Model Order Reduction for Scanning Electrochemical Microscope: The treatment of nonzero initial condition

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Abstract

At present time, model order reduction is a well-established technique for fast simulation of large-scale models based on ordinary differential equations, especially those in the field of integrated circuits and micro-electro-mechanical systems. We describe the application of model reduction to electrochemical simulation related to scanning electrochemical microscope. Model reduction allows us to reduce the simulation time significantly and, at the same time, it maintains the high accuracy.

Keywords

Model Order Reduction, Scanning Electrochemical Microscope, SECM

INTRODUCTION

Numerical methods such as finite difference, control volume and finite element discretization have been widely employed in electrochemistry to simulate the scanning electrochemical microscope (SECM), electrochemical reactors, etc. [1-7]. The system of ordinary differential equations obtained after the discretization is of large dimension. As result, its simulation consumes too much computer time.

In recent years, several model order reduction (MOR) methods [8-10] have been proposed in order to get a quick and accurate simulation of very large-scale integrated circuits and micro-electro-mechanical systems. They have been proved to be very efficient. However, to our knowledge they have not been applied yet for electrochemistry simulation. A model order reduction method based on projection technique is introduced in this paper in order to show the applicability of this method and its advantage over large-scale numerical simulation for the ordinary differential equation derived from finite volume discretization.

We consider as an example the SECM working in the feedback mode with the electro-chemical reaction that takes place on the electrode.

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In order to derive the partial differential equations for electrochemistry, at least one reaction between two species should be considered. Therefore, in most cases it is impossible to set the initial state of all the species equal to zero. Hence, the complete initial condition of the equation is always nonzero. It happens that for such a system, the conventional model order reduction methods [8-10] cannot be applied immediately because they deal only with a system possessing zero initial condition. In this paper, we propose a transformation technique, which avoid the nonzero initial condition so that the methods above can be successfully used to obtain an accurate solution.

The paper is arranged as follows. We first review the conventional model order reduction method based on projection technique and show its limitations when dealing with system with nonzero initial conditions. After that, we give a transformation technique, which can easily deal with a system with nonzero initial condition. Then we show the efficiency of model order reduction with numerical simulation results. Finally, some conclusions are given.

DESCRIPTION OF THE ELECTROCHEMICAL PROBLEM AND GENERAL IDEA OF MODEL ORDER REDUCTION

A feedback mode of SECM can be described by a partial differential equation (Fick's second law).

$$d\bar{c}/dt = D \cdot d^2\bar{c}/dt^2 \qquad (1)$$

The boundary conditions for the electrode boundary are derived from the Buttler-Volmer equation

$$j = k_{ox} \cdot c_{ox} - k_{Red} \cdot c_{Red}$$

When finite volume method is used to discretize (1) and the boundary condition, a system of ordinary differential equations is obtained

$$E\dot{\vec{c}}(t) + K\vec{c}(t) = F, \qquad \vec{c}(0) = \vec{c}_0 \neq 0 \qquad (2)$$

with $\vec{c} \in R^n$ being a vector of high dimension. At present, numerical integration is the most used method for simulation of system (2). When the dimension n of the system is very large, the simulation is slow. Model order reduction tries to substitute the original large dimensional system in (2) with a system of smaller size, yet with little accuracy lost. Thus, one need only simulate the reduced system of small size without considering the original system. In this way, simulation time and computer memory can be saved.

Model order reduction with projection technique [8-10] is the method used most often. The basic idea is to find a

projection matrix V such that the unknown vector $\vec{c}$ can be sufficiently approximated by $\vec{c} \approx V\vec{z}$, with $V \in R^{n \times q}$, $q << n$, that is

$$EV\dot{\vec{z}} + KV\vec{z} = F, \tag{3}$$

After the multiplying V^T from the left of both sides, we obtain the final reduced system with unknown state vector $\vec{z} \in R^q$, which is of much smaller size q.

$$V^T E V \dot{\vec{z}} + V^T K V \vec{z} = V^T F \tag{4}$$

CONVENTIONAL PROJECTION TECHNIQUE

In order to use the analysis from the previous section, one should be able to compute the projection matrix V.

