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Mathematical modeling of the coupled transport and electrochemical reactions in solid oxide steam electrolyzer for hydrogen production

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Abstract

A mathematical model was developed to simulate the coupled transport/electrochemical reaction phenomena in a solid oxide steam electrolyzer (SOSE) at the micro-scale level. Ohm's law, dusty gas model (DGM), Darcy's law, and the generalized Butler Volmer equation were employed to determine the transport of electronic/ionic charges and gas species as well as the electrochemical reactions. Parametric analyses were performed to investigate the effects of operating parameters and micro-structural parameters on SOSE potential. The results substantiated the fact that SOSE potential could be effectively decreased by increasing the operating temperature. In addition, higher steam molar fraction would enhance the operation of SOSE with lower potential. The effect of particle sizes on SOSE potential was studied with due consideration on the SOSE activation and concentration overpotentials. Optimal particle sizes that could minimize the SOSE potential were obtained. It was also found that decreasing electrode porosity could monotonically decrease the SOSE potential. Besides, optimal values of volumetric fraction of electronic particles were found to minimize electrode total overpotentials. In order to optimize electrode microstructure to minimize SOSE electricity consumption, the concept of "functionally graded materials (FGM)" was introduced to lower the SOSE potential. The advanced design of particle size graded SOSE was found effective for minimizing electrical energy consumption resulting in efficient SOSE hydrogen production. The micro-scale model was capable of predicting SOSE hydrogen production performance and would be a useful tool for design optimization.

Keywords: SOSE; Porous media; Multi-component mass transfer; Functionally graded materials; Electrochemical model; Thiele modulus; Wagner number

1. Introduction

The use of fossil fuels as energy sources has caused energy crisis and environmental pollution problems at a global level. Renewable energy sources, such as solar and wind, are promising to solve these problems. However, renewable energy sources are usually site-specific and intermittent. Therefore, hydrogen has been identified as an ideal energy carrier and a promising fuel to better utilize the renewable energy sources [1,2]. Hydrogen can be converted into electricity via fuel cells in an efficient and environmental manner. Due to the great promise of hydrogen fuel, there is increasingly more interest from the government, industry, and academy to develop hydrogen-related technologies.

The success of hydrogen energy highly relies on the development of hydrogen production technologies. Presently, most of hydrogen used is produced from hydrocarbon reforming, such as natural gas steam reforming [3,4]. However, the reforming of hydrocarbon is neither renewable nor clean. Hydrogen can be produced in a more environmental friendly manner by thermochemical water-splitting, photocatalytic water-splitting, or water electrolysis [5,6]. Presently, both thermochemical and photocatalytic hydrogen production methods have efficiency too low to be economically competitive. Water electrolytic hydrogen production is so far the most practical and promising technology for large-scale renewable hydrogen production [4,5]. Electrolylzers can be driven by solar cells or wind turbines together with waste heat from industry to produce hydrogen in an

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environmentally friendly manner. High-temperature solid oxide steam electrolyzers (SOSE) are more advantageous than low-temperature proton exchange membrane (PEM) electrolyzers and alkaline electrolyzers because SOSE can produce hydrogen at a high chemical reaction rate with a low electrical energy requirement [7–11]. In recent years, there are growing interests in integrating SOSE hydrogen production with nuclear power plant or geothermal energy resources for practical applications [12–14].

Most research works done on SOSE hydrogen production were experimental in nature, with an emphasis on the development of new materials to cope with high operating temperature and strong reducing/oxidizing environments required for stable and efficient operation [15–17]. Theoretical modeling studies on SOSE hydrogen production are limited in literature. Recently, an electrochemical model has been developed to obtain the *J–V* characteristics of an SOSE in hydrogen production at a macro-scale level [18,19]. However, the macro-level model was insufficient to investigate precisely the micro-structural effects, essentially needed for design optimization. Although there are a few studies on micromodeling of solid oxide fuel cell (SOFC) electrodes in the literature [20,21], these studies and results cannot be directly applied to SOSE because of different gas transport phenomena involved in SOFC and SOSE [18]. In a previous publication, it has been found that the SOFC and SOSE have different concentration overpotentials in the porous electrodes. Nevertheless, the material properties parameters can be used in the SOSE modeling since SOFC and SOSE use the same hardware but proceed in reverse direction.

