Electrochemical Kinetic Property Determination of MIECs by Comprehensive Multi-physical Coupling Model

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Abstract. Surface exchange and bulk diffusion coefficients are important electrochemical kinetic properties of mixed ionic-electronic conductors (MIECs), which are usually obtained through electrical conductivity relaxation (ECR) experiments. However, the extensively employed method is built upon the ideal diffusion described by Fick’s second law with linear absorbing boundary, which is almost impossible to achieve in actual experiments. To simulate the actual experiment system and improve the estiamtion accuracy, a comprehensive mathematical model is established to describe the coupled multi-physical processes involved, such as convection-diffusion in the surrounding atmosphere, surface exchange, bulk diffusion of MIECs, and heat transfer. A comparison between different models is carried out, and the results show that the new model established is more accurate and compatible with more complex conductivity curves.

1. Introduction

Mixed ionic and electronic conductors (MIECs) have occupied an important place as the materials for the cathode of solid oxide fuel cells (SOFCs) [1], oxygen sensors [1] and gas separation membranes [3]. Electrical conductivity relaxation (ECR) is one of the most widely used techniques to determine surface exchange coefficient and bulk diffusivity for MIECs, which has attracted more and more attention for its simplified experiments and reduced costs [4],[5].

Oxygen diffuses into or out of MIECs due to the imbalance of oxygen partial pressure, resulting in the variation of oxygen ions concentration in bulk material. The conductivity of the sample varies with the oxygen concentration and can be measured directly by using ECR technique. Therefore the information on surface exchange coefficient k and bulk diffusivity D is usually extracted by analyzing the relaxation behavior of conductivity. In actual ECR measurements, a sample fixes in a sealed container with a flowing gas mixture. The oxygen partial pressure of the gas mixture can be changed. When the sample is in equilibrium with the surrounding atmosphere, the oxygen partial pressure of the gas mixture is subject to a step change to record the transient response of the bulk material conductivity. Many physical mechanisms are involved in the ECR, and thereby, many factors may influence sample conductivity value. As the kinetic parameters k and D are determined by fitting the measured conductivity curve with corresponding theoretical predictions under identical operating
conditions, modeling in combination with inverse analysis covering all the influence factors is of significant importance to obtain accurate estimations.

In literatures, the Fick’s second law with linear absorbing boundary are usually used to describe the bulk diffusion and surface exchange processes in materials [5],[7]. This model focuses on the diffusion process within the bulk material, without regard to the influences from the surrounding atmosphere, hence only applicable when the surrounding atmosphere is stagnant, evenly distributed and its response time switched to another steady state is instantaneous or negligible. There are a large number of investigations on kinetic parameters predictions from an analytic solution of such model [8], as well as error analysis and optimization of the estimated results [7]. However, accurate estimations are hard to be determined and controlled because the ideal state is almost impossible to achieve in actual experiments. Some ECR curves obtained in the experiments deviate from the standard curve derived by the Fick’s second law [9],[10],[11]. In this situation, the Fick’s second law is invalid. The influences of gas velocity and operating temperature are still unknown. Therefore it would be of great significance to develop a comprehensive model that is close to actual experiments and able to be compatible with more complex conductivity curves.

In this work, a new and comprehensive model is established to describe the coupled multi-physical processes involved in the real ECR experiment system, and a inverse algorithm with the direct numerical approach coherently embedded is developed to determine the bulk diffusivity $D$ and surface exchange coefficient $k$ for MIECs. A comparison between different models is carried out, and the results show the new model established is more accurate and compatible with more complex conductivity curves.

