Parametric Model Order Reduction for Scanning Electrochemical Microscopy: Fast Simulation of Cyclic Voltammogram

L. H. Feng[1], D. Koziol[2], E. B. Rudnyi[2], and J. G. Korvink[2]
[1]ASIC & State Key Laboratory, Microelectronics Department, Fudan University, China. lhfeng@fudan.edu.cn
[2]IMTEK-Institute for Microsystem Technology, University of Freiburg, Freiburg, Germany

Abstract

We propose the use of parametric model reduction for fast simulation of cyclic voltammograms. The model for a cyclic voltammogram is treated as a system with a parameter (applied voltage) to be preserved during model reduction. The voltage is preserved in the symbolic form during model reduction and we can accurately simulate the cyclic voltammograms with a reduced system by spending much less time and memory as compared with direct simulation based on the original large-scale model.

1. Introduction

Model order reduction allows us to find an accurate low-dimensional approximation for a high-dimensional system of ordinary differential equations (ODEs) obtained after the discretization in space by the finite element method [1][2]. A formal and computationally efficient procedure based on the Arnoldi algorithm takes as input the system of ODEs in the form

$$E d\vec{x}/dt + K\vec{x} = bu \qquad (1)$$

with a state vector $\vec{x}$ and convert it to a similar system

$$\hat{E} d\vec{z}/dt + \hat{K}\vec{z} = \hat{b}u \qquad (2)$$

that, however, has much smaller dimension of the state vector $\vec{z}$.

In many engineering applications, the matrix K depends on parameters that should be preserved in the symbolic form. For example, these are film coefficients [3] in simulation of a thermal problem and the flow velocity in simulation of an anemometer [4]. In order to treat these important cases, conventional model reduction should be extended to parametric model reduction.

In our paper we present an application of parametric model reduction to scanning electrochemical microscopy (SECM) [5]. In the next section, we construct a mathematical model for SECM that after discretization in space produces a high-dimensional ODE system. Then we introduce the parametric model reduction technique in section 3 and discuss how it can be applied to the SECM model in section 4. In section 5, the simulation results are presented. Finally, we give conclusions.

2. Case study

We consider a cylindrical electrode operating in the feedback mode of SECM as shown in Figure 1. The computation domain under a 2D-axisymmetrical approximation includes the electrolyte under the electrode. We assume that the concentration does not depend on the rotation angle. A single chemical reaction takes place on the electrode:

$$Ox + e^- \underset{k_b}{\overset{k_f}{\Leftrightarrow}} Red \qquad (3)$$

According to the theory of SECM [6], the species transport in the electrolyte is described by diffusion only. The diffusion partial differential equations are given by Fick's second law as follows

$$dc_1/dt = D_1 \cdot \nabla^2 c_1 \qquad (4)$$

$$dc_2/dt = D_2 \cdot \nabla^2 c_2 \qquad (5)$$

The Buttler-Volmer equation has been used to describe the reaction rate on electrode surfaces for the chemical reaction (3)

$$j = k_{Ox} \cdot c_{Ox} - k_{\mathrm{Re}d} \cdot c_{\mathrm{Re}d} \qquad (6)$$

The reaction constants for the forward reaction and the backward reaction are given as follows

$$k_f = k_{Ox} = k^0 e^{\left(\frac{\alpha z F(E-E^0)}{RT}\right)} \qquad (7)$$

$$k_b = k_{\mathrm{Re}d} = k^0 e^{\left(\frac{-(1-\alpha) z F(E-E^0)}{RT}\right)} \qquad (8)$$

where k^0 is the heterogeneous standard rate constant, and $\alpha = 0.5$ is an empirical transmission factor for a heterogeneous reaction. F is the Faraday-constant, R is the gas constant, T is the temperature and n is the number of exchanged electrons per reaction. This allows us to write the boundary conditions at the electrode as follows:

$$\nabla c_1 \cdot \vec{n} = j \quad \text{and} \quad \nabla c_2 \cdot \vec{n} = -j \qquad (9)$$

The control volume method has been used for the spatial discretization of the equations above. The resulting system of ordinary differential equations is as follows

$$E d\vec{c}/dt + K\{U(t)\}\vec{c} = b, \vec{c}(0) = \vec{c}_0 \neq 0 \qquad (10)$$

where E and $K\{U(t)\}$ are system matrices, $\vec{c} \in R^n$ is the vector of unknown concentrations. R^n means that there are n elements in the vector $\vec{c}$ and n is usually referred to as the dimension of the system (10). The vector b is the load vector, which arises as a consequence of the Dirichlet boundary conditions imposed at the bulk of the electrolyte.

