An approximate analytical model of reduction of carbon dioxide in solid oxide electrolysis cell by regular and singular perturbation methods

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ABSTRACT

The objective of this study was to describe the behaviour of carbon dioxide reduction in Solid Oxide Electrolysis Cell (SOEC) in an easy way, so that it can be further applied to cell unit analysis. In this article, an approximate analytical model was established. Concentration overpotential, activation overpotential and Ohmic overpotential were carefully expressed. Regular perturbation method (RPM) was firstly used to get implicit solutions. Then singular perturbation method (SPM) was further developed. Combining RPM and SPM, explicit solutions describing gas concentration and overpotential distributions along electrode were accessible. Calculating time was largely saved, with clear and concise expressions of electrochemical process. Similar to fluid boundary, by comparing ionic current to operating current, a precise description of electrochemical reaction boundary layer (approximate 6%-11% electrode) was developed. It gave us a deeper understanding of the mechanism where electrochemical reaction happens and how it is influenced in SOEC. Using similar analytical models, comparisons of overpotential and ionic current distribution, gas concentration distribution between Solid Oxide Fuel Cell (SOFC) and SOEC in a CO_2-CO binary system were given, with ratio of reactant/product varying from 0.5 to 2.0. Meanwhile, analysis on important impact factors through analytical way in SOEC system, such as current density (from 0 to 0.3 A cm^{-2}), temperature (973 K and 1073 K), triple phase boundary (TPB), was provided.

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1. Introduction

With the high pace of modern economic development and fossil fuel consumption, the way of capturing, storage and reutilizing of the main greenhouse gas CO_2, has been investigated for a long time [1–3]. A new electrolysis method in SOEC, electrolyzing carbon dioxide to carbon monoxide and oxygen ($CO_2-CO + 1/2O_2$), was preferred [4,5]. CO can be converted to valuable hydrocarbon through Fischer Tropsch reaction [6]. Meanwhile, O_2 can serve as a long-term oxygen support for military or space facility [7]. SOEC is reverse process of SOFC in principle and consumes less energy, compared with Alkaline or PEM electrolyze. And it can be integrated with other kinds of renewable energy, such as nuclear, solar, and wind [8–10]. Moreover, highly efficient CO_2 and steam co-electrolysis for synthetic fuels production at high temperature can be achieved by the same mechanism [11,12].

Many researchers focused on inspecting the mechanism of SOFC and SOEC through numerical simulations, by simulink, CFD and COMSOL. Shi developed a model to describe heterogeneous reactions and electrochemical elementary charge transfer reactions in CO_2-CO SOEC system [13]. It predicted effects of operating conditions on the cell performance, and suggested low CO content could help reduce carbon deposition. Ni developed 1-D and 2-D SOEC models to investigate performance of CO_2 reduction [14]. Gas velocity, electrode permeability and inlet gas composition were carefully investigated. Narasimhaiah used modified Butler-Volmer equation and considered multi-step single-electron transfer reactions [15]. But the complexity of SOEC makes it difficult to grasp every detailed impact factor only basing on numerical solutions. Even those models agreed well with experimental data, essential impact factors under different operating conditions were still hard to figure out. The conclusion often depended on empirical analysis without solid theoretical support. So some researchers built analytical SOEC models to study CO_2 reduction, such as Zhang [16]. It indicated five different strategies to implement the carbon dioxide electrolysis. Grondin built a 3D simulation, taking gas flow velocity, species concentrations and current density into account. And it announced

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Nomenclature

Abbreviation

A/C	anode/channel interface
A/E	anode/electrolyte interface
C/C	cathode/channel interface
C/E	cathode/electrolyte interface
LSM	lanthanum strontium manganate
PEM	proton exchange membrane
PEN	positive-electrolyte-negative
RPM	regular perturbation method
ScSZ	scandium stabilized zirconium
SOEC	solid oxide electrolysis cell
SOFC	solid oxide fuel cell
SPM	singular perturbation method
TPB	triple phase boundary
YSZ	yttrium stabilized zirconium

