OPTIMIZATION OF A FRACTAL ELECTRODE-LEVEL CHARGE TRANSPORT MODEL

by

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Original scientific paper
https://doi.org/10.2298/TSCI200301108L

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, solid oxide fuel cell, optimization, variational principle, semi-inverse method, brackets, approximate solution, fractal calculus, fractal derivative*

Introduction

Solid oxide fuel cells (SOFC) [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:

$$\nabla(-\sigma_{\text{ion}}\nabla\phi_{\text{ion}}) = \nabla(\sigma_{\text{el}}\nabla\phi_{\text{el}}) = j \tag{1}$$

where ϕ is the potential, σ – the conductivity, the subscripts *ion* and *el* refer to ion ionic conducting phase and the electronic conducting phase, respectively, and j – the electrochemical reaction rate, which can be described by the following Butler-Volmer (BV) equation [1]:

$$j = j_0(\mathrm{e}^{\alpha\tau} - \mathrm{e}^{-\beta\tau}) \tag{2}$$

where τ is the overpotential defined as the potential difference between the two phases, α and β – the temperature-related constants.

For 1-D case, the electrode-level charge transport model in dimensionless form can be expressed [1]:

$$\frac{\mathrm{d}^2 y}{\mathrm{d}\xi^2} = k(\mathrm{e}^{\alpha y} - \mathrm{e}^{-\beta y}) \tag{3}$$

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$$y'(0) = N_0 \tag{4}$$

$$y'(1) = N_1 \tag{5}$$

where y is dimensionless overpotential, $\xi = x/l$, x – the co-ordinate in the thickness direction, l – the electrode thickness, k, α, β, N_0 and N_1 – the constants, whose physical meanings are given in [1].

Bao and Bessler [1] applied the Adomian decomposition method to the aforementioned 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 [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 aforementioned 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.

Fractal electrode-level charge transport model

Equation (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):

$$\nabla^{(\eta,\mu,\lambda)}[-\sigma_{\text{ion}}\nabla^{(\eta,\mu,\lambda)}\phi_{\text{ion}}] = \nabla^{(\eta,\mu,\lambda)}[\sigma_{\text{el}}\nabla^{(\eta,\mu,\lambda)}\phi_{\text{el}}] = j \tag{5}$$

where $\nabla^{(\eta,\mu,\lambda)}$ is defined:

$$\nabla^{(\eta,\mu,\lambda)} = i\frac{\partial}{\partial x^{\eta}} + j\frac{\partial}{\partial y^{\mu}} + k\frac{\partial}{\partial z^{\lambda}} \tag{6}$$

and the fractal derivative is defined [15-17]:

$$\frac{\partial \phi_{\text{ion}}}{\partial x^{\eta}}(x_0, y, z) = \Gamma(1+\eta)\lim_{\substack{x-x_{0\to\Delta x}\\ \Delta x\neq 0}}\frac{\phi_{\text{ion}}(x,y,z) - \phi_{\text{ion}}(x_0,y,z)}{(x-x_0)^{\eta}} \tag{7}$$

where η is the two-scale dimension, Δx – the smallest porosity, and porous size less than Δx is ignored.

A fractal modification of eqs. (3)-(5) gives:

$$\frac{\mathrm{d}^2 y}{\mathrm{d}\xi^{2\eta}} = k(\mathrm{e}^{\alpha y} - \mathrm{e}^{-\beta y}) \tag{8}$$

$$\frac{\mathrm{d}y}{\mathrm{d}\xi^{\eta}}(0) = N_0 \tag{9}$$

$$\frac{\mathrm{d}y}{\mathrm{d}\xi^{\eta}}(1) = N_1 \tag{10}$$

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

Fractal variational principle

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

$$J(y)=\int_0^1\left[\frac{1}{2}\left(\frac{\mathrm{d}y}{\mathrm{d}\xi^\eta}\right)^2+k\left(\frac{1}{\alpha}\mathrm{e}^{\alpha y}+\frac{1}{\beta}\mathrm{e}^{-\beta y}\right)\right]\mathrm{d}\xi^\eta \tag{11}$$

Proof. The stationary condition of eq. (11) is:

$$\frac{\partial L}{\partial y}-\frac{\mathrm{d}}{\mathrm{d}\xi^\eta}\left[\frac{\partial L}{\partial y^{(\eta)}}\right]=0 \tag{12}$$

where $y^{(\eta)}=\mathrm{d}y/\mathrm{d}\xi^\eta$, L is the Lagrange function defined:

$$L=\frac{1}{2}\left(\frac{\mathrm{d}y}{\mathrm{d}\xi^\eta}\right)^2+k\left(\frac{1}{\alpha}\mathrm{e}^{\alpha y}+\frac{1}{\beta}\mathrm{e}^{-\beta y}\right) \tag{13}$$

Equation (12) leads to the following Euler-Lagrange equation:

$$k(\mathrm{e}^{\alpha y}-\mathrm{e}^{-\beta y})-\frac{\mathrm{d}}{\mathrm{d}\xi^\eta}\left(\frac{\mathrm{d}y}{\mathrm{d}\xi^\eta}\right)=0 \tag{14}$$

which is eq. (8).

