nonessential (i.e., they are present in large excess or constitute inert products). For simplicity we

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assume that process (1) is the only current carrier neglecting the contributions of the other reactions (bracketed \(e^\prime\)). The oxidation step of adsorbed HCO in Eq. (2) and the oxidation of adsorbed CO in Eq. (4) are modeled with a mass action rate law, the other reactions with the Butler–Volmer rate law. The relevant adsorbed species and free adsorption sites are denoted by \(x_1 = \ce{H2O849}\), \(x_2 = \ce{O}\), \(x_4 = \ce{HCO}\), and \(x_5 = \ce{CO}\). Then the kinetic equations are given by

\[
\begin{align*}
\dot{x}_1 & = -3k_1x_1^2e^{\gamma_1}\phi + 2k_3x_4 - k_3x_1x_3 + 2k_4x_2x_5 + k_5x_2e^{-\gamma_2}\phi, \\
\dot{x}_2 & = k_3x_1e^{\gamma_1}\phi - k_4x_2x_5 - k_5x_2e^{-\gamma_2}\phi, \\
\Phi & = k_7 - k_1x_1^2e^{\gamma_1}\phi, \\
\dot{x}_4 & = k_1x_1^2e^{\gamma_1}\phi - k_2x_4, \\
\dot{x}_5 & = k_2x_4 - k_3x_2x_5,
\end{align*}
\]

where \(k_0\) corresponds to the symmetry factor of the charge transfer and \(k_7\) is the total \(\ce{H20850}/\ce{H20850}\) current. Thus the third equation of Eq. (6) represents Kirchhoff’s law, i.e., the total current \(k_7\) (equal to the migration current) is the sum of the capacitive current \(\Phi\) and the reaction current \(k_1x_1^2e^{\gamma_1}\phi\). By a substitution\(^{11}\) the exponential terms can be eliminated

\[
\begin{align*}
\dot{x}_3 & = e^{\gamma_1}\phi, \\
\dot{x}_5 & = k_6x_3\Phi, \\
\dot{x}_3 & = k_6x_3\Phi, \\
\dot{x}_5 & = k_6x_3\Phi.
\end{align*}
\]

The following kinetic equations are obtained:

\[
\begin{align*}
\dot{x}_1 & = -3k_1x_1^2x_3 + 2k_2x_4 - k_3x_1x_3 + 2k_4x_2x_5 + k_5x_2x_3^{-1}, \\
\dot{x}_2 & = k_3x_1x_3 - k_4x_2x_5 - k_5x_2x_3^{-1}, \\
\dot{x}_3 & = k_6x_3^2k_1x_1^2x_3, \\
\dot{x}_4 & = k_1x_1^2x_3 - k_2x_4, \\
\dot{x}_5 & = k_2x_4 - k_3x_2x_5.
\end{align*}
\]

Note that the kinetic term with a negative exponent (arising from the reduction reaction) does not pose formal problems in the mathematical analysis.

One can readily see that there is a conservation relation of the total number of adsorption sites

\[
x_1 + x_2 + 3x_4 + x_5 = \text{const.}
\]

III. EXISTENCE PROOFS OF BIFURCATIONS USING SNA

We use SNA (Ref. 12) in order to check analytically for kinetic instabilities in the model—for details of the procedure, which is only sketched here, see Refs. 13 and 14. In SNA, a reaction mechanism of \(n\) species and \(r\) reactions is completely specified by two \(n \times r\) matrices: the stoichiometric matrix \(N\), which contains the (positive or negative) stoichiometric change of each species in each reaction, and the kinetic matrix \(\kappa\), which contains the respective kinetic exponents, assuming that the kinetics of the \(j\)th reaction is given (or can be approximated) by power laws \(k_j\Pi x_i^{\gamma_j}\), where \(x_i\) denotes the concentration of the \(i\)th species. The rate constants \(k_j\) are left unspecified and assumed to be able to take on any non-negative value (complete parameter set). The elements of \(N\) and \(\kappa\) can be written down explicitly or encoded in a network diagram as the number of barbs and feathers on the reaction arrows (Fig. 1).

