

Consideration of reversed Boudouard reaction in solid oxide direct carbon fuel cell (SO-DCFC)

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The direct carbon fuel cell (DCFC) has attracted researcher's attention recently, due to its high conversion efficiency and its abundant fuel, carbon. A DCFC mathematical model has developed in two-dimensional, lab-scale, and considers Boudouard reaction and carbon monoxide (CO) oxidation. The model simulates the CO production by Boudouard reaction and additional electron production by CO oxidation. The Boudouard equilibrium strongly depends on operating temperature and affects the amount of produced CO and consequentially affects the overall fuel cell performance. Two different operating temperatures (973 K, 1023 K) has been calculated to discover the CO production by Boudouard reaction and overall fuel cell performance. Moreover, anode thickness of the cell has been considered to find out the influence of the Boudouard reaction zone in fuel cell performance. It was found that in high temperature operating DCFC modeling, the Boudouard reaction cannot be neglected and has a vital role in the overall fuel cell performance.

Key words: Direct carbon fuel cell, CFD, Boudouard reaction, Carbon monoxide, Carbon fuel

Introduction

On the global agenda, the conversion of solid carbonaceous fuels in carbon fuel cell which especially operates at high temperatures are in great interest as in needs for the efficient and clean environmental technology. More than 80% of the global primary energy demands on fossil fuels, even though coal-fired power plants conversion efficiency is only 30 to 35%. Moreover, coal-fired plants emit a copious amount of CO₂ and other pollution sources into the environment. However, despite the low efficiency and high emissions, the coal would be the most dominating fuel in global electricity generation market through 2050 [1, 2]. This is because coal is the most copious and widely distributed fuel on this planet. For this reason, direct carbon fuel cells (DCFC) have become promising alternative devices which converts the chemical energy of carbon into electrical energy directly with high efficiency [3-5].

Modeling and experimental studies of solid oxide direct carbon fuel cells (SO-DCFCs) have been reported recently by several researchers, and numerous SOFC models considered the ionic, and electronic conduction, gas transportation, and the electrochemical kinetics by hydrogen, syngas, and methane [6-9]. Zhao et al. [10] developed the SO-DCFC model with carbon

fuel by CH₄ cracking which considers the global carbon gasification reactions, and evaluate the effect of exchange current density and CO diffusion coefficients on the cell performance. However, the model was not experimentally validated, and the carbon gasification kinetics were not considered.

In this paper, we developed a non-isothermal kinetic model, which considers CO production by reversed Boudouard reaction in the anode chamber and the electrochemical oxidation of CO as additional fuel. The various CO and CO₂ inlet gas composition were considered to discover the influence of reversed Boudouard reaction in DCFC, and the anode thickness which can be considered as Boudouard reaction zone. The results and the process of developing this model will give the guideline on modeling DCFC system in forwarding studies.

DCFC Configuration

System description

In this study, a 2D steady-state model of the DCFC was used. The DCFC model contains five layers, which is graphite anode layer (GAL), anode catalyst layer (ACL), electrolyte (ELEC), cathode catalyst layer (CCL) and cathode gas diffusion layer (CGDL). Fig. 1(a) shows the scheme of DCFC, and the dimensions used in this model (Fig. 1(b)).

Model assumptions

The following major assumptions were made to build this model.

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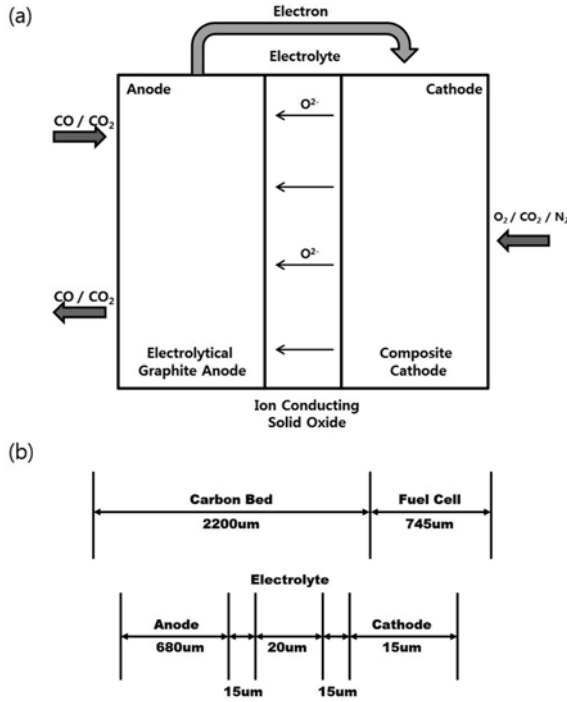


Fig. 1. Scheme of the direct carbon fuel cell (DCFC) (a) Generic illustration of the direct carbon fuel cell (b) physical dimension of the model domain.