With the assumption that the initial condition of the system is zero ($\vec{c}_0 = 0$), conventional method of constructing V is based on the transfer function of the original system (2). In the case of system (2), we are not interested in the complete state vector $\vec{c}$ but in a few outputs computed as linear combinations of concentrations, i.e.

$$\vec{y} = L\vec{c} \tag{5}$$

Then the Laplace transformation of (2)(5) with initial condition $\vec{c}_0 = 0$ is as follows

$$sEC(s) + KC(s) = FU(s)$$
$$Y(s) = LC(s) \tag{6}$$

the transfer function is defined as

$$H(s) = Y(s)/U(s) = L(sE + K)^{-1} F \tag{7}$$

By choosing a expansion point, $s = s_0 + \sigma$, $H(s)$ can be expanded into series around s_0

$$H(\sigma) = \sum_{i=0}^{\infty} LM^i r \sigma^i$$

where $M^i = -(s_0 E + K)^{-1} E$, $r = (s_0 E + K)^{-1} F$

If the projection matrix V is constructed as follows

$$spancolumn\{V\} = span\{(r, \ Mr, \cdots, M^j r\} \tag{8}$$

the reduced system (4) approximates the original system quite well, the more terms are included in the right hand side of (8), the more accurate is the reduced system. One is referred to [9] and it references for detailed theoretical proof.

Conventional method of computing V only treats things in a general way, that is, it always has an assumption that the initial condition of the system must be zero so that the transfer function in the form of (7) can be obtained. However from the Laplace transformation of system in (2)

$$\int_0^\infty E\dot{\vec{c}} e^{-st} dt + \int_0^\infty K\vec{c} e^{-st} dt = \int_0^\infty F e^{-st} dt$$

after integration, we actually obtain

$$sEC(s) + KC(s) = FU(s) + E\vec{c}_0$$
$$Y(s) = LC(s)$$

and

$$H(s) = Y(s)/U(s) =$$
$$L(sE + K)^{-1} F - L(sE + K)^{-1} E\vec{c}_0 /U(s) \tag{9}$$

The expression in (9) is dependent on $\vec{c}_0$. When $\vec{c}_0 = 0$, it is just the expression of $H(s)$ in (7) which corresponds to the first part of $H(s)$ in (9). But in our case, $\vec{c}_0$ is nonzero. If only the first part in (9) is considered to construct the projection matrix V as in (8), the resulting reduced model may probably be inaccurate, as the nonzero initial condition cannot be maintained accurately in the reduced model.

One reason is that with the reduced model we cannot describe well all-possible initial conditions. That is, from $\vec{c}_0 \neq 0$, a normal way to obtain the initial condition of the reduced system is by projection $\vec{z}_0 \approx V^T \vec{c}_0$. However, if we use such $\vec{z}_0$ to compute the initial condition of the original system we obtain $\vec{c}_0 \approx V\vec{z}_0 = VV^T \vec{c}_0$. It is clear that we can only obtain an approximate nonzero initial condition $VV^T \vec{c}_0$. The latter is a projection of the original $\vec{c}_0$ to the low-dimensional subspace and it will be very inaccurate if $\vec{c}_0$ is far away from the subspace spanned by V. This happens to be the case in our example of scanning electrochemical microscope. In the next section we will propose a method with which the above problem can be easily avoided.

PROJECTION TECHNIQUE WITH TRANSFORMATOIN

For system (2), define a new unknown variable $\tilde{\vec{c}} = \vec{c} - \vec{c}_0$, then we obtain a new system of $\tilde{\vec{c}}$

$$E\dot{\tilde{\vec{c}}} + K\tilde{\vec{c}} = F + K\vec{c}_0, \tilde{\vec{c}}(0) = 0,$$
$$\tilde{Y}(t) = L\tilde{\vec{c}} \tag{10}$$

