Modeling of Molten Hydroxide Direct Carbon Fuel Cell – Effect of Carbonate Formation

Joseph R. Ortenero*, Cluadine D. Doma, Ron Joshua M. Rubin, Katherine Cecile Kristie Vida R. Reyes, Vergel C. Bungay

Department of Chemical Engineering, De La Salle University, 2401 Taft Ave, Manila 0922, Philippines
joseph.ortenero@dlsu.edu.ph

The utilization of energy continues to increase every year due to urbanization, population growth, and industrial activity. Conventional thermal power plants that operate on fossil fuels supply not less than 80 % of the world's primary energy. To lessen the dependence of humans on conventional energy sources that are heavy carbon dioxide emitters, alternative energy generation methods such as Direct Carbon Fuel Cells (DCFC) can be developed during the transition to renewable energy. Direct carbon fuel cells have high overall system efficiency. No fuel pre-treatment is needed, and the emitted CO_2 can be easily sequestered because it is concentrated and has high purity. However, the development of DCFC is still in its early stages, and further research must be done for DCFC to be available for commercial purposes. In this study, the effect of carbonate formation and reverse Boudouard reaction have been incorporated into the electrochemical model for molten hydroxide DCFC. The effect on the performance of the fuel cell is determined through the resulting power density and temperature profile. A power density of 0.0634 W/cm^2 can be obtained at a current density of 0.2 A/cm^2 from the power density curve. The voltage efficiency can be as high as 56 % at 923 K. The gas present in the anode may be considered to consist of only CO_2 due to negligible CO formation, while carbonate formation is significant. An electrochemical and transport model of DCFC is necessary to compensate for the shortcomings of experimental data. In addition, mathematical modeling could be used to complement experimental results in optimizing the performance of DCFC.

1. Introduction

The utilization of energy has increased over the past decades since humans have become more dependent on them (Fan et al., 2021). The rise in the demand for energy and power resulted in various challenges, such as serious environmental pollution, global warming, climate change, and depletion of global energy resources. To mitigate the impact of increasing consumption of fossil fuel on the environment, investment in alternative and renewable sources of energy, such as solar and wind, and conversion technologies, such as fuel cells, must be prioritized (Ortenero et al., 2022). Currently, there is still a massive reliance on coal, oil, and natural gas to meet the world's demand for energy (Russo et al., 2023). Conventional thermal power plants that operate by burning fossil fuels supply not less than 80 % of the world's primary energy (Song et al., 2020). These power plants, however, generate power with efficiency limited to only 40 % due to the Carnot cycle efficiency limit governing a thermodynamic system (Kacprzak et al., 2013). One of the main approaches for addressing the environmental impacts of energy-conversion systems is enhancing the system so that it can efficiently deliver energy from a source (Seferlis et al., 2021). Coal, a carbon-rich material, is forecasted to remain a major energy source for power production for many years (Badwal et al., 2017).

To lessen the dependence of humans on conventional energy production methods that may soon harm the environment significantly, alternative energy generation methods must be developed and utilized. These alternative energy generation methods aim to minimize the devastating effects of traditional power generation systems by improving efficiency and consequently reducing carbon dioxide emissions.

An alternative to traditional methods of energy generation is a fuel cell. A fuel cell is an electrochemical device that converts the chemical energy of a fuel into electricity through several electrochemical reactions. It has been