Note that an \(n \times r\) matrix of rank \(d\) (\(\leq n\)) has an \(r-d\) dimensional right null space (rns) and an \(n-d\) dimensional left null space (lns). The lns of the stoichiometric matrix \(N\), \(v^\top v = 0\), contains the conservation constraints, while the intersection of the rns with the non-negative orthant represents the set of all stationary solutions. It forms a convex cone and can therefore be parametrized as a non-negative linear combination of the vectors pointing along its edges, usually referred to as extreme currents \(E_i\). These are subnetworks of the full reaction network that cannot be further simplified without violating the stationary state condition. Consequently, in SNA the complete set of stationary states can be written down in closed form as a linear combination \(\Sigma j_i E_i\) with non-negative coefficients \(j_i\) of a certain number of indecomposable subnetworks \(E_i\). For the mechanism described above there are seven reactions, five species, and one constraint \((r = 7, n = 5, d = 4)\). The current cone therefore is three-dimensional. In this case the cone is spanned by three extreme currents shown in Fig. 1.

\[A = \text{diag}(h),\]

where \(N_e\) denotes the stoichiometric matrix renormalized for a given current \(\Sigma j_i E_i\) and hence dependent on the \(j_i\); i.e.,

\[E_1, E_2, E_3, \quad D_{CM}(E_1+E_2+E_3)\]

FIG. 1. Extreme currents \(E_i\) of the system given by Eq. (8). \(E_1\) represents the formation and the reduction of surface oxygen, \(E_2\) contains the oxidation of MeOH via HCO and CO, and \(E_3\) contains the preset galvanostatic current which formally leads to an autocatalysis of \(X_6\). The species symbols \(X_i\) are connected by arrows denoting the reactions. The positive (positive) stoichiometric coefficients of products are given by the number of barbs on the arrow, the negative ones of reactants are presented by the total number of feathers, while the kinetic exponent of a reactant is symbolized by the number of left feathers. By convention no feathers are shown if stoichiometric and kinetic coefficients are both unity. The kinetic exponent for \(x_1\) is \(-1\) for the reduction of oxygen. In the current matrix diagram \(D_{CM}\), the diagonal elements are the numbers in front of the \(X_i\), the positive (negative) influence of a species on another (off-diagonal elements) are denoted by full (dashed) arrows (numerical value given by the number of barbs). The feedback loops and the \(\beta\) for the stoichiometry given by the chosen current can be read from the \(D_{CM}\).
of the three extreme currents. It is advantageous to not use the conservation constraint until later (see Sec. IV).

A sufficient condition for a kinetic instability somewhere in parameter space is \( \exists \beta_i < 0 \). A necessary and sufficient condition for a saddle-node bifurcation is a change of sign of \( \alpha_i \), respectively \( \Sigma \alpha_d \) in the presence of conservation constraints. A necessary and sufficient condition for a Hopf bifurcation has been given elsewhere, but it is only really needed for nonautocatalytic networks (i.e., when no \( \beta_i \) becomes negative). In the present context, we therefore use a (simpler) sufficient condition.

A network contains a Hopf bifurcation if there exists a species \( X_i \) with reciprocal concentration \( h_i \) and a natural number \( k < d \) such that for some current:

(a) the sum over all \( \alpha_k \) which depend on \( h_i \) is negative and
(b) the sum over all \( \alpha_d \) which depend on \( h_i \) remains positive.

This condition can be tested using the \( \beta_i \). Criteria (a) and (b) lead to two inequalities for \( h_i \) (possibly including some \( j_i \)). If these do not contradict each other, the existence of a Hopf bifurcation is guaranteed. Criterion (a) actually implies that there is a positive feedback loop (autocatalysis) involving \( k \) species, which gives rise to an unstable steady state. Criterion (b) reflects the existence of a negative feedback loop involving at least one additional species (\( d > k \)) and thus (indirectly) also a different time scale. The above condition therefore just represents a precise formulation of the well-known argument that oscillations can be due to the interplay of a fast autocatalysis and a negative feedback loop occurring on a slower time scale.

For the existence proofs we choose a simple combination \( E_1 + E_2 + E_3 \), the corresponding current matrix diagram \( D_{CM} \) is also shown in Fig. 1. Choosing \( X_1 \) (exponential of the potential) as reference variable the relevant principal minors of \( S = -N_x \kappa' \) can be read directly from the \( D_{CM} \) (without explicit calculation of the full matrices \( S \) and \( A \)) and result in

\[
\begin{align*}
\beta_2(X_3, X_1) &= -8, \\
\beta_3(X_3, X_1, X_2, X_4) &= 8, \\
\beta_2(X_3, X_2) &= 4, \\
\beta_4(X_3, X_1, X_4, X_5) &= -8, \\
\beta_2(X_3, X_4) &= \beta_2(X_3, X_5) = 2, \\
\beta_6(X_3, X_2, X_4, X_5) &= 2.
\end{align*}
\]

The other \( \beta_4 \) as well as \( \beta_5 \) are equal to zero. Consequently, the condition for a saddle-node bifurcation is a change of sign in the expression

\[
8h_2h_1 - 8h_3h_1 + 2h_2h_2,
\]

which can readily happen as \( h_1 \) increases (i.e., the CO coverage decreases).