In this investigation, a comprehensive mathematical model was developed to study the performance of SOSE at a micro-scale level. Unlike previous macro-level models for SOSE, which assume the electrochemical reactions to occur only at the electrode–electrolyte interface, the present micro-scale model considers the coupled mass transport and electrochemical reactions inside the porous electrodes. Parametric analyses were performed to study the effects of operating and micro-structural parameters on SOSE performance. Advanced design of particle size graded SOSE was investigated to reduce electrical energy consumption for efficient hydrogen production.

2. Model development

The model developed in the present study consists of the basic cathode (H_2 electrode), electrolyte, and anode (O_2 electrode). As shown in Fig. 1, the mechanisms involved in the porous H_2 electrode are (1) transport of H_2O (steam) from the cathode surface to the reaction site through pores by diffusion and transport of e^- from the current collector (H_2 electrode surface) to reaction sites through electronic conductors, (2) reaction of H_2O and e^- to form O^{2-} and H_2 at reaction sites, and (3) transport of H_2 from reaction sites to the surface of cathode through the porous medium by diffusion and transport of O^{2-} from reaction sites to electrolyte through ionic conductor. At the anode side, O^{2-} transporting in the ionic conductors is oxidized to e^- and O_2. The electrons produced are transported through electronic conductors to the anode surface and O_2 are transported to the anode surface through the porous electrode by permeation. For simplicity, the similar schematic of anode is not depicted in this paper.

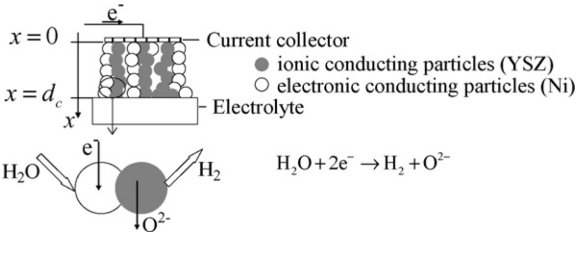

Fig. 1. Schematic of the composite cathode (H_2 electrode) of a SOSE and illustration of its electrochemical mechanisms for hydrogen production.

2.1. The cathode

Charge balance in the electronic/ionic conductors

$$\nabla \cdot J_{\mathrm{e,c}} = -S_{\mathrm{V}} J_{\mathrm{n,c}} = -\nabla \cdot J_{\mathrm{i,c}} \qquad (1)$$

where $J_{\mathrm{e,c}}$ and $J_{\mathrm{i,c}}$ are the current densities in the electronic and ionic conductors, respectively (A/m^2); S_{V} is the electrochemically active internal surface area per unit volume of the porous H_2 electrode (m^2/m^3); $J_{\mathrm{n,c}}$ (A/m^2) is the transfer current density per unit of reactive surface area.

The volumetric surface area (S_{V}) can be determined by statistical properties of binary powder mixtures [20–22],

$$S_{\mathrm{V}} = \pi \sin^2\theta r_{\mathrm{e}}^2 n_{\mathrm{t}} n_{\mathrm{e}} n_{\mathrm{i}} \frac{Z_{\mathrm{e}} Z_{\mathrm{i}}}{6} P_{\mathrm{e}} P_{\mathrm{i}} \qquad (2)$$

where θ is the contact angle between the electronic and ionic conductors; r_{e} is the radius of the electronic conductors; n_{t} is the total number of particles per unit volume; n_{e} and n_{i} (equal to $1 - n_{\mathrm{e}}$) are the number fractions of electronic and ionic conductors, respectively; P is the probability of a conductor connected with the porous medium; subscripts e and i represent electronic and ionic conductors, respectively.

The values of n_{t} and n_{e} can be determined by the following expressions [20],

$$n_{\mathrm{t}} = \frac{1 - \varepsilon}{(4/3)\pi r_{\mathrm{e}}^3 [n_{\mathrm{e}} + (1 - n_{\mathrm{e}})(r_{\mathrm{i}}/r_{\mathrm{e}})^3]} \qquad (3)$$

and

$$n_{\mathrm{e}} = \frac{\Phi}{\Phi + (1 - \Phi)/(r_{\mathrm{i}}/r_{\mathrm{e}})^3} \qquad (4)$$

where ε is the porosity of the electrode, r_{i} the radius of the ionic conductors and Φ is the volumetric fraction of electronic conductors in the porous electrode.

The average coordination number for electronic/ionic conductors can be determined, respectively by [20,23,24]

$$Z_{\mathrm{e}} = 3 + \frac{3}{n_{\mathrm{e}} + (1 - n_{\mathrm{e}})(r_{\mathrm{i}}/r_{\mathrm{e}})^2} \qquad (5)$$