- The operation of the DCFC is to be steady-state, isothermal and isobaric.
- The gas diffusion follows the ideal gas mixture in a homogeneous pore structure.
- The electrochemical reaction only occurs at the anode/cathode active layers.
- The reversed Boudouard reaction only occurs at the anode layer.
- The solid and electrolyte phase potentials are considered to describe the electron and proton transport, respectively.

Electrochemical modeling of a DCFC system

In order to simulate the charge transfer, the general Butler-Volmer equation was used to calculate the activation polarizations for anode and cathode, respectively.

$$j = j_o \left\{ \exp\left(\alpha \frac{nF\eta_{act}}{RT}\right) - \exp\left((1-\alpha) \frac{nF\eta_{act}}{RT}\right) \right\} \quad (1)$$

The apparent charge transfer-coefficient α takes value in the range 0-1 and is typically assigned as 0.5 for fuel cells [11]. The anode exchange current density $j_{o,an}$ is related to the charge transfer resistance R_{ct} and is given by following;

$$j_{o,an} = \frac{RT}{nFR_{ct}} \quad (2)$$

$$R_{ct} = 30.79 + 1.48 \exp\left(-\frac{T}{28.58}\right) \quad (3)$$

The values in equation (3) are obtained from a regression analysis of the data published by Peelen et al. [12].

In anode, total volumetric current density is the sum of two electrochemical reactions of C and CO.

$$j_{total} = j_c + j_{CO} \quad (4)$$

Where j_{total} is total volumetric current density; j_c , j_{CO} is the current density of electrochemical reaction by C and CO. However, in the cathode, only O_2 electrochemical reduction corresponds to total volumetric current density (j_{O_2}), and the equations are described below:

$$j_c = A_{v,an} j_{o,c} \left(\frac{C_c}{C_{ref,c}} \right)^{0.5} \left(\exp\left(\frac{\alpha F \eta_c}{RT}\right) - \exp\left(\frac{-\alpha F \eta_c}{RT}\right) \right) \quad (5)$$

$$j_{CO} = A_{v,an} j_{o,CO} \left(\frac{C_{CO}}{C_{ref,CO}} \right)^{0.5} \left(\exp\left(\frac{\alpha F \eta_{CO}}{RT}\right) - \exp\left(\frac{-\alpha F \eta_{CO}}{RT}\right) \right) \quad (6)$$

$$j_{O_2} = A_{v,cat} j_{o,O_2} \left(\frac{C_{O_2}}{C_{ref,O_2}} \right)^{0.5} \left(\exp\left(\frac{\alpha F \eta_{O_2}}{RT}\right) - \exp\left(\frac{-\alpha F \eta_{O_2}}{RT}\right) \right) \quad (7)$$

Here, $A_{v,an}$ and $A_{v,cat}$ are active specific surface areas for the anode and cathode electrodes. j_o is the exchange current density which represents the activity of the electrodes. The $j_{o,CO}$ was assumed to be 0.45 times that of H_2 oxidation in SOFC [13].

Reversed boudouard reaction in direct carbon fuel cell

The Boudouard reaction is the redox reaction of a chemical equilibrium mixture of carbon monoxide and carbon dioxide at a given temperature.



The Boudouard reaction equilibrium is strongly temperature dependent, as are the kinetics of the forward and reverse reaction. From about 873 K, the equilibrium shifts to the right of reaction (8); above 973 K, both thermodynamic equilibrium and kinetics cause the reverse Boudouard reaction to take place vigorously [14].

Nakagawa et al. [15] demonstrated the feasibility of a direct carbon solid oxide fuel cell (DC-SOFC) and proposed the mechanism of the fuel cell as the cycle of

Table 1. Parameters for Boudouard reaction rate [22].

Parameters	Value	Unit
k_{rb}	4.016×10^8	m/s
E_{rb} / R	29,790	K

the two reactions; the electrochemical oxidation of CO which produces CO_2 at the anode (reaction (9))



Moreover, the reversed Boudouard reaction with CO_2 and C as reactants and CO as a product (reaction (8)). It has been reported that for DC-SOFCs which conventional Ni-based anodes, the rate of the electrochemical oxidation of CO is several times lower than that of H_2 [16-19]. If the cell operates with reactions (8) and (9), then the cell performance should be improved by both of the reactions. While the rate of reaction (9) determines the cell performance directly, its reactant gas CO has to be provided by reaction (8), and also the reactant gas CO_2 of reaction (8) has to be provided by reaction (9). So, the two reactions are related closely in giving a satisfying cell performance.