The sufficient condition for a Hopf bifurcation requires

\[
0 > -8h_1 + 4h_2 + 2h_4 + 2h_5,
\]

\[
0 < 8h_2h_1 - 8h_3h_1 + 2h_2h_2.
\]

Both conditions obviously be met if \( h_1 \) is sufficient large and \( h_5 \) small (e.g., \( h_1 = h_2 = h_3 = h_4 = 1, h_5 < 1 \)). To summarize, for decreasing CO coverage one first expects a Hopf, then a saddle-node bifurcation.

### IV. APPLICATION OF ALGEBRAIC GEOMETRY

While SNA allows existence proofs of local bifurcations (as well as some indirect guesses about the parameters), it cannot give conditions for the more natural kinetic parameters. Using ideas from algebraic geometry one can, however, fill this gap, i.e., it allows to derive restrictions for the stationary solutions in convex parameters and a one-to-one mapping back into kinetic parameters.

To start with, it is necessary to explicitly write down the (more intuitive and pictorial) concepts of SNA. Via the polynomial expressions of the kinetic equation in Eq. (8) the stoichiometric matrix \( N \) and the flux vector \( v \) comprising the monomial reaction rates can be formulated. It holds that

\[
x = N v(k, x)
\]

where \( k = (x_i) \) is the vector of rate constants for the five reactions:

\[
N = \begin{pmatrix}
-3 & 2 & -1 & 2 & 1 & 0 & 0 \\
0 & 0 & 1 & -1 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 1 & 1 \\
1 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & -1 & 0 & 0 & 0
\end{pmatrix},
\]

\[
v(x, k) = \begin{pmatrix}
k_1 x_1^2 x_3 \\
k_2 x_4 \\
k_3 x_1 x_3 \\
k_4 x_2 x_5 \\
k_5 x_2 x_5^{-1} \\
k_1 k_6 x_1^2 x_3^2 \\
k_6 k_7 x_3
\end{pmatrix}.
\]

Following SNA (Ref. 12), the cone is defined by

\[
K_v = \{ v \in R^m | N v = 0, v \geq 0 \} = (\ker N \cap R_+^m) = \left\{ \sum_{i=1}^n j_i E_i, j_i \geq 0 \forall i \right\}.
\]
\[ v(j) = \sum_{i=1}^{n} j_i E_i, \quad j_i \geq 0 \quad \forall \, i, \]

with the extreme currents \( E_i \) and the reformulated flux vector \( v(j) \)

\[
E_1 = \begin{pmatrix}
0 \\
0 \\
1 \\
1 \\
0 \\
0
\end{pmatrix}, \quad E_2 = \begin{pmatrix}
1 \\
0 \\
0 \\
0 \\
0 \\
1
\end{pmatrix}, \quad E_3 = \begin{pmatrix}
0 \\
0 \\
0 \\
0 \\
1 \\
1
\end{pmatrix},
\]

\[
\Rightarrow v(j) = j_1 E_1 + j_2 E_2 + j_3 E_3 = \begin{pmatrix}
j_2 \\
j_2 \\
j_1 + j_2 \\
j_1 \\
j_3 \\
j_3
\end{pmatrix}. \tag{16}
\]

### A. Restrictive binomials and stationary solutions

The cone (14) restricts the set of stationary solutions. Further restrictions result from the image of the monomial mappings \( \mathbb{R}^n \rightarrow \mathbb{R}^r, x \rightarrow v(k,x) \) from the concentration space into the space of reaction rates. Generally, the number of \( x_i \) is smaller than the number of monomials \( v(k,x) \); hence the image of this mapping is not the full reaction rate space and there must exist some restrictions on \( v \). These take the form of **restrictive binomials** and their derivation requires some concepts of ideal theory. We refer to Ref. 17 for the ideal theory in general and for application to chemical kinetics see Refs. 18–22.