2. Synthesizing modeling and inverse algorithm

2.1. Coupled modeling of multi physical-chemical processes in the material and the surrounding atmosphere

The schematic illustration of the core experimental section is shown in figure 1. A MIEC cuboid bulk sample lies in the center of a cylindrical tube with the two ends sealed. A gas mixture with two components is supplied into the tube, flowing over the sample surface and providing the sample with the surrounding atmosphere, with certain oxygen partial pressure distribution. Two couples of silver wires (yellow and green wires) are attached to either end of the sample through silver paste to supply current and measure voltage respectively. The whole tube is heated by a test furnace, which can offer uniform heating and temperature control. At first, the sample is in equilibrium with the surrounding atmosphere, then the gas flow rate ratio of the two components is changed, and a new oxygen partial pressure distribution in the surrounding atmosphere forms. As a result, the equilibrium state at the gas/solid interface breaks, and oxygen is either released from or incorporated into the crystal lattice through surface exchange and bulk diffusion. The relaxation time of the sample to the new equilibrium depends on the response time of the surrounding atmosphere approaching a steady state. Therefore the relaxation process is governed by the flow of the gas mixture, oxygen exchange at the gas/solid interface, oxygen diffusion in the surrounding atmosphere, and bulk material.

Suppose the velocity of oxygen is identical with that of the gas mixture in the tube. The Navier-Stokes equation for compressible fluid is applied to describe the velocity and stress distributions of the oxygen in the surrounding atmosphere.

Momentum conservation equation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[ -\mathbf{p} I + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) I \right] + \mathbf{F}$$  (1)

Mass fraction conservation equation of oxygen in the gas mixture:

$$\frac{\partial c_g}{\partial t} + \nabla \cdot (-D_{OA} \nabla c_g) + \mathbf{u} \cdot \nabla c_g = 0$$  (2)

$D_{OA}$ represent the diffusivity of oxygen in the surrounding atmosphere, which depends on the temperature and pressure of gas mixture.
The diffusion process of oxygen within the bulk material is described as:

\[
\frac{\partial c}{\partial t} + \nabla \cdot (-D \nabla c) = 0
\]  

(4)

Linear reaction kinetic is assumed to describe the surface exchange between the gaseous and solid phases. A test furnace offers uniform heating and temperature control to the tube. In this situation, radiation heat transfer and heat-transfer are neglected due to diffusion in the system so that we can write the heat conservation equation as:

\[
\frac{\partial}{\partial t} (\rho C_p T) + \nabla \cdot (\rho C_p u T) = \nabla \cdot (k \nabla T) + Q
\]  

(6)

Where \( Q \) is the ohmic loss depending on the sample conductivity.

| Boundary                  | Inlet                     | Outlet                        | Other boundaries |
|---------------------------|---------------------------|-------------------------------|------------------|
| Laminar flow              | Normal velocity \( U \)   | Pressure and non-viscous stress \( p_0 = 0 \) | No-slip          |
| Mass transfer             | Oxygen partial pressure \( p_{O,2} \) | \(- \mathbf{n} \cdot D_{OA} \nabla c_g = 0 \) | Insulation       |
| /Oxygen concentration \( c_2 \) |                           |                               |                  |

The Fick’s second law with linear absorbing boundary, which has been extensively employed in existing literatures, is summarized in Table 2.

| Fick’s second law with linear absorbing boundary |
|------------------------------------------------|
| Diffusion equation                     | \( \frac{\partial c}{\partial t} = D \nabla^2 c \) |
| Boundary condition                     | \(-D \frac{\partial c}{\partial n} \bigg|_{\Gamma} = k(c_2 - c) \) |
| Initial condition                      | \( c(t, x, y, z) \bigg|_{t=0} = c_1 \) |
The conductivity of MIEC is in proportion to the charge carrier density, which are either oxygen ion or electron-hole here. We could obtain the oxygen ion concentration field \(c(t,x,y,z)\) by solving the coupled Equations (1)-(6). If the apparent conductivity is normalized as:

\[
\sigma_n(t) = \frac{\sigma(t) - \sigma_1}{\sigma_2 - \sigma_1}
\]  

(7)

Where \(\sigma(t), \sigma_1\) and \(\sigma_2\), are the apparent conductivities of the sample at time \(t\), initial and final equilibrium states, respectively. Then the oxygen ions concentration \(c_0\) can be linked to the normalized conductivity [7]:

\[
\sigma_n(t) = \frac{\sigma(t) - \sigma_1}{\sigma_2 - \sigma_1} = \frac{c_0(t) - c_{0,1}}{c_{0,2} - c_{0,1}}
\]  