The transformed system (10) possesses zero initial conditions by the definition. And its input-output $H(s)$ relation will be independent of $\vec{c}_0$. It is not difficult to prove that

$$H(s) = L(sE + K)^{-1} \tilde{F} = \sum_{i=0}^{\infty} M^i \tilde{r} \sigma^i$$

where $\tilde{F} = F + K\vec{c}_0$, $\tilde{r} = (s_0 E + K)^{-1} \tilde{F}$,

M is defined as above. The projection matrix $\tilde{V}$ can be computed in a similar way as

$$spancolumn\{\tilde{V}\} = span\{(\tilde{r}, M\tilde{r}, \cdots, M^j \tilde{r}\} \tag{11}$$

Since $\tilde{V}$ is constructed based on $H(s)$ of the system in (10), model order reduction should be done on system (10) so

that reasonable accuracy can be kept, with the same way as in (3)(4).We obtain the reduced system of small size

$$\widetilde{V}^T E \widetilde{V} \ddot{\vec{z}} + \widetilde{V}^T K \widetilde{V} \vec{z} = \widetilde{V}^T F \qquad (12)$$

The original unknown vector $\vec{c}$ can be computed by $\vec{c} = \widetilde{\vec{c}} + \vec{c}_0 \approx \widetilde{V} \vec{z} + \vec{c}_0$. Thus, the nonzero initial condition is preserved exactly, since $\vec{z}_0 = \widetilde{V}^T \widetilde{\vec{c}}_0 = 0$. The accuracy of the reduced system in (12) will only depend on the accuracy of projection matrix $\widetilde{V}$, which is easily to be met by adding more terms into the right hand side of (11).

NUMERICAL EXPERIMENTS

In this section, we present some simulation results to show the efficiency of the model order reduction techniques in the second section.

Figure 1 shows the scheme of the scanning electrochemical microscope for which the partial differential equation in (1) is derived.

The size of the original system in (2) is $n=16915$. The size of the reduced system in (4) and (12) is $q=100$, that is the unknown vector $\vec{z} \in R^{100}$.

The simulation errors between the solution of original system and the solution derived by the reduced system are estimated in Figure 2 to Figure 5. The error is defined as

$$error = [\sum_{i=1}^{n}(y_i - \hat{y}_i)^2]^{1/2} / [\sum_{i=1}^{n} y_i^2],$$

where $y = (y_1, y_2, \cdots y_n)^T$ is the solution computed by direct simulation of system (2), $\hat{y}$ is the solution computed by reduced system in (4) or (12). We assume the solution derived by direct integrate simulation as the exact solution. In order to put the errors of the two different methods for model order reduction into one figure, we use the logarithmic plot. The dashed line is the error by conventional method where the projection matrix is computed by (8), the solid line is the error by proposed transformation method in (11)(12).

In Figure 2 and Figure 3, we give the plot of the solution for current and the solution at node 7864. In each of the two figures, we compare the approximate solution by conventional model reduction method with the exact solution. One can see that the low-dimensional subspace of the dimension of 100 cannot reproduce initial conditions for the nodes close to the electrode (see Figure 2) and as a result it cannot reproduce the current. Figure 2 shows that for this node 7864, $VV^T \vec{c}_0$ is almost zero even if $\vec{c}_0 = 1$. The solutions derived by the proposed method are indistinguishable with the exact solutions if they are plotted together.

The errors of the reduced model by conventional method and the proposed method are plotted in Figure 4 and Figure 5. It can be seen that the errors between the exact solution and the approximate solution computed by the proposed transformation method are very small (below 1e-6).

Whereas the error of the conventional model reduction method is large. Therefore, the reduced smaller size system in (12) is a good substitution for the original system in (2), and the model order reduction method is a promising technique to enhance the simulation process in electrochemistry.
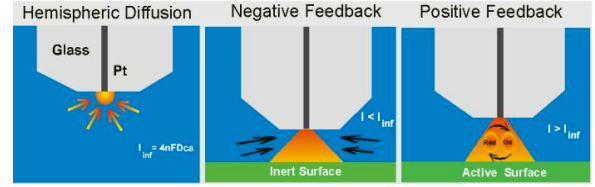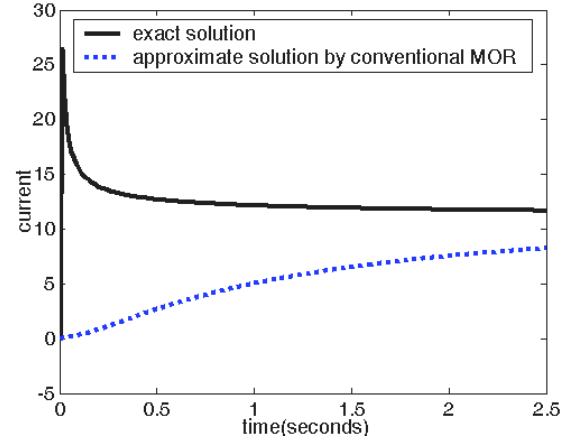