shown that fuel cell system efficiency can reach as high as 85 %, considering all the operations involved in the conversion of the fuel to electrical energy (Giddey et al., 2012). This is more than twice the efficiency of traditional power plants. Fuel cells transform stored chemical energy from fuels and oxides into useful electrical energy through redox reactions. It is not limited by the Carnot efficiency, which sets the limit to traditional power plants. A type of fuel cell, Direct Carbon Fuel Cell (DCFC), directly oxidizes carbon-rich materials into electricity, resulting in higher efficiency. The carbon dioxide emitted from the reactions can be easily sequestered without the use of expensive separation technology (Ozalp et al., 2022). However, the development of DCFC is still in its early stage, and further research must be done for DCFC to be available for commercial purposes. The study of Zecevic et al. (2004) developed a DCFC set-up using molten hydroxide in a humid atmosphere. Their findings suggest that molten hydroxide as an electrolyte can improve the ionic conductivity and reactivity towards carbon and can reduce the melting point of the mixture. However, their results also reported the unnecessary formation of carbonate in the products, causing chemical instability. Zecevic et al. (2004) discovered that an increase in the amount of water in the fuel cell results in a lower concentration of carbonate formation due to Le Chatelier's principle.

DCFCs in general, have been known for their extremely high theoretical efficiency and are regarded as one of the most efficient carbon-based processes for power generation (Ozalp et al., 2022). However, in scaling up and practical commercialization, engineering and process aspects need to be put into consideration, as well as the fundamental performance and behavior of both electrodes. Because of this, DCFC electrodes are modeled and optimized for the best observed electrochemical performance, as there are numerous alternative approaches to designing each electrode. A clear and accurate model, as well as an optimal design of the DCFC, will serve as the foundation for a commercial-scale power plant that utilizes the energy offered by these fuel cells (Elleuch et al., 2012).

Further analysis is required to improve the design of DCFC and optimize the different factors which contribute to the overall efficiency of the cell. Since this technology is still developing, only limited data are available on the design and optimum value of parameters critical to the operation of the DCFC. In addition, because DCFCs come in an array of types, depending on the electrolyte used, models for each variation must be developed to optimize it, as well as compare performance with other types of DCFC. Most existing DCFC models assume a molten carbonate electrolyte, leaving research gaps in the study and development of other electrolyte variations. In addition, problems such as carbonate formation in MHDCFC affect the performance of the cell. Theoretical modeling is necessary to understand the dynamics of carbonate formation for improved fuel cell performance. This study improves on the existing modeling study by considering the effect of carbonate formation on the performance of a molten hydroxide DCFC.

2. Direct Carbon Fuel Cell

Direct carbon fuel cell (DCFC) is an example of a special type of high-temperature fuel cell. DCFC resembles other high-temperature fuel cells, such as the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC), in terms of configuration and theoretical principles. It differs from MCFC and SOFC by the type of fuel that it uses. Solid carbon is directly fed into the anode compartment, where it will be electro-oxidized to carbon dioxide at high temperatures and produce electrical energy. The reaction is given by Eq(1):

$$C + 4OH^- \rightarrow CO_2 + 2H_2O + 4e^- \tag{1}$$

Being the only type of fuel cell that utilizes solid fuel, the DCFC possesses attractive features such as great thermodynamic advantages over other types of fuel cells. Both the reactant and products: carbon and carbon dioxide, exist as pure substances in separate phases. This property may allow the full conversion of the reactant and a theoretical fuel utilization efficiency of 100 %. This leads to a practical efficiency of around 80 %, making the DCFC potentially one of the most efficient systems in electrochemical power generation (Jiang et al., 2017). In addition, solid carbon-rich fuels in the form of coal, biomass, organic waste, etc., are both abundant and easy to obtain.

2.1 Molten Hydroxide DCFC

Molten hydroxide is a promising material due to its low melting point, high ionic conductivity, and high reactivity towards carbon. In a patented simple cell design that employs molten hydroxide electrolyte, a maximum current density of about 250 mA cm^{-2} and conversion efficiency not less than 60 % was achieved. Results of this study also showed that MHDCFC contains high water concentration, reduced carbonate formation, and increased ionic conductivity of the melt (Zecevic et al., 2005). At temperatures between 673 K and 723 K, maximum power and current density were achieved for DCFC with an equimolar mixture of NaOH – KOH in the electrolyte (Kacprzak et al., 2013). Xing et al. (2020) addressed the challenge of an increase in polarizations at low temperatures and scaled-up levels. However, the essential CO formation was not considered by the model. The

result of the model showed that ohmic polarization increased with an increase in fuel mass at low temperatures, while the increase in the active specific surface area from 100 to 1,500 m^2 reduced activation polarization (Xing et al., 2020).

