Modeling electrochemical resistance with coal surface properties in a direct carbon fuel cell based on molten carbonate

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HIGHLIGHTS

- Activation and ohmic polarization were modified by experimental results.
- The charge transfer was calculated by the surface oxygen groups.
- The electrolyte resistance takes into account Si concentration.
- The absolute average deviations were less than 10%.

ARTICLE INFO

ABSTRACT

In this study, a numerical model of activation and ohmic polarization is modified, taking into account the correlation function between surface properties and inner resistance. To investigate the correlation function, the surface properties of coal are changed by acid treatment, and the correlations between the inner resistance measured by half-cell tests and the surface characteristics are analyzed. A comparison between the model and experimental results demonstrates that the absolute average deviations for each fuel are less than 10%. The numerical results show that the sensitivities of the coal surface properties affecting polarization losses change depending on the operating temperature. The surface oxygen concentrations affect the activation polarization and the sensitivity decreased with increasing temperature. The surface ash of coal is an additional index to be considered along with ohmic polarization and it has the greatest effect on the surface properties at 973 K.

1. Introduction

The direct carbon fuel cell (DCFC) operates by using solid carbonaceous fuels, unlike the thermodynamic system dominated by the Carnot cycle. This fuel cell system directly converts the chemical energy of solid carbon into electrical energy [1]. The advantages of the DCFC are its higher efficiency and lower CO_2 emissions in comparison with existing power generation facilities. In addition, compared to other fuel cells that use gas fuel sources such as hydrogen and methane, the DCFC can use diverse fuels, such as coal, biomass, refuse fuel, and all kinds of hydrocarbons; these solid fuels have a high energy density in terms of both volumetric and mass density [2–4].

DCFCs are broadly divided into the molten carbonate DCFC, the solid oxide DCFC, and the hybrid DCFC [1]. The various DCFC systems have problems, which include low power density, poor fuel supply system, and low durability. To solve these problems caused by using solid carbon as a fuel, many researchers have conducted experimental and numerical research into DCFCs. Part of the DCFC research has presented anode mechanisms for the DCFC and DCFC modeling. Modeling research is a useful method to understand the reaction mechanism between the solid fuel, electrolyte, and electrode, and to improve the fuel cell system design. DCFC modeling researchers have been devoted to the study of comprehensive DCFC models. Zhang et al. [5] had established the numerical model of fluidized bed electrode DCFC. The activation polarization and ohmic polarization were more dominant the performance of the fluidized bed electrode DCFC than concentration polarization. The numerical model showed good agreement with experimental data until 700 A m^{-2}, while it showed large difference between measured data and numerically calculated data at high current density region.

Liu et al. [6] simulated the effect of packed-bed anode on DCFC cell performance. Low reactivity of graphite was caused by high anode activation polarization. Accordingly, one of the important parameters was the reaction rate of solid carbon with operating temperature. The

Nomenclature

A_{ct}	a constant related to charge-transfer resistance
A_s	a constant related to electrolyte resistance
B_{ct}	a constant related to charge-transfer resistance
B_s	a constant related to electrolyte resistance
c_{is}	concentration of species i at electrode surface (mol·m^{-3})
c_{ib}	concentration of species i at bulk (mol·m^{-3})
C_{so}	concentration of oxygen functional groups on the fuel surface ($0.03 < C_{so} < 0.181$)
C_s	concentration of silicon on the fuel surface ($0.07 < C_s < 0.11$)
D_i	diffusivity of dissolved gases i (m^2·s^{-1})
E_{cell}	cell voltage (V)
E_N	open-circuit voltage (V)
E_s	voltage at the electrode surface (V)
E_b	voltage in the bulk (V)
E^0	theoretical voltage (V)
F	Faraday's constant (C·mol^{-1})
G	Gibbs free energy (J)
H	enthalpy (J)
j	current density (A·m^{-2})
j_{lim}	limiting current density (A·m^{-2})
$j_{0,an}$	anode exchange current density (A·m^{-2})
$j_{0,cat}$	cathode exchange current density (A·m^{-2})
j_0^0	concentration-independent exchange current density (A·m^{-2})
K_i	solubility of dissolved gas i (mol·m^{-3}·atm^{-1})
n	number of electrical charge transfers in an electrochemical

