Solid State Ionics 295 (2016) 78–89

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Elementary reaction modeling and experimental characterization of solid oxide direct carbon-assisted steam electrolysis cells

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ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form 11 July 2016
Accepted 11 July 2016
Available online xxxx

Keywords:
Solid oxide direct carbon-assisted electrolysis cell (SO-DCEC)
Cell performance
Heterogeneous chemistry
Elementary reaction model
Carbon monoxide

ABSTRACT

A detailed one-dimension mechanistic model for solid oxide direct carbon-assisted steam electrolysis cell (SO-DCEC) is well developed by considering heterogeneous elementary reactions in both the carbon bed and the cell, coupling with mass and charge transfer processes. The model is calibrated and validated by experimental data from a button cell test with different anode carrier gases at 800 °C. The experimental and modeling results show that using CO_2 instead of argon gas as the carrier gas benefits the cell performance. A mismatching between CO production in the carbon bed, its diffusion from the carbon bed to the cell and its consumption in the cell results in different transition zones in the cell polarization curve. A concept of producing H_2 and CO simultaneously in the SO-DCEC system is proposed, and analyses indicate that working voltages of the cell and the carbon bed height greatly influence the system performance and production rates of gaseous fuels.

1. Introduction

Currently, the demand for hydrocarbon fuels keeps increasing especially in developing countries like China and India, which challenges the truth that the supply of commercially usable hydrocarbon resources is limited in the world. Moreover, environmental issues such as global warming and air pollution caused by the traditional utilization of hydrocarbon fuels become more and more severe. To address these two severe problems, hydrogen is an ideal substitution for hydrocarbon fuels as a potential fuel and an energy storage medium [1,2], for reasons that: (1) Hydrogen is an "infinite" source of energy which can be generated from other renewable sources, although no direct natural source exists for it. (2) Hydrogen is environmentally friendly since it produces water only as the combustion and oxidation product.

The development of efficient systems for hydrogen production is a crucial issue before the widely use of hydrogen. Most of hydrogen is presently produced by the steam reforming of methane, however this approach has the drawback that it cannot employ renewable energies like solar or wind energy which is totally carbon-free. Also, its reaction device is so large that it is not particularly amenable to a reliable and highly distributed hydrogen supply infrastructure [3]. Another alternative method is producing hydrogen by water electrolysis, which produces a high purity hydrogen containing no CO unlike steam reforming and also suitable for distributed generation. Hydrogen generation by high-temperature electrolysis of water vapor using solid oxide electrolysis cells (SOEC) has been demonstrated to be a high-efficiency method [4–7]. The main disadvantage of electrolysis is the high electricity consumption. For the reason that electricity is an high quality and expensive form of energy, the cost of hydrogen production by electrolysis is as expensive as 2–3 times of that by steam reforming of methane [4]. And in essence, the electricity consumed mainly comes from the grid which produced from the fossil fuels, that means the steam electrolysis process actually is not absolutely carbon-free.

Recently, there has been renewed interest in using solid oxide fuel-assisted electrolysis cell (SOFEC) for electrolytic production of hydrogen. In SOFEC steam is fed into the cathode just as in SOEC, but fuels (like carbon, CO, CH_4, biomass and other hydrocarbon fuels) are sent into the anode to facilitate the removal of oxygen from steam. It is obviously that adding assisting fuels significantly decreases the energy demand based on thermodynamics principle. Therefore, large amounts of electric power can be saved when the cell works in the SOFEC mode [8]. Several studies have demonstrated the use of anodic gaseous fuels in assisting steam electrolysis both experimentally and numerically [2–4,9]. Experiments performed on single cells by Martinez-Frias et al. [4] showed a voltage reduction of as much as 1 V when compared to the SOEC by natural gas-assisted electrolysis, and the system efficiency was up to 70% with respect to primary energy incorporating the cell with a heat recovery system.

Using carbon or carbonaceous solids for carbon-assisted hydrogen production offers several advantages over those gaseous fuel-assisted performance such as: the abundance of cheaper and low-quality fuel sources including coal and biomass, high theoretical efficiency, and high CO_2 emission reduction potential. Experiments done on a SOFEC

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http://dx.doi.org/10.1016/j.ssi.2016.07.003
0167-2738/

with a single carbon bed at the anode by Lee et al. [1] confirmed the concept of spontaneous hydrogen production and cogeneration of electricity. Xu et al. [10] developed a 2D DC-SOEC numerical model for syngas production at two different electrodes with easy control of H_2/CO ratio, which is helpful for subsequent process to synthesize other chemicals from syngas.

The performance of SOFEC with carbon as the assistant fuel relies on the coupling of carbon gasification and electrochemical reactions. The typical operating temperature of the carbon bed as well as the cell ranges from 600 to 1000 °C [11]. The cell performance decays seriously when the temperature is above 800 °C. However, the reaction rate of carbon gasification strongly depends on temperature, which is relatively slow below 800 °C [12]. Hence accelerating the reaction rate of carbon gasification to match the optimal operating temperature of the cell is crucial for improve the performance of the cell. It has been demonstrated that alkali metals are effective catalysts for carbon gasification [12–16], which are widely used for reducing the gasification reaction temperature in coal conversion processes. Li et al. [16] experimentally proved the improvement of the SO-DCFC performance by carbon catalytic gasification.