There are two important differences between Eq (10) and (1). First, the matrix K depends on the voltage that in turn depends on time in the simulation of a cyclic voltammogram. This feature must be preserved in the reduced model. Second, the initial condition of the system is always nonzero in our case, i.e. $\vec{c}_0 \neq 0$.

3. Parametric model reduction

The theory of model reduction is based on the use of the Laplace transform of Eq (1):

$$\begin{aligned}(sE+K)x &= bu\\ y &= cx\end{aligned} \tag{11}$$

where s is the Laplace variable, x is the Laplace transform of the vector $\vec{x}$ and y is the output: a linear transformation of the state vector that produces a desired observation.

The first parametric model reduction method in [7] deals with a two-parameter system that extends the previous equation as follows

$$\begin{aligned}(s_1E_1+s_2E_2-E_0)x &= bu\\ y &= cx\end{aligned} \tag{12}$$

In addition to the Laplace variable s_1, the authors assumed that the system matrix K depends on its own parameter, $K = s_2E_2 - E_0$, that they wanted to preserve in the symbolic form.

They derived the reduced model as

$$\begin{aligned}(s_1\hat{E}_1+s_2\hat{E}_2-\hat{E}_0)z &= \hat{b}u\\ \hat{y} &= \hat{c}z\end{aligned} \tag{13}$$

where

$$\hat{E}_1 = V^TE_1V, \hat{E}_2 = V^TE_2V, \hat{E}_0 = V^TE_0V, \hat{b} = V^Tb, \hat{c} = cV$$

and the projection matrix V is computed based on the parameter transfer function of (12)

$$h(s_1,s_2) = c(s_1E_1+s_2E_2-E_0)^{-1}b \tag{14}$$

$h(s_1,s_2)$ was expanded into doubled series of both s_1 and s_2,

$$\begin{aligned}h(s_1,s_2) &= -c[I-(E_0^{-1}E_1s_1+E_0^{-1}E_2s_2)]^{-1}E_0^{-1}b\\ &= -c\sum_{i=0}^{\infty}(E_0^{-1}E_1s_1+E_0^{-1}E_1s_2)^iE_0^{-1}b\\ &= -c\sum_{j=0}^{\infty}\sum_{k=0}^{j}[F_k^j(E_0^{-1}E_1,E_0^{-1}E_2)s_1^{j-k}s_2^k]E_0^{-1}b\end{aligned}$$

where F_k^j is the matrix before $s_1^{j-k}s_2^k$. For example,

$$\begin{aligned}&F_0^1 = E_0^{-1}E_1, F_1^1 = E_0^{-1}E_2, F_0^2 = (E_0^{-1}E_1)^2\\ &F_1^2 = (E_0^{-1}E_1)(E_0^{-1}E_2)+(E_0^{-1}E_2)(E_0^{-1}E_1)\\ &F_2^2 = (E_0^{-1}E_2)^2,\cdots\end{aligned} \tag{15}$$

The moments of the transfer function with respect to the two parameters are

$$-cF_k^j(E_0^{-1}E_1,E_0^{-1}E_2)E_0^{-1}b \tag{16}$$

The projection matrix V is computed based on the moments in (16), that is

$$colspan\{V\} = span\{\bigcup_{m=0}^{j}\bigcup_{k=0}^{m}F_k^m(E_0^{-1}E_1,E_0^{-1}E_2)E_0^{-1}b\} \tag{17}$$

Theorem 4 in Ref [4] proves that

$$cF_k^m(P^{-1}E_1,P^{-1}E_2)P^{-1}b = \hat{c}F_k^m(\hat{P}^{-1}\hat{E}_1,\hat{P}^{-1}\hat{E}_2)\hat{P}^{-1}\hat{b},$$
$$0 \le k \le m \le j+1$$

and this guarantees the accuracy of the reduced model.