	reaction (mol)
P	pressure in the gas phase (atm)
P_{CO2}	partial pressure of CO_2 in the gas phase (atm)
P_{O2}	partial pressure of O_2 in the gas phase (atm)
R	ideal gas constant (J·mol·K^{-1})
R_{ce}	resistance of all components except for anode (Ω·m^2)
R_{ct}	charge-transfer resistance (Ω·m^2)
R_s	electrolyte resistance (Ω·m^2)
S	entropy (J·K^{-1})
T	temperature (K)
α	apparent charge transfer coefficient
δ_{an}	thickness of anode (m)
δ_{cat}	thickness of cathode (m)
δ_e	thickness of the electrolyte in DCFC (m)
η_{act}	activation polarization (V)
η_{con}	concentration polarization (V)
η_{ohm}	ohmic polarization (V)
ν_e	stoichiometric coefficient of electrons
ν_i	stoichiometric coefficient of species i

Subscripts

act	activation
an	anode
cat	cathode
con	concentration
ct	charge transfer
lim	limit
ohm	ohmic

carbon particle size and height of the packed bed significantly affected cell performance, because these parameters were associated with the effective surface area and transportation path. Li et al. [7] simulated anode reaction in molten carbonate considering multiple-step of electrochemical reaction of graphite and carbon black. The structure and crystallite size of solid carbon had an influence on the electrochemical reactivity because of the fraction of active carbon. Alexander et al. [8] modeled the electrochemical reaction of carbon bed and validated experimental results of button cell. They demonstrated the relationship between cell geometry and performance and the trade-off between cell efficiency and power density in solid oxide DCFC. Zhang et al. [9] investigated a packed-bed anode DCFC with a molten carbonate electrolyte and graphite, and the polarization losses were expressed by electrode kinetics, ionic resistance of the cell components, and transportation of reactant and product. The real contact area between neighboring particles decreased due to the vertical gravitational force of a graphite particle moving from bottom to top, which increased the corresponding constriction resistance. In each slab on the anode, the ohmic polarization of the carbon phase was three times larger than that of the electrolyte phase.

The effect of gases from solid fuel was considered an important subject. Xu et al. [10] developed the 2D numerical model of cogeneration of CO and electricity in solid oxide DCFC and validated with Liu et al.'s experimental results [11]. Through the comparison of electrolyte-supported DCFC and anode-supported DCFC, the configuration affected to the characteristic of electrical power and CO generation. They also investigated the thermal behaviors with various operating condition and the gasification effect when H_2O and CO_2 were supplied in anode [12,13]. Elleuch et al. [14] investigated the effects of CO and CO_2 on theoretical potential using the thermodynamic equilibrium method. The results indicated that when the reaction of CO production (Boudouard reaction) was considered, the theoretical potential was higher than that in only CO_2 reactions, and the theoretical potential value increased as temperature increases. Chen et al. [15] established a

1D electrochemical reactor model in molten carbonate considering multiple electrochemical and chemical reactions. From the numerical analysis, the electrochemical mechanism of carbon was faster than the Boudouard reaction and the DCFC performance was restricted by the anode reaction and ohmic losses. In addition, the optimization of thickness of carbon bed was needed to improve carbon utilization because of carbon efficiency with distance from current collector.

Yu et al. [16] reported a solid oxide-DCFC model considering gasification and electrochemical reactions. The carbon gasification model was validated by experiment and the effect of carrier gas on cell performance was analyzed. The model that coupled gasification and electrochemical reactions showed that the physical properties such as bed height, char conversion, and fuel utilization affected cell performance. In addition, they experimentally investigated the effect of potassium salt which is catalyst of carbon gasification and proposed the reaction mechanism and kinetics data [17].

Even though there have been several modeling studies on the DCFC, most of them have considered pure solid carbon, such as graphite particles, carbon black, and activated carbon, because of the irregular properties of coal and biomass. Therefore, the surface properties of coal, which forms the triple-phase boundary between the electrode and the molten electrolyte, such as the presence of oxygen-functional groups, surface pores, and ash, were not considered in the simulation of anode polarization, even though each of these surface properties have been the focus of experimental research into the DCFC [18–20].

The objective of this study is to model the polarization losses of a DCFC considering the surface properties of fuel. For the comparison between electrochemical reactions and surface properties, bituminous coal and coal treated with HCl and HNO_3 were used as fuels. In order to reduce the effect of volatile matter on DCFC performance, bituminous coal with low volatility was selected rather than sub-bituminous coal or lignite coal. Fig. 1 shows the schematic diagram of the DCFC composed of two electrodes and molten carbonate electrolyte. As shown in Fig. 2, the resistances described in this paper are determined by an