



Short communication

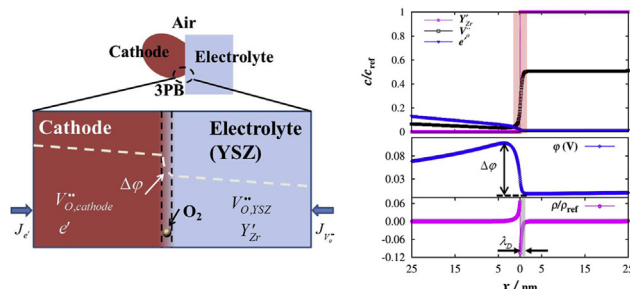
Oxygen vacancy diffusion across cathode/electrolyte interface in solid oxide fuel cells: An electrochemical phase-field model

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HIGHLIGHTS

- Electrochemical model on the ionic transport across cathode/electrolyte interface.
- Cell heterogeneity and interfaces are efficiently described in phase-field model.
- Nonlinear current/overpotential relationship is verified.
- Interfacial equilibrium states of oxygen vacancy and electron are revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

An electrochemical phase-field model is developed to study electronic and ionic transport across the cathode/electrolyte interface in solid oxide fuel cells. The influences of local current density and interfacial electrochemical reactions on the transport behaviors are incorporated. This model reproduces two electrochemical features. Nernst equation is satisfied through the thermodynamic equilibriums of the electron and oxygen vacancy. The distributions of charged species around the interface induce charge double layer. Moreover, we verify the nonlinear current/overpotential relationship. This model facilitates the exploration of problems in solid oxide fuel cells, which are associated with transport of species and electrochemical reactions at high operating temperature.

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1. Introduction

The high operating temperature (700–1000 °C) of Solid Oxide Fuel Cells (SOFC) subjects the cell to conditions that shorten lifetime, mainly due to the accelerated performance degradation [1,2]. One way to mitigate this problem is to reduce the operating temperature to intermediate temperature (500–700 °C) but keep both reaction

activity and ionic diffusivity at high levels [3–5]. A detailed understanding of the oxygen reduction reaction and oxygen transport across the cathode/electrolyte interface is one of the first important steps toward this goal. Although direct experimental observations can provide valuable knowledge of the diffusion processes, numerical models are indispensable because the modeling results can be used to optimize structural designs and determine optimal operation conditions of SOFC [6,7]. Further, a deeper understanding of the physical properties can be reached through fitting the experimental data to a numerical model [8,9]. Most existing models treat the electrode and electrolyte separately [10–12], thus are

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difficult to describe the ionic/electronic diffusion across the electrode/electrolyte interface. In this letter, a continuum model is developed to explore the electrochemical reaction kinetics and the transport of oxygen vacancies and electrons across the cathode/electrolyte interface in SOFC. Establishing such a continuum model is essential because the physical, chemical and electrochemical properties of the interface can be different from the bulk electrolyte or electrode phase due to atomic scale inter-diffusion and/or segregation, and because the oxygen vacancy/electron diffusion across the cathode/electrolyte interface imposes a significant influence on the cation inter-diffusion across the interface as well.

2. Model

In the model, mixed ionic–electronic conductor (e.g., (La,Sr)MnO₃ and (La,Sr)FeO₃) and yttria stabilized zirconia (YSZ) are considered as cathode and electrolyte, respectively. Fig. 1a schematically depicts the transport of oxygen vacancy/electron across the cathode/electrolyte interface at three-phase (i.e., cathode, electrolyte and air) boundaries (3PB). Accordingly, lattice oxygen atoms $O_{O,YSZ}^{\times}$ are generated by the gaseous oxygen (O_2) in the air phase through the reaction, i.e., $(1/2)O_2 + 2e' + V_{O,YSZ}^{\times} \rightarrow O_{O,YSZ}^{\times}$, and then diffuse through vacancy exchange into the YSZ electrolyte. Here the electron e' is provided by the cathode, while the oxygen vacancy $V_{O,YSZ}^{\times}$ in the oxygen ion conductor YSZ is generated through yttrium doping of the host ZrO₂, i.e., $Y_2O_3 + 2Zr_{Zr}^{\times} + O_O^{\times} \rightarrow 2Y'_{Zr} + V_O^{\times} + 2ZrO_2$. Equilibrium is reached when the interfacial electrochemical reaction consumes the same amount of V_O^{\times} and e' .

We use a composition order parameter C which continuously changes from 0 to 1 to describe the cathode ($C=0$), electrolyte ($C=1$), and their interface ($0 < C < 1$), as shown in Fig. 1b. Cahn–Hilliard equation is used to describe the phase evolution around 3PB in SOFC [13], i.e.,

$$\frac{\partial C}{\partial t} = \nabla \cdot M \nabla \left(\frac{\partial f(C)}{\partial C} - \kappa \nabla^2 C \right), \quad (1)$$