This method was extended to systems with more than two parameters in Ref [8], where the linear system with p parameters was defined as

$$\begin{aligned}(s_1E_1+s_2E_2+\cdots+s_pE_p-E_0)x &= bu\\ y &= cx\end{aligned} \tag{18}$$

Since c does not contribute to the projection matrix V, the series expansion of only vector x instead of the transfer function is considered in [8]. From (18), we have

$$\begin{aligned}x &= -[I-(s_1E_0^{-1}E_1+\cdots+s_pE_0^{-1}E_p)]^{-1}E_0^{-1}bu\\ &= -\sum_{m=0}^{\infty}[s_1E_0^{-1}E_1+\cdots+s_pE_0^{-1}E_p]^mE_0^{-1}bu\\ &= \sum_{m=0}^{\infty}\sum_{k_2=0}^{m-(k_3+\cdots+k_p)}\cdots\sum_{k_{p-1}=0}^{m-k_p}\sum_{k_p=0}^{m}\\ &[F_{k_2,\cdots k_p}^m(E_0^{-1}E_1,\cdots,E_0^{-1}E_p)bu]s_1^{m-(k_2+\cdots+k_p)}s_2^{k_2}\cdots s_p^{k_p}\end{aligned}$$

where $F_{k_2,\cdots,k_p}^m$ is defined similarly to (15).

The projection matrix V is constructed by the terms in the series above, that is

$$colspan(V) = span\{\bigcup_{m=0}^{m_q}\bigcup_{k_2=0}^{m-(k_p+\cdots+k_3)}\cdots\bigcup_{k_{p-1}=0}^{m-k_p}\bigcup_{k_p=0}^{m}F_{k_2,\cdots k_p}^mE_0^{-1}b\} \tag{18}$$

We can expand (18) to show it more clear:

$$\begin{aligned}&colspan(V) = span\{E_0^{-1}b,(E_0^{-1}E_1)E_0^{-1}b,(E_0^{-1}E_2)E_0^{-1}b\cdots,\\ &(E_0^{-1}E_p)E_0^{-1}b,(E_0^{-1}E_1)^2E_0^{-1}b,\\ &[(E_0^{-1}E_1)(E_0^{-1}E_2)+(E_0^{-1}E_2)(E_0^{-1}E_1)]E_0^{-1}b,\cdots,\\ &[(E_0^{-1}E_1)(E_0^{-1}E_p)+(E_0^{-1}E_p+E_0^{-1}E_1)]E_0^{-1}b,\\ &(E_0^{-1}E_2)^2E_0^{-1}b,[(E_0^{-1}E_2)(E_0^{-1}E_3)+\\ &(E_0^{-1}E_3)(E_0^{-1}E_2)]E_0^{-1}b,\cdots,[(E_0^{-1}E_2)(E_0^{-1}E_p)\\ &+(E_0^{-1}E_p)(E_0^{-1}E_2)]E_0^{-1}b,\cdots,(E_0^{-1}E_p)^mE_0^{-1}b\}\end{aligned}$$

In Ref [8], there is a similar theorem that can prove that the moments included in (18) are the same for the reduced model. In the next section, we will show how this method can be applied to the model from section 2.

4. Parametric model reduction for the SECM model

For the SECM model in (11), the system matrix K depends on the voltage that plays the role of the input function, that is, it changes in time. According to the SECM theory, we can express this dependence as follows

$$K = G + s_1D_1 + s_2D_2$$

where G, D_1, D_2 are constant matrices and s_1 and s_2 are the functions of the voltage applied on the electrode

$$s_1(t) = e^{u(t)},\ s_2(t) = e^{-u(t)}$$

with $u(t) = v(t) - v_0$ were v_0 is the reference voltage.

As result, the system (11) can be re-written into the following form:

$$Ed\bar{c}/dt + G\bar{c} + (s_1D_1 + s_2D_2)\bar{c} = b \qquad (19)$$

where the two scalar functions $s_1(t), s_2(t)$ are considered as parameters.

The next problem is that the initial condition of system (11) is not equal to a zero vector, $\bar{c}_0 \neq 0$. The Laplace transformation for (19) produces

$$(sE + s_1D_1 + s_2D_2 + G)x(s) = bu(s) + E\bar{c}_0 \qquad (20)$$

where *x(s)* is the Laplace transformation of $\bar{c}$. Eq (20) is different from (17) with *p*=3. This means that (18) cannot be used yet to construct the projection matrix based on (20). However, we can first do a vector transformation on (19) by $\tilde{\bar{c}} = \bar{c} - \bar{c}_0$ and obtain a new system in respect to $\tilde{\bar{c}}$ [9]

$$\begin{aligned} &Ed\tilde{\bar{c}}/dt + G\tilde{\bar{c}} + (s_1D_1 + s_2D_2)\tilde{\bar{c}} = \\ &b + G\bar{c}_0 + s_1D_1\bar{c}_0 + s_2D_2\bar{c}_0 \end{aligned} \qquad (21)$$