MHDCFC relies on electrochemical reactions to generate energy from carbon, with the formation of CO_2 as a product. However, CO can also be found in the gas mixture. The presence of the compound can be explained by the Boudouard equilibrium reaction given by Eq(2):

$$2CO \rightleftharpoons CO_2 + C \tag{2}$$

It has been thoroughly researched that as the reaction is a function of temperature, a shift to the left, towards the side of carbon monoxide, occurs at high temperatures. It has been established that at temperatures above 700 °C, CO formation via reverse Boudouard reaction is vigorous, and at lower temperatures, CO is almost reduced to zero (Ido and Kawase, 2020). This is due to a large positive enthalpy of reaction of about 172 kJ mol^{-1} that does not favor the production of CO under ambient conditions but does so at high temperatures when the $-T\Delta S$ entropic term begins to dominate and produces a negative free energy (Ozalp et al., 2022).

The main drawback of DCFC using molten hydroxide in the electrolyte is the generation of carbonates. The chemical instability of the electrolyte offsets the mentioned advantages of using hydroxides and consequently reduces the cell performance and shortens the cell operation (Jiang et al., 2017). Hemmes and Cassir (2011) reported that carbonates are formed via the electrochemical reaction that takes place between hydroxide and carbon at the anode, as described in Eq(3).

$$C + 6OH^- \rightarrow CO_3{}^{2-} + 3H_2O + 4e^- \tag{3}$$

Only a few studies provided compelling results in trying to resolve the historical carbonate formation in MHDCFC.

3. Modelling of Molten Hydroxide DCFC

The following are the reactions that occur at the anode and cathode of a molten hydroxide DCFC in addition to Eq(1) to Eq(3).

$$2OH^- + CO_2 \rightarrow CO_3{}^{2-} + H_2O \tag{4}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{5}$$

The potential difference in the cell is defined as the open circuit voltage (OCV). The OCV is the cell operating voltage when there is no current flowing through the circuit (Xing et al., 2017). Specifically, for MHDCFC, OCV can be calculated using the Nernst equation shown in Eq(6),

$$E_N = E_0 + \frac{RT}{nF}\ln\left(\frac{P_{O_2}}{P_{CO_2}}\right) \tag{6}$$

where E_N is the OCV, E_0 is the OCV in the standard state, P_{O_2} is the pressure of O_2 in the cathode, P_{CO_2} is the pressure of CO_2 in the anode, R is the universal gas constant, T is the operating temperature, n is the number of electrons participating in the electrochemical reactions and F is the Faraday's constant.

The cell operating voltage when a current is flowing through the circuit is lower than the OCV due to the polarization losses. An expression to determine the cell operating voltage (V_{cell}) can be described in Eq(7).

$$V_{cell} = E_N - \eta_{ohm} - \eta_{act} - \eta_{conc} \tag{7}$$

where $\eta_{ohm}, \eta_{act}, \eta_{conc}$ are the ohmic, activation, and concentration polarizations.

The summary of the relationship between the different equations for electronic charge transport in anode and cathode is shown in Figure 1. The transport parameters were taken from the study of Song et al. (2020). The electronic charge transport constants and cell geometry parameters were taken from Xing et al. (2020).

