

Model Reduction in the Design of Alkaline Methanol Fuel Cells

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Abstract—In this paper, it is shown that the electrochemical kinetics of alkaline methanol oxidation can be reduced by setting certain fast reactions contained in it to a steady state. As a result, the underlying system of Ordinary Differential Equations (ODE) is transformed into a system of Differential-Algebraic Equations (DAE). We measure the precision characteristics of such transformation and discuss the consequences of the obtained model reduction.

Keywords—modeling of complex systems; observational data and simulations; advanced applications; mathematical chemistry.

I. INTRODUCTION

In this short paper, we continue our research [1] on mathematical modeling of alkaline methanol oxidation, a process relevant for the design of efficient fuel cells. The considered reaction network is shown in Figure 1 left. It connects 6 reagents θ_i by 12 reactions r_j . The kinetics is described by the system of Ordinary Differential Equations (ODE):

$$\alpha_i d\theta_i/dt = F_i = \sum_j C_{ij} r_j, \quad (1)$$

where α_i are constant coefficients, for the case of ODE set to $\alpha_i = 1$; $\theta_i \in [0, 1]$ are surface coverages for the reagents; C_{ij} is a structural matrix relating production rates F_i and reaction rates r_j . The reaction rates are polynomial functions of θ_i , whose coefficients depend on the applied voltage $\eta(t)$. The voltage is a function of time, set in these experiments to a saw-like profile. The explicit form of all functions can be found in [1]. Here, only the structure of this system is important. Note that some reactions in Figure 1 are deselected (grayed out) by setting the corresponding matrix entries to zero. We have also reassigned normalization factors between F_i and r_j , so that both are measured in the same units (s^{-1}).

The experimental measurements are performed using the technique of Cyclic Voltammetry (CV) [2]), in a setup shown in Figure 1 right. The measured quantity is a cell current, in the model given by the expression:

$$I_{cell} = F A C_{act} F_7, \quad F_7 = \sum_j C_{7j} r_j, \quad (2)$$

where F – Faraday constant, A – geometric electrode area, C_{act} – a surface concentration of Pt catalyst. Here, we add the 7th row in the structural matrix and omit the practically vanishing capacitance term $C_{dl} d\eta/dt$. The described mathematical model fits the experimental data well, as shown in Figure 3 left. Further improvements of the method are described in Section II and the results are discussed in Section III.

II. IMPROVEMENTS OF THE METHOD

In this paper, we draw attention to Figure 2, which depicts the evolution of production and reaction rates. It is visible that

some r_j compensate each other, resulting in almost zero F_i . This common property, also noted in [3], means that some of the reactions proceed so fast that they are almost permanently in equilibrium. One production rate is not in equilibrium. It is also characterized by the presence of only one reaction: $F_6 = r_{12}$. Thus, in the equations, one can switch off the dynamic terms for all reagents except for the 6th, so that $\alpha_i = \delta_{i6}$. As a result, the ODE system is replaced by an equivalent system of Differential-Algebraic Equations (DAE). Mathematica v11 can be used to solve DAE systems with the same efficiency as ODE.

III. DISCUSSION

After the replacement by DAE, the CV plot in Figure 3 left changes slightly, as well as the detailed evolution of θ_i , shown in Figure 3 center. An interesting property that immediately catches the eye is the temporal asymmetry of the profiles for some reagents. Since the voltage is an even periodic function, if all reactions were in equilibrium, all θ_i would be even periodic. They would behave like red or black lines, corresponding to OH_{ad} and free Pt in Figure 3. Deviation from this behavior for magenta and brown, that is, $COOH_{ad}$ and PtO , is a purely dynamic effect. The consequence of this effect is the observed mismatch (hysteresis) for the increasing and decreasing branches of the CV plot. In line with this work, it is important that DAE provides the same profiles as ODE. Figure 3 right measures the deviation between the DAE and ODE, for θ_i , in the same colors, as well as the deviation of I_{cell} relative to its maximum, shown in gray. As a result, the transition from ODE to DAE results in 0.8% maximal variation for θ_i and 2.5% for I_{cell} , proving a good accuracy of the DAE representation.