For the new system, the initial condition is exactly zero, $\tilde{\bar{c}}_0 = \bar{c}_0 - \bar{c}_0 = 0$. After the Laplace transformation, (21) becomes,

$$\begin{aligned} &sEx(s) + Gx(s) + (s_1D_1 + s_2D_2)x(s) \\ &= \tilde{b}u(s) \end{aligned} \qquad (22)$$

with $\tilde{b} = b + G\bar{c}_0 + s_1D_1\bar{c}_0 + s_2D_2\bar{c}_0$.

Eq (22) is now similar to (17), except that the vector *b* in (17) does not depend on parameters while the vector $\tilde{b}$ depends on two parameters. However, it is relatively easy to deal with this by comparison of the right sides in (18) and (22). In (18), the vector *b* is one of the base vectors to span the subspace for matrix *V,* and in (22) the vector $\tilde{b}$ should play the same role as b. The vector $\tilde{b}$ is actually the linear combination of three vectors, $(b + G\bar{c}_0), D_1\bar{c}_0, D_2\bar{c}_0$, so that when we construct the projection matrix *V* according to (18), we replace the vector *b* in (18) by the three vectors above, that is, by a matrix $B = (b + G\bar{c}_0, D_1\bar{c}_0, D_2\bar{c}_0)$ so that it is independent of the parameters. We construct the projection matrix *V* for (22) according to (18) as

$$\begin{aligned} &colspan(V) = span\{G^{-1}B, (G^{-1}E)G^{-1}B, (G^{-1}D_1)G^{-1}B, \cdots, \\ &(G^{-1}D_2)G^{-1}B, (G^{-1}E)^2G^{-1}B, [(G^{-1}E)(G^{-1}D_1) + \\ &(G^{-1}D_1)(G^{-1}E)]G^{-1}B, \cdots, [(G^{-1}E)(G^{-1}D_2) + \\ &(G^{-1}D_2 + G^{-1}E)]G^{-1}B, (G^{-1}D_1)^2G^{-1}B, \cdots, (G^{-1}D_2)^jG^{-1}B\} \end{aligned}$$

The reduced model is of the form

$$\hat{E}dz/dt + \hat{G}z + (s_1\hat{D}_1 + s_2\hat{D}_2)z = \hat{b} \qquad (23)$$

where,

$$\begin{aligned} &\hat{E} = V^TEV, \hat{G} = V^TGV, \hat{D}_1 = V^TD_1V, \\ &\hat{D}_2 = V^TD_2V, \hat{b} = V^T\tilde{b}. \end{aligned}$$

After obtaining the solution *z* in (23), we can return back to the solution $\tilde{\bar{c}}$ in (21) by $\tilde{\bar{c}} \approx Vz$, and the original solution $\bar{c}$ in (11) can be computed by $\bar{c} = \tilde{\bar{c}} + \bar{c}_0$.

In the next section, we will show the efficiency of parametric model reduction for the simulation of the voltammogram by means of numerical experiments.

5. Simulation results

The discretization of the SECM device shown in Fig. 1 resulted in a system of ordinary differential equations (10) with the dimension of the state vector equal to 16912. The method described in the previous section produced a reduced model with dimension 202.

Figure 2 to Figure 5 show the simulation results of the original and reduced models. The voltage had a triangular waveform:

$$\begin{cases} u = u + at, & 0 < t < t_{u_{\max}} \\ u = u - at, & t_{u_{\max}} < t < t_{u_0} \end{cases}$$

The figures display the current as a function of voltage (not in time) as this is the usual way to represent voltammograms. The solid line is the result computed by full simulation of the original large model, the dashed line is the result computed by the small reduced model. The results of the reduced model are accurate for a wide range of the dynamic behavior when the value of du/dt changes by three orders of magnitude (0.0005-0.5).