We assume that the solution can be expressed:

$$y=\ln(a+b\xi^\eta+c\xi^{2\eta}) \tag{15}$$

The boundary conditions, eqs. (9) and (10), become:

$$\frac{b}{a}-N_0=0 \tag{16}$$

$$\frac{b+2c}{a+b+c}-N_1=0 \tag{17}$$

Equations (16) and (17) can be written in simpler forms:

$$g(a,b,c)=b-aN_0=0 \tag{18}$$

$$h(a,b,c)=b+2c-N_1(a+b+c)=0 \tag{19}$$

Putting eq. (15) into eq. (11) results in*:*

$$J(a,b,c)=\int_0^1\left\{\frac{1}{2}\left(\frac{b+2c\xi^\eta}{a+b\xi^\eta+c\xi^{2\eta}}\right)^2+k\left[\frac{1}{\alpha}(a+b\xi^\eta+c\xi^{2\eta})^\alpha+\frac{1}{\beta}(a+b\xi^\eta+c\xi^{2\eta})\right]^{-\beta}\right\}\mathrm{d}\xi^\eta \tag{20}$$

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

$$J_a \mathrm{d}a + J_b \mathrm{d}b + J_c \mathrm{d}c = 0 \tag{21}$$

$$g_a \mathrm{d}a + g_b \mathrm{d}b + g_c \mathrm{d}c = 0 \tag{22}$$

$$h_a \mathrm{d}a + h_b \mathrm{d}b + h_c \mathrm{d}c = 0 \tag{23}$$

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

$$J_a = \frac{\partial J}{\partial a} = \int_0^1 \left\{ -\frac{(b+2c\xi^\eta)^2}{(a+b\xi^\eta+c\xi^{2\eta})^3} + k[(a+b\xi^\eta+c\xi^{2\eta})^{\alpha-1} - (a+b\xi^\eta+c\xi^{2\eta})^{-\beta-1}] \right\} \mathrm{d}\xi^\eta$$

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

$$< J, g, h >_{a,b,c} = \begin{vmatrix} J_a & J_b & J_c \\ g_a & g_b & g_c \\ h_a & h_b & h_c \end{vmatrix} = 0 \tag{24}$$

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

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

As illustrating examples, we consider three simple cases to show the solution process.

Case 1. $k = \alpha = \beta = N_0 = N_1 = 1.$ Under the assumption, from eqs. (16) and (17), we have $a = b$ and $a = c$, and eq. (20) can be simplified:

$$J(a) = \int_0^1 \left[\frac{1}{2}\left(\frac{1+2\xi^\eta}{1+\xi^\eta+\xi^{2\eta}} \right)^2 + a + a\xi^\eta + a\xi^{2\eta} + \frac{1}{a+a\xi^\eta+a\xi^{2\eta}} \right] \mathrm{d}\xi^\eta \tag{25}$$

The stationary condition of eq. (25) reads:

$$\frac{\mathrm{d}J}{\mathrm{d}a} = \int_0^1 \left[1+\xi^\eta+\xi^{2\eta} - \frac{1}{a^2(1+\xi^\eta+\xi^{2\eta})} \right] \mathrm{d}\xi^\eta = 0 \tag{26}$$

From which we can identify a easily:

$$a = \sqrt{\frac{\int_0^1 (1+\xi^\eta+\xi^{2\eta})^{-1} \mathrm{d}\xi^\eta}{\int_0^1 (1+\xi^\eta+\xi^{2\eta}) \mathrm{d}\xi^\eta}} = \sqrt{\frac{\pi \dfrac{\sqrt{3}}{9}}{\dfrac{11}{6}}} = 0.574 \tag{27}$$

