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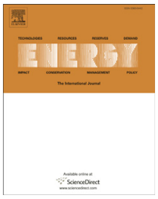

Performance analysis of a direct carbon fuel cell with molten carbonate electrolyte

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ABSTRACT

The model of a packed bed anode DCFC (direct carbon fuel cell) with molten carbonate as an electrolyte and graphite as a fuel is established to globally evaluate its performance. Thermodynamic-electrochemical analyses on the performance of the DCFC are implemented, in which the activation overpotential, ohmic overpotential, and concentration overpotential are taken as the main sources of voltage losses. The analytical expressions for the cell voltage, power output, efficiency, and entropy production rate are derived, from which the general performance characteristics are discussed in detail. At the anode, the ohmic overpotential in each slab resulting from the carbon phase is found to be about three orders of magnitude larger than that resulting from the electrolyte phase. The radius of the real contact area between two neighboring graphite particles decreases at an accelerating rate as one goes up in the bed, and the corresponding constriction resistance will increase at an accelerating rate. The decrease in the operating current density and anode dimension and the increase in the operating temperature will lessen the overall ohmic overpotential. The effects of the operating current density, operating temperature and anode dimension on the performance are discussed, and the optimum criteria for some important performance parameters are determined.

1. Introduction

Despite the growing concern about the increase in greenhouse gas emissions and climate change, coal will continue to be a significant source of energy for next several decades [1]. Nowadays, coal is mainly utilized by converting to electric power through coal-fired power plants, however, this method is not only a low-efficiency process, but also emits substantial amounts of greenhouse gases and pollutants, such NO_x, SO_x, etc. It is urgent to investigate a new and high-efficiency technology for coal to be used for power generation [2]. Fuel cell, can be fueled by gaseous, liquid, and even solid fuel, is regarded as a promising technology which will play an important role in the future low-carbon economy [3–6].

DCFC (direct carbon fuel cell) is an electrochemical device that directly converts the chemical energy of carbon into electricity, which has been considered as an alternative choice for coal utilization. DCFC has several unique attractive merits [7–9]: (1) it offers great thermodynamic advantages over other fuel cells as the theoretical thermal efficiency can be close to 100%; (2) the solid carbon fuel is easy for transport and storage and can be widely obtained from coal, coke, biomass, and even wastes; (3) DCFC releases lower emissions than coal-firing power plant and the conversion from carbon directly to carbon dioxide in DCFC may bring up a convenient pathway for CO_2 capture; (4) DCFC system is mechanically simple because no reformers or heat engines are required. DCFCs can be mainly classified into three types according to their electrolytes: molten hydroxide [10–12], molten carbonate [13–15], and solid oxide electrolyte DCFCs [2,16,17]. However, the DCFC with molten electrolytes (e.g., Li_2CO_3/K_2CO_3 eutectic melt) were found to be the most attractive approach, because the molten carbonates have high stability and electrical conductivity, low volatility and toxicity, and relatively low melting points [18].

Besides the studies on experimental test and cell prototype design [13,19–21], some important modeling and simulation studies on the molten carbonate electrolyte DCFC had been carried out. Liu et al. simulated the performance of a direct carbon fuel cell

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based on molten carbonate electrolyte by considering the electrochemical reaction dynamics, mass-transfer, and the electrode processes [22]. Li et al. examined the performance of a molten carbonate electrolyte DCFC by using carbon black and graphite as the fuels, and found that the charge transfer steps as well as the oxygen ion absorption steps are both important for the reaction rate [23]. Hemmes et al. studied the performance of a CO_2-producing DCFC system, a system efficiency of around 78% was obtained and the process responsible for the major exergy losses was determined by an exergy analysis [14]. However, further research is still necessary to deeply understand the performance characteristics of the DCFC based on molten carbonate electrolyte.

In this work, a theoretical model of a packed bed anode DCFC using molten carbonate as an electrolyte and graphite as a fuel is developed, in which multiple irreversible losses in electrochemical reactions such as activation overpotentials, ohmic overpotentials, and concentration overpotentials are considered. The variation with the position of the packed of the ohmic overpotential at the anode side bed will be showed in detail. Based on thermodynamic-electrochemical analysis, some performance parameters such as the cell potential, efficiency, power density, and entropy production rate are derived to reveal the general performance characteristics of the DCFC system. The effects of some operating conditions and design parameters on the performance of the DCFC will be discussed, and the optimum criteria for the performance parameters will be given.