(8)

2.2. Inverse algorithm

As illustrated above, we can get the apparent conductivity relaxation history of a sample directly in ECR experiments. Then the determination of the \(k\) and \(D\) values is turned into a parameter estimation/inverse problem, i.e., finding the closest \(k\) and \(D\) so that the calculated conductivity is matchable with the experimental data under identical operating conditions. The matching error between experimental measurement and model predictions is defined as:

\[
J(\mathbf{w}^T) = \sum_{i=1}^{Nt} [\sigma_n(t_i, \mathbf{w}^T) - Y_{meas}(t_i)]^2
\]  

(9)

where \(\mathbf{w} = [k, D]^T\) is the estimated kinetic parameter vector; the discrete time \(t_i\), \(i = 1, 2 \ldots, Nt\), represent the sampling points; \(\sigma_n(t_i, \mathbf{w}^T)\) and \(Y_{meas}(t_i)\) are normalized conductivities predicted by the model and measured in the experiment at the sampling time \(t_i\). To minimize the matching error, the derivative of \(J(\mathbf{w}^T)\) with respect to vector \(\mathbf{w}\) is set to be zero:

\[
\mathbf{X}^T(\mathbf{w})[\sigma_n^T(\mathbf{w}^T) - Y_{meas}^T] = 0
\]  

(10)

where \(\sigma_n = [\sigma_n(t_1, \mathbf{w}), \sigma_n(t_2, \mathbf{w}), \ldots, \sigma_n(t_{Nt}, \mathbf{w})]\), \(Y_{meas} = [Y_{meas}(t_1), Y_{meas}(t_2), \ldots, Y_{meas}(t_{Nt})]\), and \(\mathbf{X}(\mathbf{w})\) is the sensitivity matrix defined as,

\[
\mathbf{X}(\mathbf{w}) = \left[\frac{\partial \sigma_n(t_1)}{\partial \mathbf{w}}, \frac{\partial \sigma_n(t_2)}{\partial \mathbf{w}}, \ldots, \frac{\partial \sigma_n(t_{Nt})}{\partial \mathbf{w}}\right]^T
\]  

(11)

A group of nonlinear algebraic equations can be obtained by expanding Eqn. (10). However, it is hard to solve for kinetic parameter vector \(\mathbf{w}\) from Eqn. (10) analytically, instead, the Levenberg-Marquardt iterative method [12] is resorted. The kinetic parameter vector \(\mathbf{w}\) is expanded in a Taylor series, only the first-order terms remain and thus an iterative formula of Eqn. (10) is obtained:

\[
\left[\left(\mathbf{X}(s)\right)^T \mathbf{X}(s) + \mu(s)\Omega(s)\right] \mathbf{w}^{(s+1)} = \left[\left(\mathbf{X}(s)\right)^T \mathbf{X}(s) + \mu(s)\Omega(s)\right] \mathbf{w}^{(s)} - \left(\mathbf{X}(s)^T \sigma_n^T(\mathbf{w}^T) - Y_{meas}^T\right)
\]  

(12)

where \(s\) is the number of iterative steps, \(\mu\) is the damping factor, and:

\[
\Omega = diag(\mathbf{X}^T \mathbf{X})
\]  

(13)

One can obtain the \(k\) and \(D\) values through the iteration of eq. (12). However, the estimation of \(k\) and \(D\) is a typical ill-posed problem which has no unique solution but a set of solutions depending on the measurement noise and expected confidence levels. The measurement noise of the experimental conductivity \(Y_{meas}\) is assumed to satisfy normal distribution with standard deviation \(S_Y\), then one can calculate the standard deviation of estimated parameters \(S_w\) through the following expression:

\[
S_{w_j} = S_Y \sqrt{\left[\mathbf{X}^T \mathbf{X}\right]^{-1}}_{jj}, j = 1,2
\]  

(14)
A 95% confidence level is generally considered in engineering applications. Accordingly, the uncertainty of the estimated $k$ and $D$ can be known as:

$$w_j - 1.96 S_{w_j} \leq w_j \leq w_j + 1.96 S_{w_j}, j = 1, 2$$  \hspace{1cm} (15)