The restrictive binomials can be found after a basis change of the ideal \( I \) which is generated by the reaction rates \( v_j \) and their corresponding monomials \( v_j(k,x) \)

\[
I = \langle v_1 - k_1 x_1^2 x_3, v_2 - k_2 x_4, v_3 - k_3 x_1 x_3, v_4 - k_4 x_2 x_5, v_5 - k_5 x_2 x_1, v_6 - k_6 x_3^2 x_1, v_7 - k_7 x_3 \rangle. \tag{17}
\]

The set of zeros of the basis elements of an ideal \( I \) is equal to the set of zeros of the whole ideal. The set of zeros of a binomial ideal is called its variety \( V(I) \). It is trivial that the reaction rates lie in the set of zeros of these binomials. The variety of Eq. (17) consists of points \( (x,v) \). In this variety there are no restrictions on \( x \), but the variables \( v \) must lie in the image of the monomial mapping of the reaction rates for given \( x \). These restrictions may be found after a change of the basis of Eq. (17). Note that the variety of an ideal is not affected by a change of the basis (Hilbert’s basis theorem).

The basis of choice in the present context is a so-called **Gröbner** basis (GB) (Ref. 17), which requires to choose a monomial order and exhibits a tendency to separate variables. For the desired separation of the variables \( v_j \) and \( x_i \) the pure lexicographic order is used. The resulting GB of the ideal (17) contains the restrictive binomials (bold binomials in GB)

\[
\text{GB} = \langle k_1 k_6 v_3^2 - v_6 k_3^2 v_7 v_1 - k_7 v_6 v_7 k_4 x_5 x_2, -k_6 v_1 k_5 x_4 + v_5 v_6 k_4 x_5 - v_1 + k_2 x_4, -v_7 k_4 k_7 x_5, k_6 k_7 k_8 - v_7 v_5, v_7 k_3 x_1 - k_6 k_7 v_3, v_6 x_1 k_3 - k_6 v_3 v_4, k_3 k_2 x_3 v_4 - v_3 v_5 k_4 x_5 - v_1 k_3 + k_1 x_3 v_3 \rangle, \tag{18}
\]

which depend only on the reaction rates and span the so-called **deformed toric ideal** \( V^{\text{def,tor}} \)

\[
V^{\text{def,tor}} = \langle k_1 k_5 v_3^2 - v_6 k_5^2 v_7 - v_3 - k_7 v_6 \rangle. \tag{19}
\]

The reaction rates are confined to the deformed toric variety \( V^{\text{def,tor}} \) and additionally we know that the non-negative stationary reaction rates are confined to the cone \( K_o \) [Eq. (14)]. Hence, the non-negative stationary reaction rates must lie in the intersection of the deformed toric variety and the cone

\[
V^{\text{def,tor}} \cap K_o. \tag{20}
\]

Since we have not yet used any conservation constraint, this intersection generally has a dimension equal to the number of constraints \( n-d \). Consequently, the number of restrictive binomials is in general \( r-n \). With \( v_1 = j_2, v_3 = j_1 + j_2, v_6 = j_3, \) and \( v_7 = j_3 \), see Eq. (16), we obtain the deformed toric variety

\[
0 = k_1 k_5 (j_1 + j_2)^2 - j_3 k_3^2, \tag{21}
\]

\[
0 = j_3 j_2 - k_1 j_3.
\]

This leads to the intersection of the convex cone \( K_o \) and the deformed toric variety \( V^{\text{def,tor}} \) (20). Since there is exactly one conservation relation (9) the intersection represents a curve. As curve parameter we arbitrarily choose the convex coordinate \( j_1 \) (* \( \Rightarrow \) O equilibrium)

\[
j_1 = j_1, \quad j_2 = k_7, \quad j_3 = \frac{k_6 (j_1 + k_7)}{k_3^2}. \tag{21}
\]

and the curve in \( \mathbb{R}^{2}_{\geq 0} \) is given by

\[
v(k,j_1) = \begin{pmatrix}
k_7 \\
k_7 \\
(j_1 + k_7) \frac{k_5}{k_3} \\
(j_1 + k_7)^2 k_6 \frac{k_5}{k_3^2}
\end{pmatrix}. \tag{22}
\]
\{ x \in \mathbb{R}^n_{\geq 0} | \exists k_i \geq 0 \quad \text{with} \quad N_U(k, x) = 0 \}, \quad (23)

is mapped onto the intersection set of the deformed toric variety and the cone
\{ v \in V(\text{defvar}), v \geq 0, N_U = 0 \}. \quad (24)

In one direction the mapping is given by \( v : x \mapsto v(k, x) \). The inverse mapping (from the intersection curve to the set of stationary concentrations) is \( v^{-1} : v(k, j) \mapsto x(k, j) \) and can be calculated by the Hermite normal form algorithm. For details and proofs of this relationship see Refs. 18 and 21.

