OPTIMIZATION OF A FRACTAL ELECTRODE-LEVEL CHARGE TRANSPORT MODEL

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A fractal electrode-level charge transport model is established to study the effect the porous electrodes on the properties of solid oxide fuel cells. A fractal variational principle is used to obtain an approximate solution of the overpotential distribution throughout electrode thickness. Optimal design of the electrode is discussed.

Keywords: Fuel cell, SOFC, optimization, variational principle, semi-inverse method, brackets, approximate solution, fractal calculus, fractal derivative

1. Introduction

Solid oxide fuel cells (SOFCs)[1-4] are mainly formed by a mixture of an ionic conductor and an electronic conductor. According to Ohm’s law, the charge transfer in two phases is

\[ \nabla \cdot (-\sigma_{\text{ion}} \nabla \phi_{\text{ion}}) = \nabla \cdot (\sigma_{\text{el}} \nabla \phi_{\text{el}}) = j \]  

(1)

where \( \phi \) is the potential, \( \sigma \) conductivity, the subscriptions “ion” and “el” refer to, respectively, ion ionic conducting phase and the electronic conducting phase, \( j \) is the electrochemical reaction rate, which can be described by the following Butler–Volmer (BV) equation[1]

\[ j = j_0 (e^{\alpha \tau} - e^{-\beta \tau}) \]  

(2)

where \( \tau \) is the overpotential defined as the potential difference between the two phases, \( \alpha \) and \( \beta \) are temperature-related constants.

For one-dimensional case, the electrode-level charge transport model in dimensionless form can be expressed as[1]

\[ \frac{d^2 y}{d \xi^2} = k (e^{\alpha y} - e^{-\beta y}) \]  

(3)

\[ y'(0) = N_0 \]  

(4)

\[ y'(1) = N_1 \]  

(5)

where \( y \) is dimensionless overpotential, \( \xi = x/l \), \( x \) is coordinate in the thickness direction and \( l \) is electrode thickness, \( k \), \( \alpha \), \( \beta \), \( N_0 \) and \( N_1 \) are constants, whose physical meanings are given in Ref.[1].

Bao and Bessler[1] applied the Adomian decomposition method to the above system, some alternative approaches to the problem include the variational iteration method[5,6], the homotopy perturbation method[7,8], and others, see a complete review on various analytical methods in Refs.[9-12].

Accurate model and computational efficiency are highly needed to optimize electrode-level and cell-level systems and to control fuel cells, however the above model cannot take into account the effect of porous structure of electrodes on its properties, a fractal modification is much needed, and a fractal variational principle is established in this paper.
2. Fractal electrode-level charge transport model

Eq.(1) cannot model the effect of the porous structure and unsmooth boundary of electrodes on the charge transport. It was reported that the surface morphology will greatly affect mass, heat and ion transport[13,14]. Considering the porous electrodes, we modify Eq.(1) as

\[ \nabla^{(q,\mu,\lambda)} \cdot ( \sigma \nabla^{(q,\mu,\lambda)} \phi_{el} ) = j \]

where \( \nabla^{(q,\mu,\lambda)} \) is defined as

\[ \nabla^{(q,\mu,\lambda)} = i \frac{\partial}{\partial \eta} + j \frac{\partial}{\partial \mu} + k \frac{\partial}{\partial \lambda} \]

and the fractal derivative is defined as[15,16,17]

\[ \frac{\partial \phi_{im}(x_0, y, z)}{\partial \xi^{(0)}} = \lim_{\Delta x \to 0} \frac{\phi_{im}(x, y, z) - \phi_{im}(x_0, y, z)}{(x-x_0)^{\eta}} \]

where \( \eta \) is the two-scale dimension, \( \Delta x \) is the smallest porosity, and porous size less than \( \Delta x \) is ignored.

A fractal modification of Eqs.(3)-(5) gives as follows

\[ \frac{d^2 y}{d \xi^{(q)}} = k(e^{\alpha y} - e^{\beta y}) \]  

\[ \frac{dy}{d \xi^{(q)}}(0) = N_0 \]  

\[ \frac{dy}{d \xi^{(q)}}(1) = N_1 \]

Fractal calculus becomes a useful tool to modeling discontinuous problems[18-21].