A comparison of this work with recent studies on DCFC modelling in terms of the cell potential and power density at various current density values are given in Figure 2. Transport equations significantly affect the nonlinearity of cell potential at increasing current density. However, since other equations and base case parameters involving MHDCFCs were adopted from the study of Xing et al. (2017), and their DCFC type is the same for this model, the obtained values were closer to their model. Other MHDCFC studies, such as the model of Guo et al. (2014) using different carbonaceous fuels, validate the trend for decreasing the cell potential values up to 0.2 to 0.4 V between 0.1 to 0.2 A/cm². Experimental values obtained from Xing et al. (2017) showed higher degradation of cell potential compared to the obtained model values for the three models.
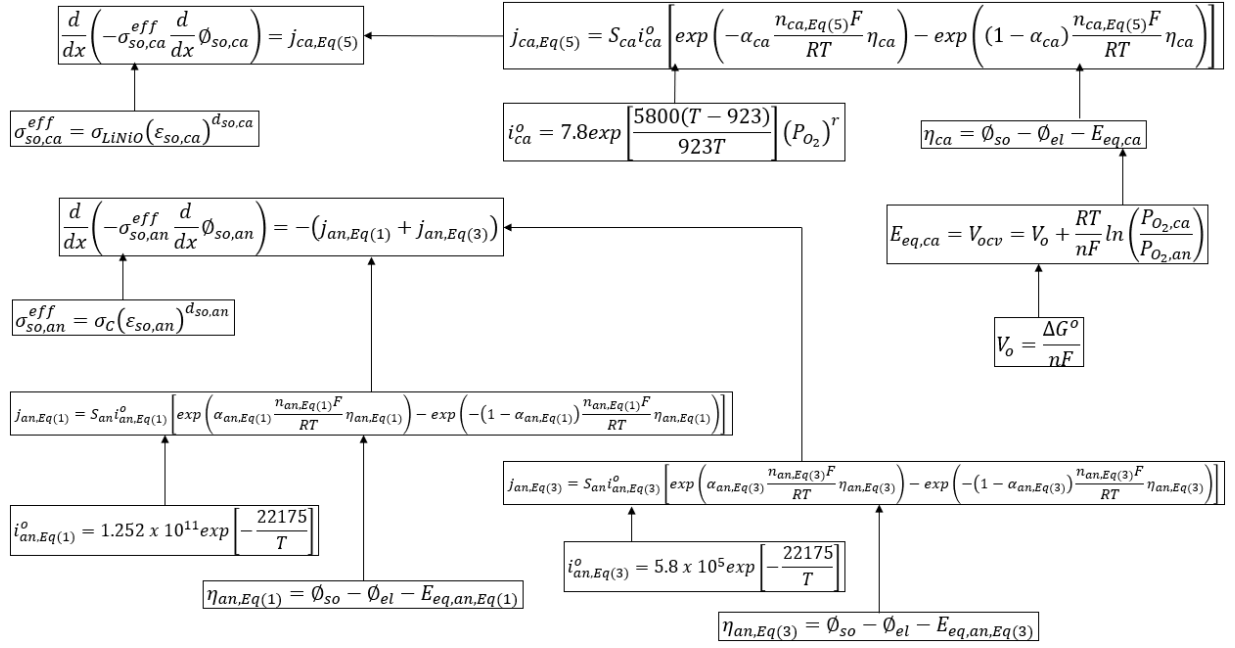
$$\frac{d}{dx}\left(-\sigma_{so,ca}^{eff}\frac{d}{dx}\emptyset_{so,ca}\right)=j_{ca,Eq(5)}$$

$$j_{ca,Eq(5)}=S_{ca}i_{ca}^{o}\left[exp\left(-\alpha_{ca}\frac{n_{ca,Eq(5)}F}{RT}\eta_{ca}\right)-exp\left((1-\alpha_{ca})\frac{n_{ca,Eq(5)}F}{RT}\eta_{ca}\right)\right]$$

$$\sigma_{so,ca}^{eff}=\sigma_{LiNiO}(\varepsilon_{so,ca})^{d_{so,ca}}$$

$$i_{ca}^{o}=7.8exp\left[\frac{5800(T-923)}{923T}\right](P_{O_2})^{r}$$

$$\eta_{ca}=\emptyset_{so}-\emptyset_{el}-E_{eq,ca}$$

$$\frac{d}{dx}\left(-\sigma_{so,an}^{eff}\frac{d}{dx}\emptyset_{so,an}\right)=-\left(j_{an,Eq(1)}+j_{an,Eq(3)}\right)$$