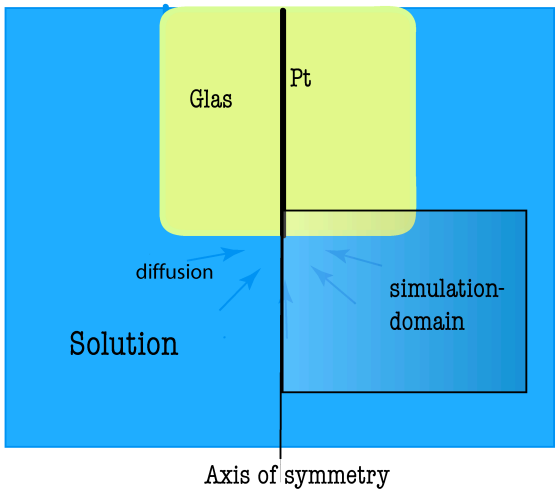

Figure 1: The computational unit.

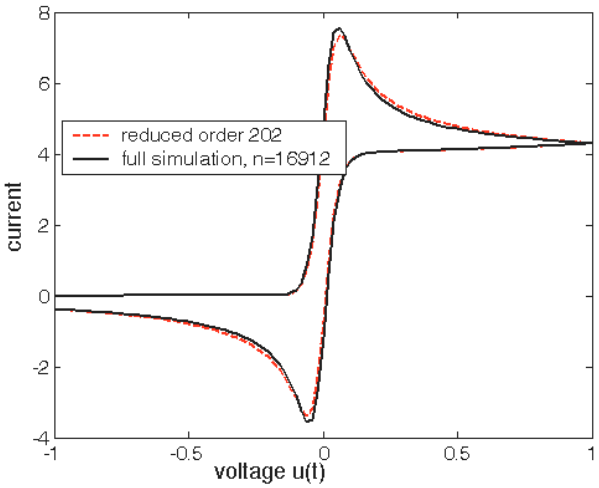

Figure 2: Simulation results of the cyclic voltammogram when $du/dt = \pm 0.5$.

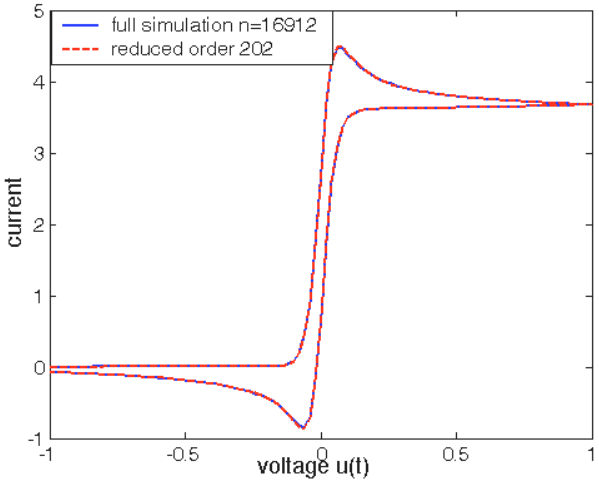

Figure 3: Simulation results of the cyclic voltammogram when $du/dt = \pm 0.05$.

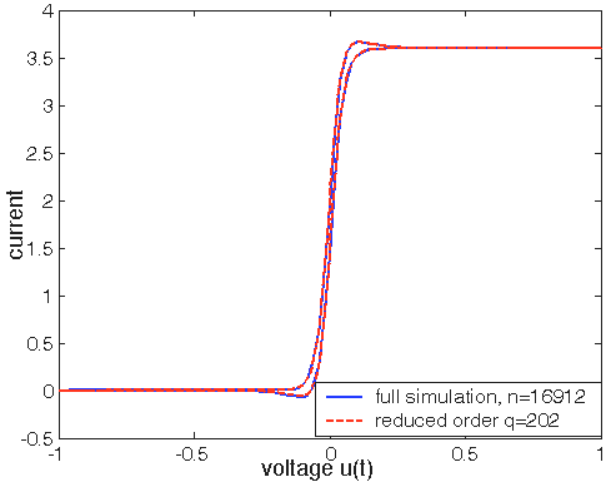

Figure 4: Simulation results of the cyclic voltammogram when $du/dt = \pm 0.005$.