3. Fractal Variational Principle

The variational principle is an effective approach to nonlinear problems[22-26]. Using the semi-inverse method[22-26], the following variational principle can be obtained:

\[ J(y) = \int_l^r \left( \frac{1}{2} \left( \frac{dy}{d \xi^{(q)}} \right)^2 + k \left( \frac{1}{\alpha} e^{\alpha y} + \frac{1}{\beta} e^{\beta y} \right) \right) d \xi^{(q)} \]

Proof. The stationary condition of Eq.(11) is

\[ \frac{\partial L}{\partial y} - \frac{d}{d \xi^{(q)}} \frac{\partial L}{\partial y^{(q)}} = 0, \]

where \( y^{(q)} = dy / d \xi^{(q)} \), \( L \) is the Lagrange function defined as

\[ L = \frac{1}{2} \left( \frac{dy}{d \xi^{(q)}} \right)^2 + k \left( \frac{1}{\alpha} e^{\alpha y} + \frac{1}{\beta} e^{\beta y} \right) \]

Eq.(12) leads to the following Euler-Lagrange equation

\[ k(e^{\alpha y} - e^{\beta y}) - \frac{d}{d \xi^{(q)}} \frac{dy}{d \xi^{(q)}} = 0 \]

which is Eq.(8).

We assume that the solution can be expressed as

\[ y = \ln(a + b \xi^{(q)} + c \xi^{(2q)}) \]

The boundary conditions, Equations(9) and (10), become

\[ \frac{b}{a} - N_0 = 0 \]  

\[ \frac{b + 2c}{a + b + c} - N_1 = 0 \]

Equations(16) and (17) can be written in simpler forms:
Putting Equation (15) into Equation (11) results in

\[ J(a,b,c) = \int_{0}^{1} \left[ \frac{1}{2} \left( \frac{b+2c}{a+b^{2}+c^{2}} \right)^{2} + k \left( \frac{1}{a} (a+b^{2}+c^{2})^{\alpha} + \frac{1}{\beta} (a+b^{2}+c^{2})^{\beta} \right) \right] d\xi^{\eta} \]  

(20)

The variational principle of Equation (11) under constraints of Equations (9) and (10) become an optimal problem to minimize \( J(a,b,c) \) under the constraints of Equations (18) and (19). The stationary conditions are [27,28]

\[ \frac{\partial J}{\partial a} = 0 \]  

(21)

\[ \frac{\partial J}{\partial b} = 0 \]  

(22)

\[ \frac{\partial J}{\partial c} = 0 \]  

(23)

where the subscript denotes the partial derivative, e.g.,

\[ \frac{\partial J}{\partial a} = \int_{0}^{1} \left( \frac{2c}{a+b^{2}+c^{2}} \right) d\xi^{\eta} \]

For arbitrary \( da, db \) and \( dc \), we have the following stationary condition [27,28]:

\[ <J,g,h>_{a,b,c} = g_{a} J_{a} + g_{b} J_{b} + g_{c} J_{c} = 0 \]  

(24)

where \( <J,g,h>_{a,b,c} \) is the bracket. Its properties are discussed in Refs. [28] (it was also called as He-bracket in Ref. [29]).

Solving Equations (18),(19) and (24) simultaneously, the constants, \( a, b \) and \( c \), may be easily determined. As a result, the overpotential distribution, Equation (15), is obtained.

**Case 1.** \( k = \alpha = \beta = N_{0} = N_{i} = 1 \). Under the assumption, from Equations (16) and (17), we have \( a = b \) and \( a = c \), and Equation (20) can be simplified as

\[ J(a) = \int_{0}^{1} \left[ \frac{1}{2} \left( \frac{2c}{1+\xi^{2}+\xi^{2}} \right)^{2} + a + a^{2} + \frac{1}{a^{2}(1+\xi^{2}+\xi^{2})} \right] d\xi^{\eta} \]  

(25)

The stationary condition of Equation (25) reads

\[ \frac{dJ}{da} = \int_{0}^{1} \left[ 1 + \frac{2c}{1+\xi^{2}+\xi^{2}} \right] d\xi^{\eta} = 0 \]  

(26)

From which we can identify \( a \) easily:

\[ a = \frac{\int_{0}^{1} (1+\xi^{2}) d\xi^{\eta}}{\int_{0}^{1} (1+\xi^{2}+\xi^{2}) d\xi^{\eta}} = \frac{\pi\sqrt{3}}{\frac{9}{11}} = 0.574 \]  

(27)

So the overpotential distribution across the thickness of the electrode becomes

\[ y = \ln(0.574(1+\xi^{2}+\xi^{2})) \]  

(28)