### 2.3. Numerical solution and computational algorithm

The commercial software COMSOL Multiphysics 5.3 is employed as the direct numerical approach to solve the mathematical model described by equations (1)-(6). A structured mesh with refined grids near gas/solid interfaces is adopted after the grid independence is validated. Then the whole direct numerical calculation of the model is embedded into the iterative loop of the inverse algorithm, which is implemented via MATLAB in combination with COMSOL. Figure 2 illustrates the flow chart of the inverse algorithm, and parameter $\varepsilon$ is the prescribed tolerance of the matching error while parameters $\beta$, $\gamma$ are employed to adjust the damping factor of the iteration procedure.

### 3. Results and discussion

Through above analysis, there are obvious differences between the model established and the Fick’s second law employed in the existing method. To understand the difference, we determine kinetic parameters for a set of normalized conductivity data respectively with these two models and the related inverse algorithm. The set of normalized conductivity data to be fitted was assigned assumed measurement noise in advance. First, we carried out direct numerical simulations using the comprehensive mode and assumed values of $k$ and $D$. Then the generated conductivity relaxation responses were added with normally-distributed random noise, of which the mean was 0 and the variance was 5% of the conductivity difference between the initial and final equilibrium states. The initial guesses of $k$ and $D$ values are chosen in a wide range to avoid local minimums of matching error. A set of estimated $k$ and $D$ values with the corresponding matching errors are finally obtained. Figure 3 shows the conductivity curves estimated by the two different models when the smallest matching error is reached.

Clearly, the set of preset normalized conductivity data somewhat deviates from perfect monotone increasing or decreasing trend. In this situation, the fitted conductivity curves by coupled multi-physical processes model are more consistent than those by Fick’s second law, which indicates the model employed in this work is more compatible with complex curves. The corresponding estimated values of $k$ and $D$ under certain operating parameters are then summarized in table III. It can be found that the estimated values of $k$ by the two models are both very close to the true value, and the estimation by new multi-physical coupling model is a little more accurate. Although both the estimated values of $D$ significantly deviate from the true value, the deviation of the estimation by new multi-physical model are much smaller and can be controlled within an order of magnitude. Since the
two models are embedded into the same inverse algorithm to determine surface exchange coefficient $k$ and bulk diffusivity $D$, it can be concluded that the comprehensive model employed in this work is more reliable and the corresponding estimated results obtained are more accurate.

Table 3 Comparison of Fick's law and the newly developed model estimated result.

| Relaxation process | Oxidation | Reduction |
|--------------------|-----------|-----------|
| Operating parameters | Inlet velocity: 1200 ml/min | Inlet velocity: 1200 ml/min |
|                     | Oxygen partial pressure: 0.021 atm → 0.062 atm | Oxygen partial pressure: 0.062 atm → 0.021 atm |
|                     | Temperature: 800 K | Temperature: 800 K |
| Preset values       | $k = 1 \times 10^{-4}$ m/s | $k = 1 \times 10^{-6}$ m/s |
|                     | $D = 1 \times 10^{-5}$ m$^2$/s | $D = 1 \times 10^{-10}$ m$^2$/s |
| Estimations by model in this work | $D = 1.14 \times 10^{-5}$ m$^2$/s | $D = 7.07 \times 10^{-10}$ m$^2$/s |
| Estimation by Fick’s second law | $D = 2.10 \times 10^{-4}$ m$^2$/s | $D = 1.36 \times 10^{-6}$ m$^2$/s |

4. Conclusions
A generic inverse analysis method is developed to determine the bulk diffusivity $D$ and surface exchange coefficient $k$ for MIECs from ECR measurement data. A comprehensive model is established and employed to describe the coupled multi-physical processes during the actual experimental procedure that is different from ideal diffusion described by Fick’s second law with linear absorbing boundary. A comparison study between different models is carried out, and the results show the new model established is more accurate and able to be compatible with more complex conductivity curves; in turn, the estimated results fitted by the new model are more reliable.

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