So the overpotential distribution across the thickness of the electrode becomes:

$$y = \ln[0.574(1+\xi^\eta+\xi^{2\eta})] \tag{28}$$

Case 2. $k=\alpha=\beta=N_1=1,$ and $N_0=0$. Similarly we have b = 0, c = a, and:

$$J(a)=\int_0^1\left[\frac{1}{2}\left(\frac{2\xi^\eta}{1+\xi^{2\eta}}\right)^2+a(1+\xi^{2\eta})+\frac{1}{a(1+\xi^{2\eta})}\right]\mathrm{d}\xi^\eta \tag{29}$$

Making the function, eq. (29), stationary, we can identify a, which is:

$$a=\sqrt{\frac{\int_0^1(1+\xi^{2\eta})^{-1}\mathrm{d}\xi^\eta}{\int_0^1(1+\xi^{2\eta})\mathrm{d}\xi^\eta}}=\sqrt{\frac{\frac{\pi}{4}}{\frac{4}{3}}}=0.767 \tag{30}$$

As a result, we obtain:

$$y=\ln[0.767(1+\xi^{2\eta})] \tag{31}$$

Case 3. $k=\beta=N_1=1,$ and $N_0=0$, and α it to be determined optimally to satisfy:

$$y(\xi=1)=\bar{y} \tag{32}$$

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

By a similar calculation, we have:

$$y(\xi)=\ln[c(1+\xi^{2\eta})] \tag{33}$$

and

$$J(c,\alpha)=\int_0^1\left[\frac{1}{2}\left(\frac{2\xi^\eta}{1+\xi^{2\eta}}\right)^2+\frac{1}{\alpha}(c+c\xi^{2\eta})^\alpha+\frac{1}{c(1+\xi^{2\eta})}\right]\mathrm{d}\xi^\eta \tag{34}$$

The stationary condition with respect to c is:

$$\frac{\partial J}{\partial c}=\int_0^1\left[(1+\xi^{2\eta})^\alpha c^{\alpha-1}-\frac{1}{c^2(1+\xi^{2\eta})}\right]\mathrm{d}\xi^\eta=0 \tag{35}$$

From eq. (35), the constant, c, can be identified:

$$c^{\alpha+1}=\frac{\int_0^1(1+\xi^{2\eta})^{-1}\mathrm{d}\xi^\eta}{\int_0^1(1+\xi^{2\eta})^\alpha\mathrm{d}\xi^\eta} \tag{36}$$

As a result, we have:

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

$$=\frac{1}{\alpha+1}\left[\ln\int_0^1(1+\xi^{2\eta})^{-1}\mathrm{d}\xi^{\eta}-\ln\int_0^1(1+\xi^{2\eta})^{\alpha}\mathrm{d}\xi^{\eta}\right]+\ln(1+\xi^{2\eta}) \tag{37}$$

By eq. (32), we have:

$$\frac{1}{\alpha+1}\left[\ln\int_0^1(1+\xi^{2\eta})^{-1}\mathrm{d}\xi^{\eta}-\ln\int_0^1(1+\xi^{2\eta})^{\alpha}\mathrm{d}\xi^{\eta}\right]+\ln 2=\bar{y} \tag{38}$$

For a fixed $\bar{y}$, from eq. (38) α can be determined, see tab. 1.

Table 1. Values of *α* for different $\bar{y}$

$\bar{y}$	0.4402	0.4285	0.4166	0.4046	0.3925	0.3805	0.3687	0.3571	0.3458
A	0.5	1	1.5	2	2.5	3	3.5	4	4.5

Discussion and conclusion

From eq. (28), we have:

$$\frac{\mathrm{d}y}{\mathrm{d}\xi}=\frac{1+\eta\xi^{\eta-1}+2\eta\xi^{2\eta-1}}{1+\xi^{\eta}+\xi^{2\eta}} \tag{39}$$

It has the following property:

$$\frac{\mathrm{d}y}{\mathrm{d}\xi}(0)=\begin{cases}1, & \eta\ge 1\\ \infty, & \eta<1\end{cases} \tag{40}$$

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 eq. (15) and validness of its solution for the whole solution domain. Other trial functions are also permitted, for example:

$$y(\xi)=\sum_{i=0}^{N}a_i\xi^{i\eta} \tag{41}$$

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:

$$y(\xi) = \ln\left[\sum_{i=0}^{M} a_i \xi^{i\eta}\right] \tag{42}$$

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

Acknowledgment

This work has been financially supported by the Public Projects of Zhejiang Province (LGG18F030013) and Research start-up fund of Ningbo University of Technology.

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Paper submitted: March 1, 2020
Paper revised: May 25, 2020
Paper accepted: June 20, 2020