$$E_{eq,ca}=V_{ocv}=V_o+\frac{RT}{nF}ln\left(\frac{P_{O_2,ca}}{P_{O_2,an}}\right)$$

$$\sigma_{so,an}^{eff}=\sigma_C(\varepsilon_{so,an})^{d_{so,an}}$$

$$V_o=\frac{\Delta G^o}{nF}$$

$$j_{an,Eq(1)}=S_{an}i_{an,Eq(1)}^{o}\left[exp\left(\alpha_{an,Eq(1)}\frac{n_{an,Eq(1)}F}{RT}\eta_{an,Eq(1)}\right)-exp\left(-\left(1-\alpha_{an,Eq(1)}\right)\frac{n_{an,Eq(1)}F}{RT}\eta_{an,Eq(1)}\right)\right]$$

$$j_{an,Eq(3)}=S_{an}i_{an,Eq(3)}^{o}\left[exp\left(\alpha_{an,Eq(3)}\frac{n_{an,Eq(3)}F}{RT}\eta_{an,Eq(3)}\right)-exp\left(-\left(1-\alpha_{an,Eq(3)}\right)\frac{n_{an,Eq(3)}F}{RT}\eta_{an,Eq(3)}\right)\right]$$

$$i_{an,Eq(1)}^{o}=1.252\times10^{11}exp\left[-\frac{22175}{T}\right]$$

$$\eta_{an,Eq(1)}=\emptyset_{so}-\emptyset_{el}-E_{eq,an,Eq(1)}$$

$$i_{an,Eq(3)}^{o}=5.8\times10^{5}exp\left[-\frac{22175}{T}\right]$$

$$\eta_{an,Eq(3)}=\emptyset_{so}-\emptyset_{el}-E_{eq,an,Eq(3)}$$

Figure 1: Model equations for electronic charge transport in both cathode and anode

In this work, the power density of the fuel cell is also increasing at low current densities. This began to stabilize at 0.0634 W/cm^2, potentially going on a downward trend at high current densities. The observed maximum power density of this model is higher than the model of Xing et al. (2020) due to a lower surface area and oxygen flow rate. The maximum power density for this model was achieved at a higher current density compared to the work of Xing et al. (2017). Experimental values from Xing et al. (2017) observed significant deviations from model values.
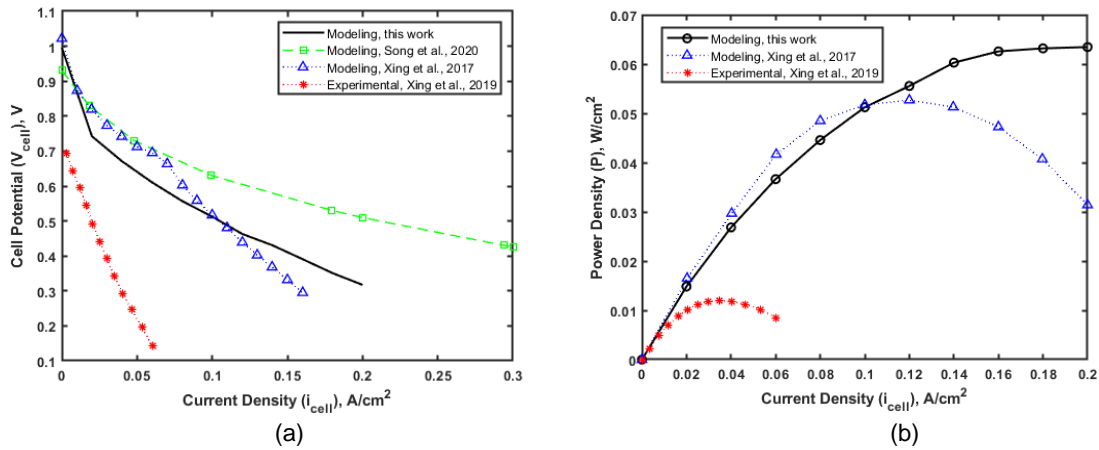