Chemical modeling of Boudouard reaction in direct carbon fuel cell

In DCFC, reversed Boudouard reaction produces CO between the chemical reaction of carbon and CO_2 which strongly depends on operating temperature [20]. Since DCFC operating temperature is 973-1223 K, the CO production (reversed Boudouard reaction) should be considered. CO also can be produced by incomplete carbon oxidation (reaction (10)),



However, the carbon incomplete oxidation ratio in DCFC is unknown; therefore, in this model, the reversed Boudouard reaction is the only CO production reaction. The reversed Boudouard reaction rate is calculated by the chemical reaction model and can be written as [21]:

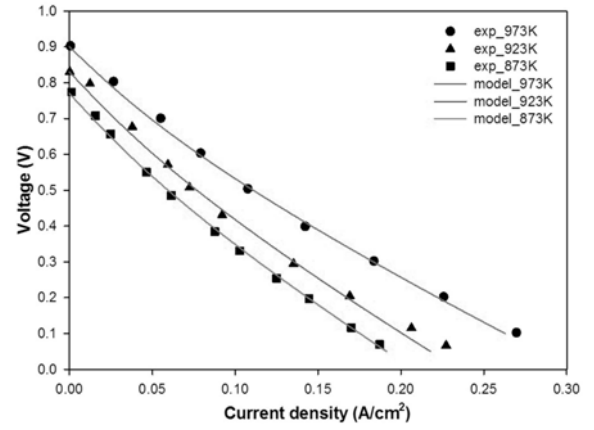
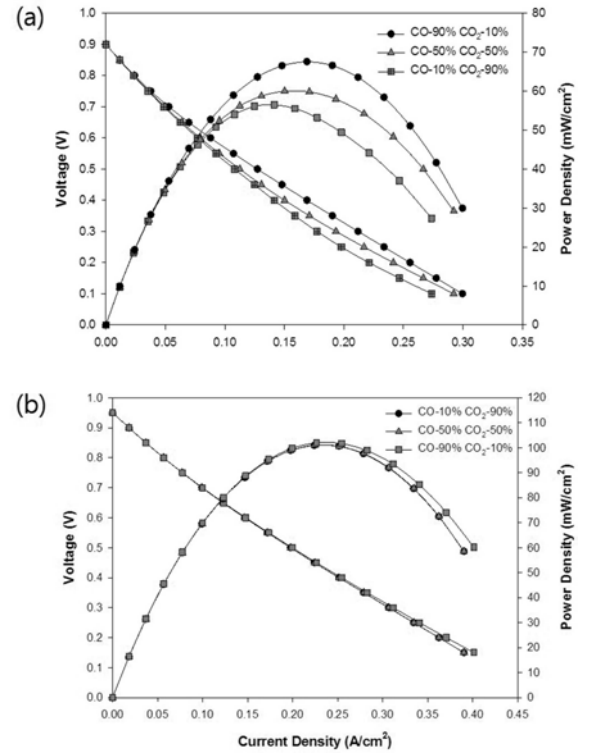
$$R_{rb} = k_{rb} \exp\left(\frac{-E_{rb}}{RT}\right) c_{\text{CO}_2} \quad (11)$$

Where R_{rb} is Boudouard reaction rate; k_{rb} is a frequency factor for the reversed Boudouard reaction; E_{rb} is activation energy of the reversed Boudouard reaction, and c_{CO_2} is molar concentration of CO_2 . The parameters for Boudouard reaction rate are described in Table 1.

Results and Discussion

Model validation

The electrochemical DCFC model was developed

**Fig. 2.** Model validation. I-V curve of DCFC model at 873 K, 923 K, and 973 K.**Fig. 3.** Various inlet gas proportion in DCFC and its performance (a) 973 K (b) 1023 K

based on the work of Elleuch et al. [23], and the input parameters and physical properties considered for the analysis are summarized in Table 3-3. The experimental data reported by Elleuch et al. [24] were compared with the developed simulation data, and as shown in Figure 3-5, the non-isothermal model at 873 K, 923 K, and 973 K was calculated, and they are in good agreement with experimental data.

Effect of reversed Boudouard reaction in DCFC

Fig. 3 shows the DCFC performance in various inlet gas compositions. Fig. 3(a) is the I-V curve of DCFC