2. A thermodynamic-electrochemical model

As illustrated in Fig. 1, the DCFC consists of a packed bed anode, a porous cathode, and a molten carbonate electrolyte sandwiched in between the two electrodes, where the anode, electrolyte, and cathode are made of graphite, Li_2CO_3/K_2CO_3 eutectic melt with a molar ratio of 32:68, and lithium doped NiO, respectively [22]. Graphite is fed to the anode in the form of solid carbon particles and get wetted with molten carbonate, and the spaces between the surrounding particles are occupied by the electrolyte. Each particle is assumed to act as a rigid sphere and packed with a simple hexagonal pattern. The height, length, and width of the packed bed anode are H, L, and W, respectively. The packed bed consists of several slabs of sphere carbon particles and the number of the slabs N_s depends on the bed height H and the diameter of the carbon particle D_c, i.e., $N_s = H/D_c$. Thus, the number of particles in each slab is $N_e = 1.14LW/D_c^2$ [24]. The possible anode and cathode electrochemical reactions in a DCFC may be as follows:

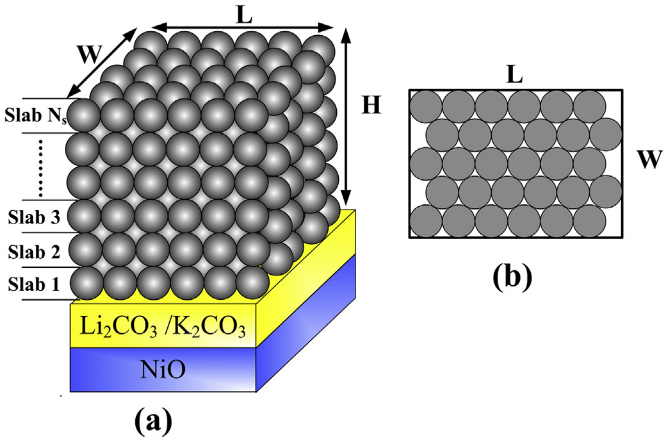

Fig. 1. (a) Schematic diagram of a packed bed anode DCFC with molten carbonate electrolyte, (b) top view of the packed bed anode.

$$\text{Anode}:\ C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^-, \tag{1a}$$

$$\text{Cathode}:\ O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}, \tag{1b}$$

or

$$\text{Anode}:\ C + CO_3^{2-} \rightarrow CO + CO_2 + 2e^-, \tag{1a$'$}$$

$$\text{Cathode}:\ O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}. \tag{1b$'$}$$

Thus, the overall cell reactions are:

$$C + O_2 \rightarrow CO_2 \tag{2}$$

or

$$C + 0.5O_2 \rightarrow CO. \tag{3}$$

Generally, the anode product gas will be a mixture of CO_2 and CO [15], and the ratio between CO_2 and CO in the mixture depends on thermodynamics (mainly temperature) and kinetics of the respective cell reactions. Although the Boudouard equilibrium (CO_2 + C ↔ CO) at the temperature of the DCFC (700–800 °C) predicts a certain amount of CO generation [14,25], it has been found that almost pure CO_2 was observed in the experiment [26]. According to the experimental results, the product of CO in the anode can be reasonably ignored, and thereby, reactions (1a′) and (3) are not considered in this work. The overall reaction (2) is exothermic, and the total energies released can be expressed as $-\Delta H = -\Delta G - T\Delta S$ [27], where $(-\Delta G)$ is the Gibbs free energy change of the reaction as the form of electrical energy, and $(-T\Delta S)$ represents the thermal energy part, T is the operating temperature, and ΔS is the entropy change of the reaction. Based on the data list in Table 1 [28,29], one can generate the curves of $(-\Delta H)$, $(-\Delta G)$, $(-T\Delta S)$ and $(\Delta G/\Delta H)$ varying with the operating temperature. As shown in Fig. 2, both the total energy $(-\Delta H)$ and the electrical energy $(-\Delta G)$ near-linearly decrease at a small slope with the increase of the operating temperature, and $(-\Delta H)$ is slightly larger than $(-\Delta G)$ as the $(-T\Delta S)$ can be assumed to be negligible with a large $(-\Delta G)$ or $(-\Delta H)$. The theoretical thermodynamic efficiency, $(\Delta G/\Delta H)$, almost keeps 100% in the typical operating temperature range of DCFC.

According to Faraday's law, the fuel consumption rate in the electrochemical reactions is determined by $\dot{q}_C = I/n_eF$, where n_e is the number of electrons transferred per mole graphite ($n_e = 4$), F is Faraday's constant, and I is the operating electric current of DCFC [27]. Therefore, the total energy released per unit time is given by

$$-\Delta\dot{H} = -\dot{q}_C\Delta h = -\frac{\Delta h}{n_eF}I, \tag{4}$$

where $(-\Delta h)$ is the molar enthalpy change which can be calculated from the data in Table 1.

Unlike the conventional fuel cells, DCFC exhibits minimal Nernst loss at the anode side of the cell as the electrochemical activity of a solid is independent of the amount of solid. The OCV (open circuit voltage) predicts that the maximum electrical potential can be obtained by reaction (2) with a specific temperature and gas concentrations and calculated by the Nernst equation [22], i.e.,

$$E = E_0 + \frac{RT}{n_eF}\ln\left[\frac{p_{O_2,\mathrm{cat}}\left(p_{CO_2,\mathrm{cat}}\right)^2}{p_{CO_2,\mathrm{an}}}\right], \tag{5}$$

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