Figure 2: Comparison of results with other DCFC models and experimental value: (a) Cell potential (V) versus current density (A cm^{-2}) polarization curves; and (b) power density (W cm^{-2}) versus current density (A cm^{-2}) curves

The gas transport characteristics in a direct carbon fuel cell were investigated and are shown in Figure 3. This illustrates the partial pressures of gas species in both the cathode and the anode that are operating at a current density and temperature of 0.1 A/cm^2 and 923 K. The anode exhibits an increase in CO_2 partial pressure to the outer region accompanied by a corresponding decrease in CO partial pressure. This occurrence can be explained by the indication of the Bouduard reaction. On the other hand, in the cathode, the partial pressure of O_2 was only considered. In a DCFC operating with molten hydroxide electrolyte, the consideration of O_2 is crucial. The cathode is responsible for the reduction of oxygen through electrochemical reactions, which can be represented by the cathodic reaction seen in Eq(7). This is essential as it enables the supply of electrons

necessary for the electrochemical process and generation of electrical current. Its overall significance is due to its involvement in reduction reactions and the overall efficiency of the fuel cell. It can be observed in Figure 3b that the partial pressure decreased to the inner region. In comparison to the study of Song et al. (2020), the drop in partial pressures do not deviate from each other. This indicated that the gas transport within the cathode does not limit the performance of the direct carbon fuel cell.
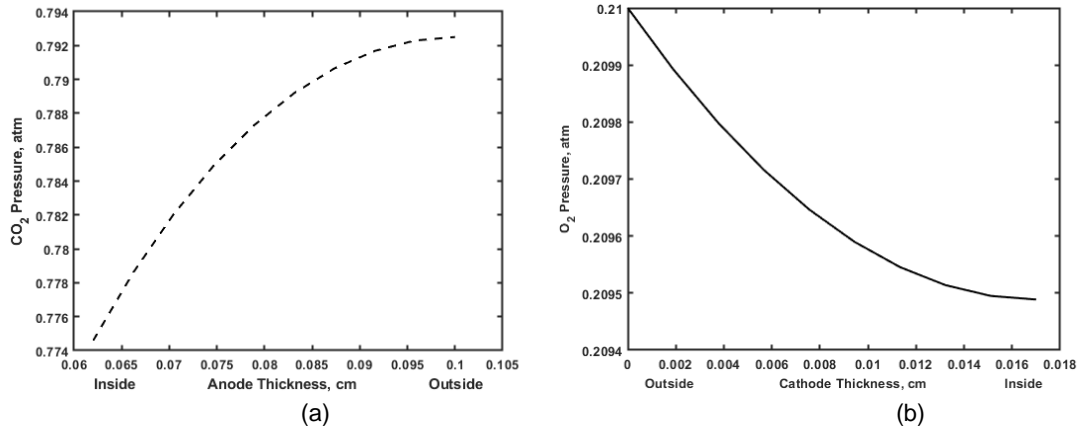
Figure 3: (a) Partial pressure of CO_2 along the thickness of anode at $i_{cell} = 0.1$ A/cm^2 and $T = 923K$ and (b) partial pressure of O_2 along the thickness of cathode at $i_{cell} = 0.1$ A/cm^2 and $T = 923$ K