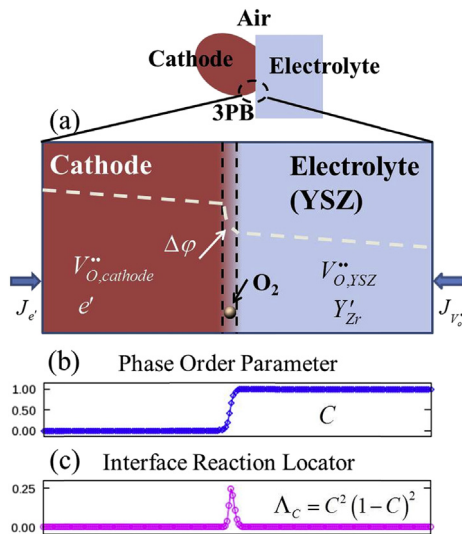


Fig. 1. (a) Schematic of the electrochemical phase-field model depicting oxygen vacancy/electron diffusion across the cathode/electrolyte interface at a 3PB site. V_O^{\times} and e' (V_O^{\times} and Y'_{Zr}) are the charge carriers in the MIEC cathode (electrolyte). An electrostatic potential drop ($\Delta\phi$) exists at the interface, where the electrochemical reaction promotes the charge transfer and consumes V_O^{\times} and e' . Oxygen (O_2) is instantly transferred to the interface from air phase. Profiles of (b) composition order parameter C and (c) interface reaction locator Λ_c .

where M (in the unit of $m^5 J^{-1} s^{-1}$, $M^* = 1$ in reduced unit) is the atomic mobility that is chosen to ensure C reaches equilibrium much faster than the oxygen vacancy and electrons, t is time, and κ is the gradient coefficient (in the unit of $J m^{-1}$, $\kappa^* = 4$ in reduced unit). The interface width is proportional to $\sqrt{\kappa}$ following diffuse-interface theory [14]. A double well potential $f(C) = 2C^2(1-C)^2$ is used as the bulk free energy to describe the two equilibrium states under zero overpotential for the cathode and electrolyte. Since the present 3PB is assumed to be immobile, C will not evolve after reaching equilibrium.

The electrochemical potential of a species i is expressed as,

$$\bar{\mu}_i = \mu_i^0 + k_B T \ln a_i + z_i e \phi, \quad i \in \{V_O^{\times}, e', Y'_{Zr}\} \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature, z_i is the charge per ion of species i , e is the elementary charge and ϕ is the electrostatic potential. μ_i^0 and $a_i = \gamma_i X_i = \gamma_i c_i V_0$ are the standard chemical potential and the activity of a species i , respectively, where γ_i is the activity coefficient, X_i is the molar fraction, c_i is the molar concentration and V_0 the molar volume that is constant in the present model. Values for all parameters are obtained from experiments at 1273 K (see Table 1). Both solid electrode and electrolyte are considered as ideal solution ($\gamma_i = 1$). $\mu_i^0 = \mu_i^{0,cathode} + [\mu_i^{0,YSZ} - \mu_i^{0,cathode}]h(C)$, in which $\mu_i^{0,cathode}$ and $\mu_i^{0,YSZ}$ are the standard chemical potential of cathode and YSZ respectively. $h(C) = C^3(6C^2 - 15C + 10)$ is an interpolating function to bridge $\mu_i^{0,cathode}$ and $i_a = -8 \times 10^6 A \cdot m^{-2}$ [15,16]. The total flux for a given species i is

$$J_i = -\frac{D_i c_i}{k_B T} \nabla \mu_i^0 - D_i \nabla c_i(x, t) - \frac{D_i z_i e c_i}{k_B T} \nabla \phi, \quad (3)$$

where D_i is the self-diffusivity. The second term on the right-hand side of Eq. (3) is the flux from the concentration gradient, and the last one describes electromigration against the gradient of electrostatic potential. The current density is $i_a = e N_A \sum_i z_i J_i$, in which

N_A is the Avogadro constant. Combining the sink term due to the interfacial reaction and the mass transport equation, the diffusion equations for the species i is given as,

$$\frac{\partial c_i(x, t)}{\partial t} = -\nabla \cdot J_i - R_i^{3PB} K \Lambda_c = \nabla \cdot \frac{D_i c_i}{k_B T} \nabla \mu_i^0 + \nabla \cdot D_i \nabla c_i(x, t) + \nabla \cdot \frac{D_i z_i e c_i}{k_B T} \nabla \phi - R_i^{3PB} K \Lambda_c, \quad (4)$$

where R_i^{3PB} is the rate constant of the chemical reaction at the 3PB. Here $R_i^{3PB} = |i_a / e N_A z_i|$ for V_O^{\times} and e' and $R_{Y'_{Zr}}^{3PB} = 0$ since Y'_{Zr} is not involved in the reaction. The function $\Lambda_c = C^2(1-C)^2$, which has nonzero values only in the vicinity of the cathode/electrolyte interface (see Fig. 1c), is introduced to limit the reaction at and near the interface. Integration of the sink term in Eq. (4) gives the same

Table 1
Values of parameters in the electrochemical phase-field model.

Parameter	Value	Parameter	Value
$D_{V_{Zr}^{\times}}$	$5 \times 10^{-20} m^2 s^{-1}$ ^a	$Z_{V_{Zr}^{\times}}$	-1
$D_{V_O^{\times}}$	$1 \times 10^{-8} m^2 s^{-1}$ ^b	$Z_{V_O^{\times}}$	2
$D_{e'}$	$2 \times 10^{-4} m^2 s^{-1}$ ^c	$Z_{e'}$	-1
ϵ	40 ^d	T	1273 K

^a Reference [19].

^b Reference [10].

^c Reference [20].

^d Reference [21].

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