In general, the Hermite normal form \( H \) of a rectangular matrix of integers \( A \) is its reduced echelon form. It holds that \( UA=H \). For our purpose the Hermite normal form \( H \) of the kinetic matrix \( \kappa \) is required: \( U \kappa = H \). Then the matrix \( U \) contains the exponents of certain slack variables \( w \) which will form monomials substituting the variables \( x \), i.e., \( x(w) \). Thereby, it is possible to represent the reaction rates in the slack variables too, \( v(w) \)

\[
\begin{pmatrix}
1 & -1 & -1 & 0 & 1 \\
0 & 0 & 0 & 1 & 0 \\
-1 & 2 & 2 & 0 & -2 \\
0 & 0 & 0 & 0 & 1 \\
0 & 1 & 0 & 0 & -1 \\
\end{pmatrix}
\begin{pmatrix}
2 & 0 & 1 & 0 & 0 & 2 & 0 \\
0 & 0 & 0 & 1 & 1 & 0 & 0 \\
1 & 0 & 1 & 0 & -1 & 2 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & -1 & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 2 & 2 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 1 & 0 \\
\end{pmatrix}
\]

By setting \( v(w) = v(k, j) \) the slack variables in dependence of the curve parameter \( w(k, j) \) can be calculated and resubstituted into \( x(w) \). Then the set of stationary concentrations in dependence of the curve parameter \( x(k, j) \) is given by

\[
\begin{pmatrix}
k_3 k_7 \\
\frac{(j_1 + k_7) k_1}{k_7 k_3} \\
\frac{k_1 (j_1 + k_7)}{k_7} \\
\frac{2 (j_1 + k_7)^3 k_1}{k_7} \\
0 \\
0 \\
\end{pmatrix}
\begin{pmatrix}
k_3 k_7 \\
\frac{(j_1 + k_7) k_1}{k_7 k_3} \\
\frac{k_1 (j_1 + k_7)}{k_7} \\
\frac{2 (j_1 + k_7)^3 k_1}{k_7} \\
0 \\
0 \\
\end{pmatrix}
\begin{pmatrix}
2 k_2 \\
\frac{2 j_1 k_1 (j_1 + k_7)^2 k_4}{k_7 k_3^2} \\
0 \\
0 \\
0 \\
0 \\
\end{pmatrix}
\]

Note that the curve in both reaction rate space \( v(k, j) \) and concentration space \( x(k, j) \) corresponds to the variety of the ideal in Eq. (17). By means of these solutions the stability of our chemical reaction system can now be analyzed.

B. Stability analysis

The Jacobian matrix \( \text{Jac}(k, j) \) for our system at steady state is given by

\[
\text{Jac}(k, j) =
\begin{pmatrix}
- k_1 (j_1 + k_7) (7 k_7 + j_1) & (2 k_7 + j_1) k_1 k_7 k_3 k_7 \\
- k_1 k_7 & - k_1 k_7 & 2 k_7 k_3^2 (2 k_7 + j_1) \\
- k_1 k_7 & k_1 (j_1 + k_7) & k_1 (j_1 + k_7) k_1 \\
- 2 j_1 k_1 (j_1 + k_7)^3 k_1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\]

To prove the occurrence of a saddle-node or a Hopf bifurcation the characteristic polynomial \( \text{cp} \) of \( \text{Jac}(k, j) \) with its coefficients \( a_i \)

\[
\text{cp} = a_4 \lambda^4 + a_3 \lambda^3 + a_2 \lambda^2 + a_1 \lambda + a_0
\]

is considered. Note that because of the conservation relation (9) the characteristic polynomial is of degree four. The coefficients \( a_4 \) and \( a_3 \) for \( \text{Jac}(k, j) \) are always positive.
intersection function can be generated by substituting the stationary solutions

$$a_0 = -3j_k^3 k_j k_i k_2 k_4 - 13 j_k^3 k_j k_i k_2 k_4 - 22 j_k^3 k_j k_i k_2 k_3 k_4 - 18 j_k^3 k_j k_i k_2 k_3 k_4 + (k_j k_i k_2 k_3 k_4 k_3 k_5 - k_j^2 k_i^2 k_3^2) j_i^3 \nonumber$$

$$+ (k_j k_i k_2 k_3 k_4 (-2 k_j k_i^2 + k_i^3 k_3)) j_i^2 + 3 j_k k_i k_2 k_3^2 k_4 + k_j k_i k_2^2 k_4^2.$$  

(30)

becomes negative for high values of $j_i$ which indicates the occurrence of a saddle-node bifurcation.