Figure.1 The computational unit
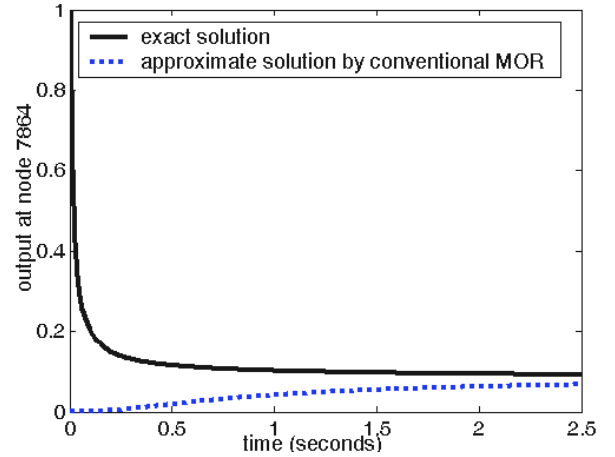

Figure. 2 Solution comparisons for the current

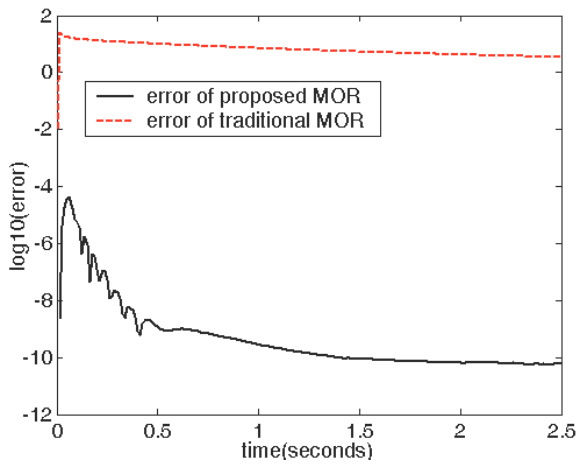**Figure. 3 Solution comparisons at node 7864**
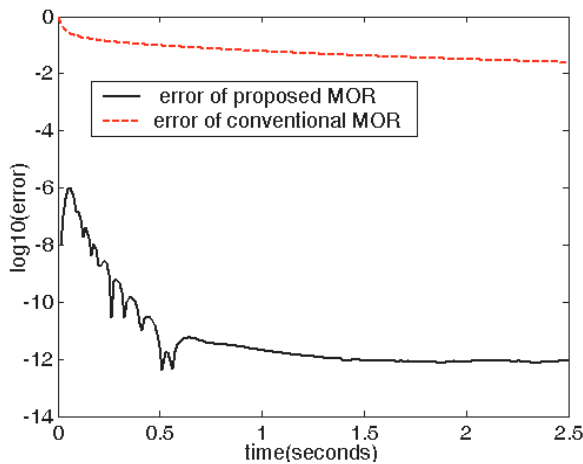
Figure. 4 Error comparisons for current

Figure. 5 Error comparisons at node 7864

CONCLUSIONS

In this paper, we propose a model reduction technique for fast simulation of the partial differential equation that arises from Scanning Electrochemiscal Microscope (SECM). We show by theoretical analysis and simulation results that model reduction works well. In order to perform model reduction on the system from SECM, we must first deal with the nonzero initial condition. We propose a transformation technique combined with the conventional model reduction method, which proves to be much more accurate than merely the conventional model reduction method.

At present, we have considered a case when the voltage is constant. However to simulate cyclic voltammogramm, the voltage should change as a function of time. This can be treated by parametric model reduction [11]. Its application

to scanning electrochemical microscope will be described in a separate paper.

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