**Case 2.** \( k = \alpha = \beta = N_{i} = 1 \), and \( N_{0} = 0 \). Similarly we have \( b = 0 \), \( c = a \), and

\[ J(a) = \int_{0}^{1} \left[ \frac{1}{2} \left( \frac{2c^{2}}{1+\xi^{2}} \right)^{2} + a(1+\xi^{2}) + \frac{1}{a(1+\xi^{2})} \right] d\xi^{\eta} \]  

(29)

Making the function, Equation (29), stationary, we can identify \( a \), which is

\[ a = \frac{\int_{0}^{1} (1+\xi^{2}) d\xi^{\eta}}{\int_{0}^{1} (1+\xi^{2})^{3} d\xi^{\eta}} = \frac{\pi/4}{\sqrt{4/3}} = 0.767 \]  

(30)

As a result, we obtain

\[ y = \ln(0.767(1+\xi^{2})) \]  

(31)
**Case 3.** \( k = \beta = N_i = 1, \) and \( N_0 = 0, \) and \( \alpha \) it to be determined optimally to satisfy

\[
y(\xi = 1) = \bar{y},
\]

where \( \bar{y} \) is prescribed overpotential at \( \xi = 1. \)

By a similar calculation, we have

\[
y(\xi) = \ln[\alpha(1 + \xi^{2\eta})]
\]

and

\[
J(c, \alpha) = \int_0^1 \left[ \frac{1}{2} \left( \frac{2\xi^{\eta}}{1 + \xi^{2\eta}} \right)^2 + \frac{1}{\alpha} \left( c + c \xi^{2\eta} \right)^a + \frac{1}{c(1 + \xi^{2\eta})} \right] d\xi^{\eta}
\]

The stationary condition with respect to \( c \) is

\[
\frac{\partial J}{\partial c} = \int_0^1 \left( (1 + \xi^{2\eta})^{-1} d\xi^{\eta} - \frac{1}{c(1 + \xi^{2\eta})} \right) d\xi^{\eta} = 0
\]

From Equation (35), the constant, \( c, \) can be identified, which is

\[
c^{a+1} = \frac{\int_0^1 (1 + \xi^{2\eta})^{-1} d\xi^{\eta}}{\int_0^1 (1 + \xi^{2\eta})^a d\xi^{\eta}}
\]

As a result, we have

\[
y(\xi, \alpha) = \ln \left[ \frac{\int_0^1 (1 + \xi^{2\eta})^{-1} d\xi^{\eta}}{\int_0^1 (1 + \xi^{2\eta})^a d\xi^{\eta}} \right] + \frac{1}{\alpha + 1} \ln \left( \frac{\int_0^1 (1 + \xi^{2\eta})^{-1} d\xi^{\eta}}{\int_0^1 (1 + \xi^{2\eta})^a d\xi^{\eta}} \right) + \ln(1 + \xi^{2\eta})
\]

By Equation (32), we have

\[
\frac{1}{\alpha + 1} [\ln \int_0^1 (1 + \xi^{2\eta})^{-1} d\xi^{\eta} - \ln \int_0^1 (1 + \xi^{2\eta})^a d\xi^{\eta}] + \ln 2 = \bar{y}
\]

For a fixed \( \bar{y} \), from Equation (38) \( \alpha \) can be determined, see table 1.

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**4. Discussion and conclusion**

From Eq.(28), we have

\[
dy \frac{d\eta}{d\xi} = \frac{1 + \eta \xi^{\eta-1} + 2\eta \xi^{2\eta-1}}{1 + \xi^{\eta} + \xi^{2\eta}}
\]

It has the following property

\[
\frac{d\alpha}{d\xi}(0) = \begin{cases} \frac{1}{\alpha}, & \eta \geq 1 \\ \infty, & \eta < 1 \end{cases}
\]

When \( \eta < 1, \) a sudden rise of potential is predicted. This property cannot be revealed by classical models. Additionally the variational approach guarantees the optimal state of all possible states \((a,b,c)\) in Equation (15) and validness of its solution for the whole solution domain. Other trial functions are also permitted, for example

\[
y(\xi) = \sum_{i=0}^{N} a_i \xi^{i\eta}
\]
where \( a_i \) are constants to be further determined using some a mathematical software, e.g., MatLab (MathWorks, Natick, MA).

If a higher accurate solution is required, we can assume that

\[
y(\xi) = \ln \left[ \sum_{i=0}^{M} a_i \xi^i \right]
\]

where \( a_i \) can be determined in a similar way as illustrated above. The obtained solution can be used to optimally design and control fuel cells.

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**References**


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