A sufficient condition for the occurrence of a Hopf bifurcation will be given if $a_j > 0$, and $a_0 > 0$, and one of the other coefficients, $a_i < 0$ for an $i$ with $0<i<d$ where $d$ being the rank of the Jacobian matrix. This condition is fulfilled for low values of $j_i$ and if $k_i k_j \gg k_2$, then the coefficients $a_3, a_4, a_5$, and $a_0$ are positive and $a_2$ and $a_1$ are negative

$$a_2 = j_j^3 k_j^4 + 11 j_k^2 k_j k_i k_2^2 + 34 j_k^3 k_j^2 k_i^2 + 7 k_i k_j k_k k_i k_2^3 + k_i k_j k_k k_i k_2^4 + k_2 k_i k_3 k_4 k_5 (5 k_2 - 7 k_i k_2) + k_i k_j k_k k_i k_2^3 + k_i k_j k_k k_i k_2^4 + k_i k_j k_k k_i k_2^5 + k_i k_j k_k k_i k_2^6,$$  

(31)

The intersection relation (9) is given by the total number of adsorption sites (sum of the adsorbed species and free adsorption sites) and forms a plane c in the concentration space which is orthogonal to the $x_3$ axis. Hence the intersection points of the plane c and curve $x(k, j_i)$, see Eq. (26), are the steady-state solutions for a given number of adsorption sites. At the point of a saddle node, the plane of the intersection relation c touches the curve of the stationary solutions $x(k, j_i)$. At the same point the intersection function $F(k, j_i, c)$ and its derivative $D_j F(k, j_i, c)$ are zero (theorem of implicit functions). The intersection function can be generated by substituting the stationary solutions $x(k, j_i)$ into the conservation relation $F(k, j_i, c) = x_1 + x_2 + 3x_4 + x_5 - c$. After factorization and elimination of all nonzero factors one obtains

$$F(k, j_i, c) = k_1^4 k_2 k_4 j_i^3 + 6 k_1^2 k_2 k_4 k_3 j_i^3 + 6 k_1^2 k_2 k_4 k_3 j_i^3 + (3 k_2^3 k_3^2 k_4 k_3 + 4 k_2^3 k_3^2 k_4 k_2 k_4 - k_2 c k_1^2 k_2 k_4) j_i^3 \nonumber$$

$$+ (6 k_2^3 k_3^2 k_4 k_3 + 4 k_2^3 k_3^2 k_4 k_2 k_4 + k_2^3 k_3^2 k_4 k_2 k_4 + k_2^3 k_3^2 k_4 k_2 k_4) j_i^2 \nonumber$$

$$+ (3 k_2^3 k_3^2 k_4 k_3 - k_2 c k_1^2 k_2 k_4 + k_2^3 k_3^2 k_4 k_2 k_4 + k_2^3 k_3^2 k_4 k_2 k_4) j_i^2 + k_2^3 k_3^2 k_4 k_2 k_4.$$  

Then the intersection function represents a polynomial in $j_i$ of degree six. For simplicity let $F(k, j_i, c)$ be expressed by

$$0 = b_j j_i^6 + b_5 j_i^5 + b_4 j_i^4 + b_3 j_i^3 + b_2 j_i^2 + b_1 j_i + b_0.$$  

(32)

Since the coefficients $b_0, b_5, b_4, and b_0$ depend only on the kinetic constants $k$ they are always positive, $b_0, b_5, b_4, b_0 > 0$. The coefficients $b_5, b_2, and b_1$,

$$b_5 = k_j k_i k_2 (4 k_2 k_1 k_2 - k_3^2 k_5 (3 k_7 - c k_2)),$$

$$b_2 = k_j^2 k_2 k_4 (k_2^2 k_2 - 2 k_3 k_5 k_3 (3 k_7 - c k_2) + k_3^3 k_5 k_2),$${}  

(33)

$$b_1 = k_j^3 k_2 k_4 (k_2 k_3 + k_3 (3 k_7 - c k_2)),$$

which depend on k and c, become negative if $3 k_7 \approx c k_2$. Consequently, two sign changes are possible in the coefficients
and therefore the polynomial may have at most two positive zeros (Descartes’ rule), so only two positive steady states are possible. For \( j_1 \to 0 \) and \( j_1 \to \infty \) the polynomial is positive, therefore the number of zeros must be even. That means there are no steady states, or exactly one saddle-node bifurcation, or exactly two steady states.