To gain insight into the complex physical phenomena governing the cell performance, it is requisite to establish validated mechanism models for cell design and operating condition optimization. Numerous SOFC (or SOEC) models concerning gas transport phenomena, ionic and electronic conduction, and electrochemical processes have been reported in literatures for syngas and methane [2,17–21]. Zhao et al. [22] developed the SO-DCFC model with carbon fuel from CH_4 cracking. Alexander et al. [23] and Yu et al. [24] developed detailed mechanism models coupling the carbon bed, fuel cell reaction and transport processes, which are based on biomass and carbon black as the fuels respectively. In these two models, the detailed carbon gasification kinetics and the diffusion processes within the carbon bed are carefully considered.

From the discussion above, it is clear that mechanism models for SOFEC with gaseous fuels at the anode and SO-DCFC with carbon gasification have been well studied separately. And only small number of experiments have been conducted on SOFEC with carbonaceous fuels at the anode. A validated mechanism model with experiments is helpful to understand the intricate phenomena in SO-DCEC performance coupling with the carbon bed gasification, as experimental studies on the SO-DCEC are rather complex, expensive and time-consuming. In this paper, a comprehensive elementary reaction kinetic model of SO-DCEC coupled with potassium catalytic gasification of a single carbon bed is developed. This model fully considers the coupling of electrochemical reactions, charge transport and mass transport processes within the cell and the thermochemical processes of the carbon bed. The modeling results are validated by experimental data obtained for an SO-DCEC button cell with different anodic carrier gases at the setting operating temperature of 800 °C. Then the anodic reaction mechanism is carefully investigated based on the experimental and numerical results. After that, the effects of the operating temperatures, carrier gas composition and carbon bed properties on the SO-DCEC performance optimization are systematically explored.

2. Model development

2.1. Model assumption and geometry

The model assumptions are listed as follows:

(1) The gases in the computational domain are ideal gases;
(2) The temperature within the carbon bed and the cell is uniform. All parameters are determined under the selected temperature;
(3) The electrodes are isotropic materials with porous and stable microstructures. And the distribution of electronic conductors and

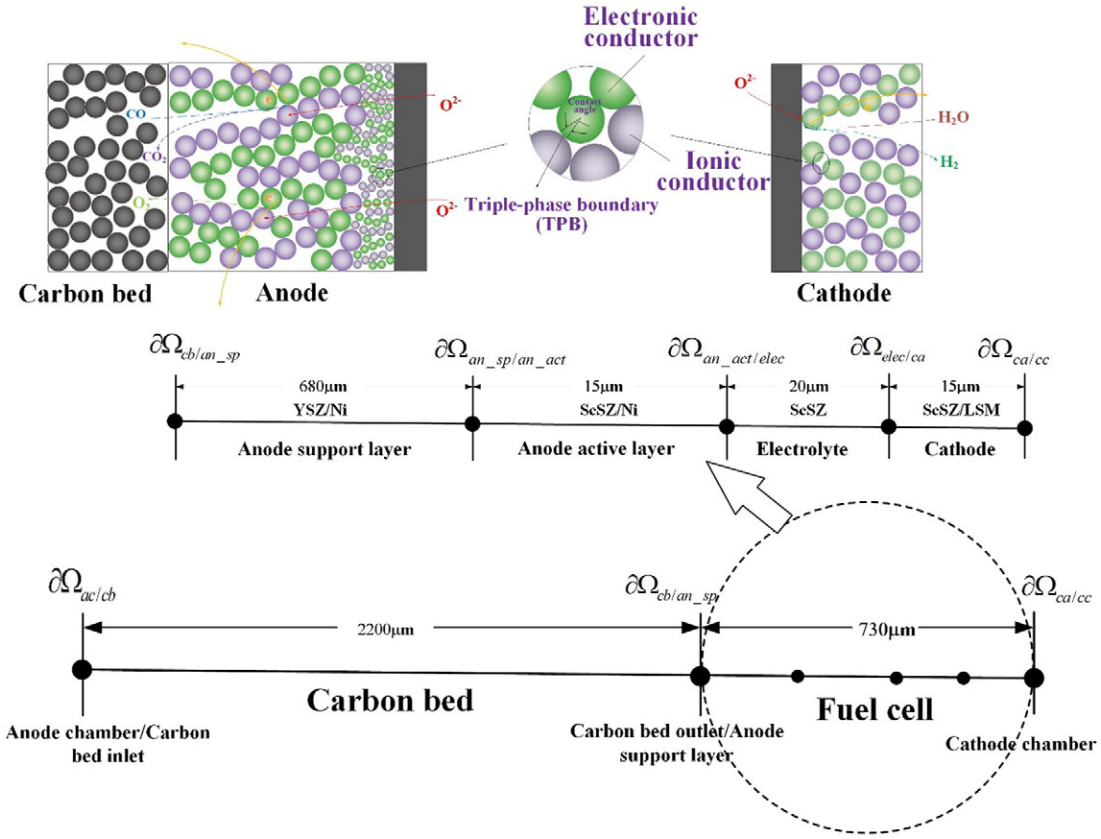

Fig. 1. Model structures, calculation domains and boundaries of fuel-assisted steam electrolysis.