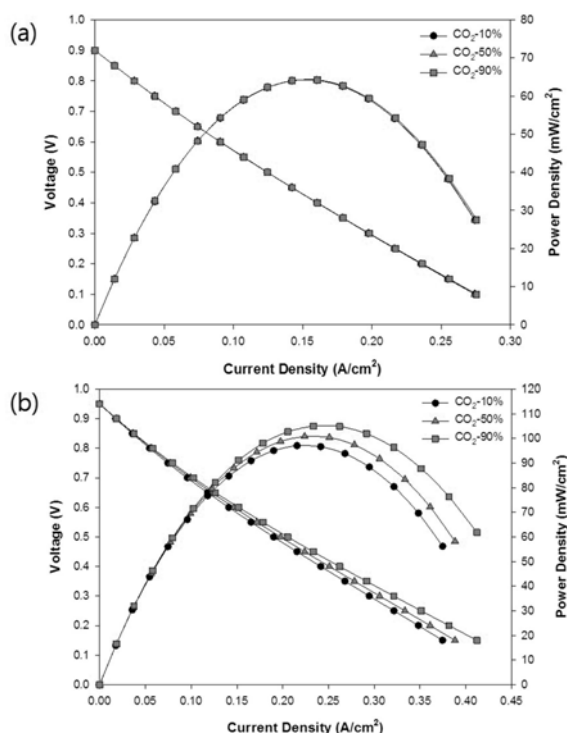


Fig. 4. Effect of reversed Boudouard reaction in DCFC (a) 973 K (b) 1023 K.

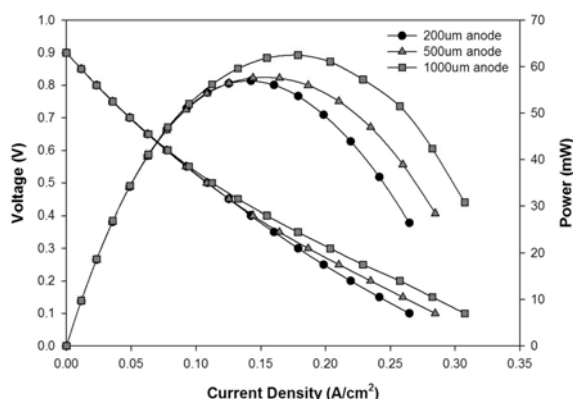


Fig. 5. Effect of reversed Boudouard reaction by various anode thickness in DCFC at 973 K.

at 973 K with different CO and CO₂ composition. As the model considers extra electrons by CO oxidation, inlet gas which contains 90% of CO gives the highest performance among other results. However, at 1023 K result, even though the inlet gas composition of CO and CO₂ varies from 10% to 90%, there is a small change in performance. To discover the effect of reversed Boudouard reaction on the overall cell performance, CO₂ inlet gas was considered independently, and the result shows in Fig. 4. Fig. 4(a) shows the result at 973 K, and since Boudouard reaction rate is influenced by operating temperature, the result at 973 K shows almost no difference with CO₂ composition change. However, at 1023 K (Fig. 4(b)), reversed Boudouard

reaction rate increases, and as a result, CO production increases and which leads the increase of cell performance.

Anode thickness and CO production in DCFC

Fig. 5 shows the DCFC cell performance in different anode thickness. As the anode thickness increases from 200 μm to 1000 μm, the cell performance increases. The reversed Boudouard reaction is a chemical reaction which is not related to the triple-phase boundary (TPB) but occurs through the anode zone. As anode thickness increases, the reversed Boudouard reaction zone increases, in conclusion, increases the amount of CO production. The produced CO by reversed Boudouard reaction oxidized at TPB and produces extra electrons which increases the overall cell performance.

Conclusions

In this study, a direct carbon fuel cell non-isothermal, the two-dimensional model was developed, and the reversed Boudouard reaction and the additional electrons by CO oxidation in the anode chamber was considered. To investigate the effect of reversed Boudouard reaction in DCFC, three different CO₂ conditions and two different operating temperatures at the anode chamber were considered. The result shows the higher the operating temperature is, the higher produced CO by reversed Boudouard reaction, and higher overall cell performance due to additional electrons by CO oxidation. We also investigate the anode thickness which affects the reversed Boudouard reaction zone, and the result shows the thicker the anode thickness is, the larger the CO production occurs. The DCFC technology is developing step so far but offers high efficiency and low cost of CO₂ capture which would be suitable for next-generation application from small systems to large centralized facilities.

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Nomenclature

A_V	active specific surface area, $\text{m}^2 \text{m}^{-3}$
C_i	molar concentration of species i, mol m^{-3}
D_{AB}	binary diffusivity coefficient of i and j, $\text{cm}^2 \text{s}^{-1}$
E_{rb}	activation energy of reversed Boudouard reaction, J
F	Faraday's constant, $96,485 \text{ C mol}^{-1}$
i	current density, A cm^{-2}
i_0	exchange current density, A cm^{-2}
$K_{\text{Boudouard}}$	Boudouard equilibrium constant
P	pressure, Pa
R	universal gas constant, $8.3145 \text{ J mol}^{-1} \text{K}^{-1}$
R_{rb}	Boudouard reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$
T	temperature, K

Greek symbols

α	transfer coefficient
η	overpotential, V

Subscripts

i	species i
j	species j