As mentioned above the location of the saddle-node bifurcation—where the curve \( x(k,j_1) \) is tangential to the plane \( c \)—can be defined by a common zero of the intersection function \( F(k,j_1,c) \) and its derivative \( D_{j_1} F(k,j_1,c) \). We differentiate the intersection function \( F(k,j_1,c) \), factorize this derivative, and eliminate all nonzero factors. Then \( D_{j_1} F(k,j_1,c) \) is given by

\[
D_{j_1} F(j,k,c) = 3j_1^3k_1^2k_4 + 13j_1^2k_1^2k_2k_7 + 22j_1^3k_1^2k_4k_2^2 \\
+ 18j_1^4k_2k_4^2k_7 + (k_4k_2^2(7k_1^2k_2^2 - k_3^2k_7))j_1^3 \\
+ (k_2k_4(3k_2^7 - k_3^2k_7))j_1^2 - 3k_5^3k_5k_3j_1 \\
- k_7^4k_2^2k_4, \tag{34}
\]

which is a polynomial in \( j_1 \) of degree seven and exhibits exactly one sign change in the coefficients. Note that the derivative \( D_{j_1} F(k,j_1,c) \) of the intersection function is equal to the coefficient \( a_0 \) multiplied by \(-1\). The polynomial in Eq. (34) is negative for \( j_1 \to 0 \) and positive for \( j_1 \to \infty \). So, there is exactly one zero for the intersection function \( F(k,j_1,c) \) and its derivative \( D_{j_1} F(k,j_1,c) \). If there are two steady states then the one at low \( j_1 \) is stable since the derivative of the intersection function (34) is negative for \( j_1 \to 0 \). For high values of \( j_1 \) this derivative [Eq. (34)] is positive and the corresponding steady state is unstable. This means on the other hand that the steady state with a high coverage of carbon monoxide is stable and the steady state with a high coverage of oxygen is unstable.

The stability analysis proves the existence of a saddle node and a Hopf bifurcation. On the conditions \( 3k_3 \ll ck_2 \) and \( k_6k_1 \gg k_2 \), a saddle node occurs for high values of \( j_1 \) and a Hopf bifurcation for low values of \( j_1 \). We choose a set of kinetic constants \( k \), which fulfill the required conditions: \( k_1 =4, k_2 = 10, k_3 = 1, k_4 = 2, k_5 = 6, k_6 = 15, k_7 = 0.1, \) and \( c = 0.6 \). In Fig. 2, the curve of the stationary solutions for \( x_1 = x_3 = 0 \), and \( x_4 = \text{CO} \) in the concentration space is shown with the plane of the conservation relation intersecting the two stationary states. The location of the Hopf bifurcation can be obtained by the Hurwitz determinants. We know that two sign changes in the coefficients \( a_0 \) of the characteristic equation of the Jacobian matrix are required for the occurrence of a Hopf bifurcation, therefore the coefficient \( a_0 \) must be positive. Further, the Hurwitz determinant of highest order \( |H_4| \) must be zero. Since \( a_0 \) is positive and \( |H_4| = a_0H_3 \) holds, \( |H_3| \) must be zero.

For mathematical reasons, the obvious choice of the control parameter is the total electrode area \( c \): for large \( c \) a stable node exists, when decreasing \( c \) first a Hopf, later a saddle-node bifurcation occurs. In between, a saddle-loop bifurcation must take place, because the limit cycle growing out from the Hopf bifurcation will at some point (before the saddle node occurs) collide with the inset of the saddle point. The exact location cannot be determined from the algebra described above, but needs to be found numerically. In experiment the same sequence has been observed when increasing the total current (corresponding to \( k_7 \)).

V. NUMERICAL SIMULATIONS

In order to do numerical integration it is advantageous to eliminate one variable using the mentioned constraint. Usually the surface area is normalized to unity, and the empty sites are eliminated (though any other variable which is part of the constraint would do); thus \( x_1 = 1 - x_2 - 3x_4 - x_5 \). The kinetic equations become

\[
\begin{align*}
x_2 &= k_3x_3(1 - x_2 - 3x_4 - x_5) - k_4x_3x_4 - k_5x_3x_5^{-1}, \\
x_3 &= k_7k_6x_3 - k_6(1 - x_2 - 3x_4 - x_5)^2x_5^2, \\
x_4 &= k_1x_3(1 - x_2 - 3x_4 - x_5)^2 - k_2x_4, \\
x_5 &= k_3x_4 - k_4x_2x_5.
\end{align*}
\tag{35}
\]

Integration was carried out with MATLAB and bifurcation diagrams calculated with Matcont Continuation Toolbox. A variable step ranging from 0.1 to \( 10^{-6} \) was adopted.