IV. CONCLUSION

The advantage of the DAE formulation obtained in this paper is that only one degree of freedom θ_6 remains in the system, to which the evolution of other reagents is strictly coupled. The model is reduced and still describes the same effects as the complete system. In particular, it explains the dynamic hysteresis of volt-ampere characteristics of the cell.

V. ACKNOWLEDGEMENT

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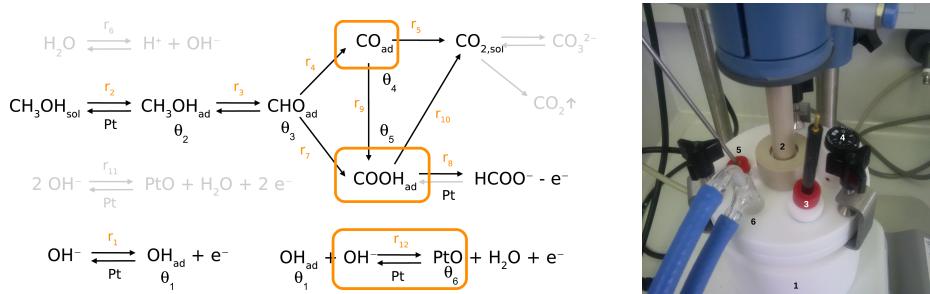


Figure 1. On the left: the chemical reactions network, the orange boxes show the reactions potentially responsible for the hysteresis effect on the CV plot. On the right: the experimental setup, consisting of a teflon cell (1) under deep vacuum, the rotating working electrode (2), the counter electrode (3), the reference electrode (4), the temperature sensor (5) and argon blow supply (6).

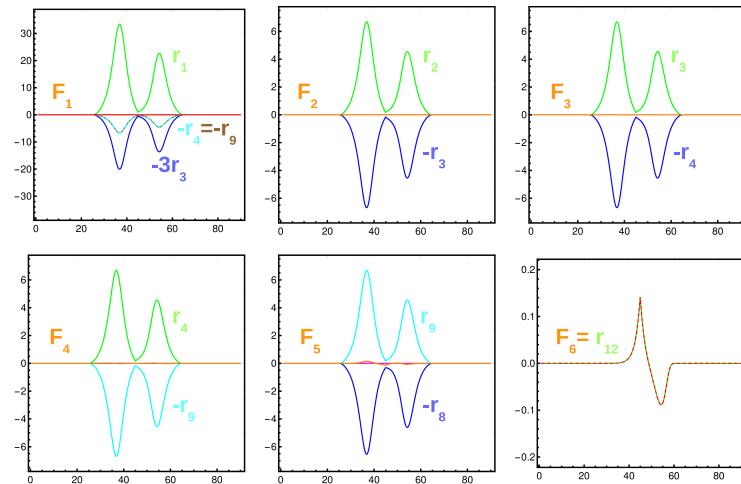


Figure 2. The plots of production rates F_i and reaction rates r_i . All production rates except F_6 show an approach to equilibrium. The horizontal axes show the time in seconds, the vertical axes: F_i and r_i in s^{-1} .

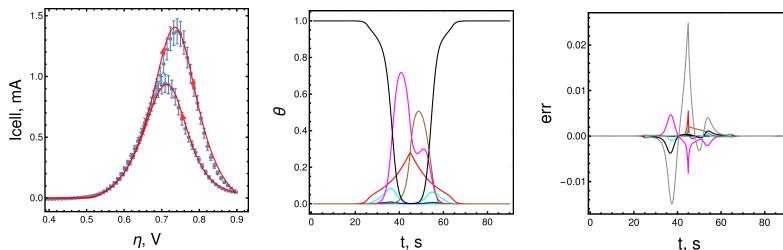


Figure 3. On the left: CV plot, blue points with error bars – the experiment, red line – the model. In the center: evolution of surface coverages, the colors (red, green, blue, cyan, magenta, brown) encode sequential θ_i , black shows the free Pt surface. On the right: ODE→DAE variations for θ_i (the same colors), relative variation for I_{cell} (in gray).

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