Figure 4 illustrates the effect of temperature on the cathode overpotential of the fuel cell. These were determined using the Butler-Volmer equation. The overpotential in the anode is greater than that in the cathode. This indicates a high activation energy requirement for the oxidation reaction in the anode. At all temperatures, the increase in overpotential in the cathode is linear, while it is nonlinear for the anode. An increase in temperature observed at constant current density decreases the overpotentials for both the anode and the cathode. However, an increase in temperature may also favor the Boudouard reaction. An increase in temperature uniformly decreases the anode overpotential, while the cathode overpotential decreases unevenly.
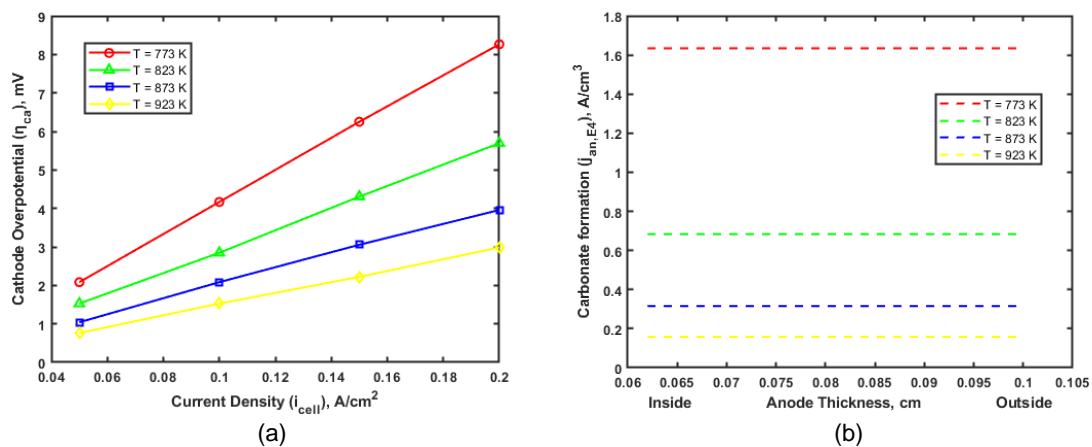

Figure 4: (a) Cathode overpotential with various cell current densities, and (b) rate of carbonate formation at $i_{cell} = 0.1$ A/cm^2

The relationship between carbonate formation and anode thickness is influenced by several factors. The distribution of reactants and products within the cell and the significance of the anode thickness affect the overall cell performance and carbonate formation. Figure 4b shows the different carbonate formations at varying temperatures. At 773 K, the carbonate formation is approximately 1.65 A/cm^3, at 823K is 0.69 A/cm^3, at 873 K is 0.3 A/cm^3, and 923 K is 0.17 A/cm^3. For the decrease in carbonate formation with increasing temperature this is influenced by factors such as the shift in Boudouard reaction towards CO and CO_2 productions instead of carbonate species that become evident at higher temperatures, enhanced hydroxide ions presence promoting

direct carbon oxidation, increased ionic conductivity facilitating the migration of carbonate ions away from the anode region, and accelerated electrochemical kinetics reducing the relative contribution of carbonate formation.

4. Conclusions

The demand for energy has led to environmental challenges associated with conventional power generation. To address these issues, alternative energy generation methods like fuel cells, particularly direct carbon fuel cells (DCFCs), offer higher efficiency and reduced carbon emissions. Further research is needed to optimize the design and performance of molten hydroxide DCFCs, especially in terms of carbonate formation. Results of this study showed that by applying the base case configurations and a 923 K temperature, the cell voltage of the modeled MHDCFC follows a nonlinear trend which agrees with the work of Song et al. (2020). The maximum power density for this study is 0.0634 W/cm^2, greater than the obtained maximum power density of Xing et al. (2017) at the same temperature. The Boudouard reaction can be observed at a minimum temperature of 600 C (873 K). The Boudouard reaction rate significantly increased as the temperature increased from 873 K to 973 K. For the carbonate formation reaction rate, increasing the operating temperature decreased the carbonate formation reaction rate due to the dominance of the Boudouard reaction at higher temperatures. Minimizing carbonate formation effects recommend the presence of sufficient water in the fuel cell to favor the reactants in Eq (3) due to Le Chatelier's principle. The unwanted Boudouard reaction may be minimized by controlling the operating temperature of the fuel cell, using high-quality materials, and by utilizing the high purity of the fuel.

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