We choose \( k_7 \) (corresponding to the galvanostatically adjusted total current) as control parameter, which is also the parameter most easily varied in experiment (other parameters given in Fig. 3). Note that an increase in \( k_7 \) has the same effect on the bifurcation sequence as a decrease in \( c \) (which corresponds to the total surface area of the electrode) since a smaller surface can only support a smaller total current. Figure 3 shows two sets of oscillations in all variables in order to visualize the relative amplitudes and phases, close to the Hopf, respectively, saddle-loop bifurcation. A one-parameter bifurcation diagram varying \( k_7 \) is shown in Fig. 4, which also gives the location and a visualization of the saddle-loop bifurcation. Both the type of kinetic instabilities and the potential oscillations are in good agreement with experiment (see Fig. 3, respectively, Fig. 6 of Ref. 4).
VI. DISCUSSION

In general a kinetic model need not include all intermediates and not even all side reactions known to be involved in the mechanism in order to explain certain prominent features of the system under consideration. The electrooxidation of MeOH is certainly more complicated than described above. However the goal of the present work was to develop the most parsimonious model compatible with the experimentally observed bifurcation structure (cf. earlier work on formic acid oxidation). A more quantitative model for applications such as fuel cells would, of course, have to consider all contributions to the overall current, and (most likely) consider some side reactions (e.g., formation of methanaldehyde and formic acid, which may build up a (small) concentration in the electrolyte, readorb, and get electrooxidized in turn). The most short-lived intermediate(s) can typically be eliminated without causing significant quantitative deviations.

The main goal of the present work was to present several tools for model development involving linear algebra, algebraic geometry and numerics. In has been demonstrated that it can be very advantageous to apply the analytical tools (SNA and toric varieties) rather than trying numerical simulations of an ODE (or even PDE or reaction-migration) system directly. Usually some rate constants are not known with the desired accuracy or cannot be measured directly. Consequently, not finding, for instance, a Hopf bifurcation (or other kinetic instabilities) numerically does not exclude their occurrence somewhere, since often there are too many unknown parameters. In contrast, SNA allows to write down all physically possible stationary states (complete parameter set in convex parameters) and there are necessary and sufficient conditions to prove or exclude the existence of local bifurcations. In order to apply SNA for large systems the extreme currents cannot be generated by hand any more, but there are good algorithms to compute them.

In principle one has to consider combinations of up to \( (r-d) \) extreme currents for a complete stability analysis, though mostly two or three are sufficient to find the bifurcations. The number of combinations of \( E_i \) which need to be considered is restricted by the fact that one should choose \( k \)-faces of the polytope (for \( k \) extreme currents) up to \( (r-d) \)-dimensional simplices (if necessary) and one only...
needs to consider additional extreme currents if they bring in additional feedback loops (or strengthen loops already present).

The algebraic methods described in Sec. IV are also in principle applicable for large systems, in particular all common computer algebra systems include an efficient algorithm to compute Gröbner bases. Still there are limitations. In the absence of conservation constraints (or other linear dependencies of some variables) the intersection of the restrictive binomials with the convex cone consists of a countable number of discrete points. Solving for these can become impossible for higher order equations. In this case it is advisable to introduce an auxiliary variable or parametrize the system in some other way and cut the resulting curve afterwards in order to obtain the stationary states. This is also the reason why (as in the example described) the constraint(s) should not be used for the analytical calculations until the very end. In complicated cases current computer algebra systems are unable to solve the restrictive binomials for the $j_i$ directly. This is of course trivial for the present example [see Eqs. (20) and (21)], but when there are more restrictions one may need to do some substitution by hand, which can be tedious and time consuming. On the other hand, computer algebra programs have been and still are improving so this may not pose serious problems in the near future any more.

When the 2 problems just mentioned have been overcome, the expressions in kinetic parameters for the stationary states can result in exceedingly complicated formulae which are impossible to interpret (the number of parameters being equal to the number of reactions $r$, respectively, $r=2$ after normalizing time and concentrations). If a significant number of rate constants are known with reasonable accuracy from experiment, these expressions can of course be greatly simplified by plugging in the numerical values, whereas a full analysis for arbitrary parameters may be intractable. A possible solution to this problem making use of factorization theory (i.e., construction of a quotient ring which retains the zeros of the original ring structure) is described elsewhere.  

VII. CONCLUSION

A combination of analytical tools (from linear algebra as well as algebraic geometry) and numerical simulations has been used to develop a model for methanol electro-oxidation. We believe that this integrated approach can help to identify the decisive steps also in other systems and contribute to the understanding of dynamic peculiarities.

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