English letters

a,b	slope rate of normalized fuel concentration
C	concentration (mol/m^3)
D	diffusion parameter (m^{2}s^{-1})
E	activation energy (kj mol^{-1})
f	nF/RT (V^{-1})
F	Faraday constant (96,384 C mol^{-1})
i	current density (A cm^{-2})
i_{ref}	exchange current density (A cm^{-2})
I	operating current density (A cm^{-2})
j	electrochemical reaction rate (mol m^{-2} s^{-1})
l	electrode/electrolyte thickness (m)
M	molecular weight (kg mol^{-1})
n	electrons transferred per reaction molecule (n = 2)
N	flux (mol m^{-2} s^{-1})
P	pressure (Pa)
r	mean pore radius of electrode
R	universal gas constant (8.314 J mol^{-1} K^{-1})
S_{TPB}	active area per unit volume (m^2 m^{-3})
T	temperature (K)
x	spatial coordinate along the electrode thickness (m)
z	dimensionless x coordinate
z_0	dimensionless thickness of the inactive layer

Greek letters

α	charge transfer coefficient
γ	reaction order
ε	porosity
ε	equilibrium potential
τ	tortuosity
σ	conductivity (S/m)
λ	mean free path
η	overpotential (V)
η	dimensionless overpotential
ϕ	potential (V)
ψ	$\psi = 1$ in cathode, $\psi = -1$ in anode
ε	characteristic length
Ω_D	collision integral
$\theta_1, \theta_2, \theta$	perturbation variables
ξ	dimensionless coordinate for the active layer
ζ_1, ζ_2	dimensionless coordinate for enlarged boundary layer
Φ_0	dimensionless parameter for mass transfer

Subscripts and superscripts

a	anode
c	cathode
e	electrolyte
eff	effective
el	electronic conducting phase
eq	equilibrium
$inact$	inactive layer
ion	ionic conducting phase
k	Knudsen
ref	reference
t	total
0	initial condition

that the model could be applied to macro-scale unit [17]. Unfortunately, there is few models considering about what is happening on the boundary layer. Because main electrochemical reaction occurs on boundary [18], boundary effect is crucial in understanding SOEC [19–21]. An analytical model describing gas concentration distribution and overpotential distribution along the electrode, especially in boundary layer, can help to grasp more detailed electrochemical and mass diffusion features.

This model concerning SOEC was mainly based on a former model which used perturbation methods to get analytical solutions in SOFC system [22]. Cathode-support SOEC (cathode thickness is 700 μm) with intermediate temperature (1073 K) was mainly studied [23–25]. This model integrated rules of Ohmic law, Butler-Volmer equation, theoretical electrolytic voltage and Fick's second diffusion law to get a comprehensive understanding of Ohmic loss, activation loss and concentration loss of CO_2 reduction in SOEC. Combining RPM and SPM, explicit expression of concentration distribution and overpotential distribution were accessible. A boundary layer effects was discovered and artificially defined. Important influential parameters, such as current density, temperature, gas composition and triple phase boundary, were carefully studied.

2. PEN transfer mathematical model

PEN (Positive-Electrolyte-Negative) is SOEC core structure. It represents electrochemical reaction, heterogeneous reaction, mass and charge transfers. Typically, Ni/YSZ is used to make cathode material. It is a kind of ceramic material that can conduct ionic and electronic currents, which also separates reactant and product on cathode/channel (C/C) and cathode/electrolyte (C/E) side. The anode side, often made by porous material LSM/ScSZ, is used to provide triple phase boundary (TPB) for oxygen production and diffusion. In accordance with our former publication [18], When cathode thickness is large enough (700 μm, both in [18] and this model), the heterogeneous reactions reach the equilibrium near the C/C interface, and major electrochemical reaction occurs nearby C/E interface. CO_2 is reduced to CO ($CO_2 + 2e - CO + O^{2-}$). While on the anode TPB, O_2 is produced ($O^{2-} - 1/2O_2 + 2e^-$). In this article, the electrolyte, cathode, and anode are made of ScSZ, Ni/YSZ, LSM/ScSZ with thickness of 20 μm, 680 μm (support layer) + 20 μm (active layer), 20 μm, as Fig. 1 shown.

This model is based on following assumptions:

1. One-dimension, isothermal and steady operating condition is considered. Temperature distributes uniformly in the whole cell, all parameters are given at a certain temperature.
2. All gases are treated as ideal gases.
3. Thickness of cathode is neglectable compared to its diameter. So convection diffusion associated with gas pressure gradient along the electrodes is ignored. The positive direction is from C/C interface to C/E interface.