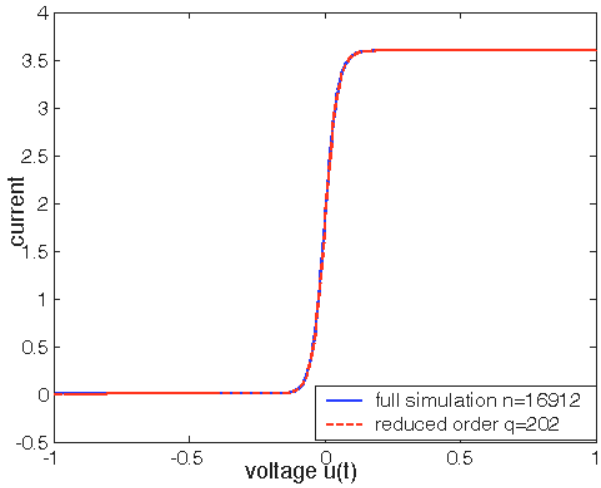

Figure 5: Simulation results of the cyclic voltammogram when $du/dt = \pm 0.0005$.

6. Conclusions

We have introduced in our paper a new parametric model order reduction technique in order to make a compact model for scanning electrochemical microscopy. The parametric model order reduction preserved the parameters in the original model into the reduced small model in the symbolic form so that the reduced small model can replace the original large model in simulation even when the values of the parameters change. At the same time, the reduced model produces solutions as accurate as the solution computed directly from the original large model. Even though the dynamic model for SECM is a time varying system, when we make use of the special structure of the system matrices, we can consider it as a parametric system. Therefore the parametric model order reduction technique can be employed to obtain a reduced small model of this system that reproduces the original system with good accuracy.

Acknowledgments

LHF is supported partly by NSFC research project 90307017, 60176017, 90207002 of China, partly by Synopsys Inc., partly by Cross-Century Outstanding Scholar's fund of the Ministry of Education of China, partly by National 863 plan projects 2004AA1Z1050 of China, Science & Technology key project of the Ministry of Education of China 02095, partly by NSF grants CCR-0098275 and CCR-0306298 of China and partly by a fund of the Alfried Krupp von Bohlen und Halbach-Stiftung of Germany. IMTEK acknowledges the partial funding by the DGF Graduirtenkolleg 'Non linear differential equations - modelling, theory, numerics, visualisation' and by operating grant of Freiburg university.

References

[1] R. W. Freund, “Reduced-order modeling techniques based on Krylov subspaces and their use in circuit simulation,” in Applied and Computational Control Signals and Circuits, vol. 1, B. N. Datta, Ed.: Birkhauser, Boston, pp. 435-498, 1999.

[2] E. B. Rudnyi, J. G. Korvink, Review: Automatic Model Reduction for Transient Simulation of MEMS-based Devices, Sensors Update v. 11, p. 3-33, 2002.

[3] L. H. Feng, E. B. Rudnyi, J. G. Korvink. Parametric Model Reduction to Generate Boundary Condition Independent Compact Thermal Model. THERMINIC 2004, 10th International Workshop on THERMAL INVESTIGATIONS of ICs and Systems, 29 September - 1 October 2004, Sophia Antipolis, France, p. 281-285.

[4] C. Moosmann, E. B. Rudnyi, A. Greiner, J. G. Korvink, M. Hornung, parameter preserving model order reduction of a flow meter, 2005 NSTI Nanotech, Nanotechnology Conference and Trade Show 2005, May 8-12, 2005.

[5] Scanning Electrochemical Microscopy, Edited by: Allen J. Bard and Michael V. Mirkin, ISBN: 0-8247-0471-1, Dekker, 2001.

[6] M. V. Mirkin, “ Theory in scanning electrochemical microscopy.” Bard, A. J. and M. V. Mirkin, Eds. (2001). New York, John Wiley & Sons. pp. 145 – 199.

[7] D. S. Weile, E. Michielssen, E. Grimme, and K.Gallivan," A method for generating rational interpolant reduced order models of two-parameter linear systems," Appl. Math. Lett. vol. 12, pp. 93-102, 1999.

[8] L. Daniel, O.C. Siong, L.S. Chay, K.H. Lee, J. White, “A Multiparameter Moment-Matching Model-Reduction Approach for Generating Geometrically Parameterized Interconnect Performance Models,” IEEE Trans. Computer-Aided Design of Integrated Circuits and Systems, vol. 23, no. 5, pp. 678-693, 2004.

[9] L. H. Feng, D. Koziol, E. B. Rudnyi, J. G. Korvink. Model Order Reduction for Scanning Electrochemical Microscope: The treatment of nonzero initial conditions. IEEE Sensors 2004, The Third IEEE conference on sensors, Vienna, Austria, Oct. 24-27, 2004, Technical Program & Abstracts, Special Session W1Le, Scanning Probe Tip Integrated Sensors, p. 257.