



Fuel Cell for Production of Electric Energy with Carbon Dioxide as One of the Cell Reactants

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ARTICLE INFO	ABSTRACT
Published Online: 12 December 2025	An electrochemical system; utilizing the sodium in the molten state, and carbon dioxide and oxygen gas mixture as the reactant species; to produce electrical energy has been formulated to predict the standard-state open-circuit voltage as a function of the cell temperature. The cell open-circuit voltage as a function of temperature can be predicted for the non-standard states of the species taking part in the overall cell reaction. In addition, the developed formulation is capable of predicting the following: The cell operational voltage, electric power density, and efficiency of the cell to deliver electric power density as a function of the cell geometric current density: For the case of the cell operation as a batch electrochemical reactor, the provided formulation can predict the open-circuit cell voltage as a function of the cell temperature, pressure, the overall reaction extent and the initial composition of the cell cathode-side reactant mixture. The rates of the reactant-species consumption and product-species production can also be predicted at a given cell geometric current density. Some examples of the computed data presented in the form of plots are given below. (1) The cell open-circuit voltage decreases from 3.26 to 2.95 volt for the increase in the cell temperature from 100 to 300°C. (2) For the cell with the solid electrolyte (sodium beta-alumina solid electrolyte) of 10μm thickness, the decrease in the cell operational voltage is of the order of 3mV at 200°C for the cell current range of 10 to 100 mA $\cdot$ cm$_{geom}^{-2}$. (3) At the cell temperature of 200°C, $\frac{P}{P_0} = 4$, the electric power density increases from about 0.033 to 0.327 W $\cdot$ cm^{-2} over the geometric current range of 10 to 100 mA $\cdot$ cm$_{geom}^{-2}$. (4) The efficiency to deliver electric power ranges from 99.98 to 99.80 over the geometric current density of range of 10 to 100 mA $\cdot$ cm$_{geom}^{-2}$ for the cell with the solid electrolyte thickness of 10μm at 200°C and $\frac{P}{P_0} = 4$.
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1. INTRODUCTION

The analyses and developments of the electrochemical systems have been carried out here at the University of Dayton since 1989 [some typical references: 1-7]. Very recently, we decided to develop a fuel cell, using carbon dioxide gas as one of the cell reactants, to generate electric power. Our current effort is focused on the development of a fuel cell system for applications in the space vehicle systems. Such fuel cell systems can take carbon dioxide from the combustion exhaust gas mixture discharged from the

combustor of a space vehicle coupled with the fuel cell. Carbon dioxide or its mixture with oxygen gas would react with the fuel cell anode-side reactant sodium in the molten state to generate electric power. This power coupled with the supersonic power of a space vehicle system is expected to result in the hypersonic speed.

On the Earth's surface, such a system can be utilized simultaneously to generate electric power and reduce the concentration levels of carbon dioxide (one of the global warming gases) from the ambient atmospheric air. Sodium

supply relative to that of lithium is unlimited [8]. Also, sodium is cheaper than lithium. Furthermore, the cell reaction product sodium carbonate is a valuable product, especially,

used in making soaps and chemicals, in cleaning and bleaching, etc. Figure 1 shows the sketch of the fuel cell system intended to be developed.

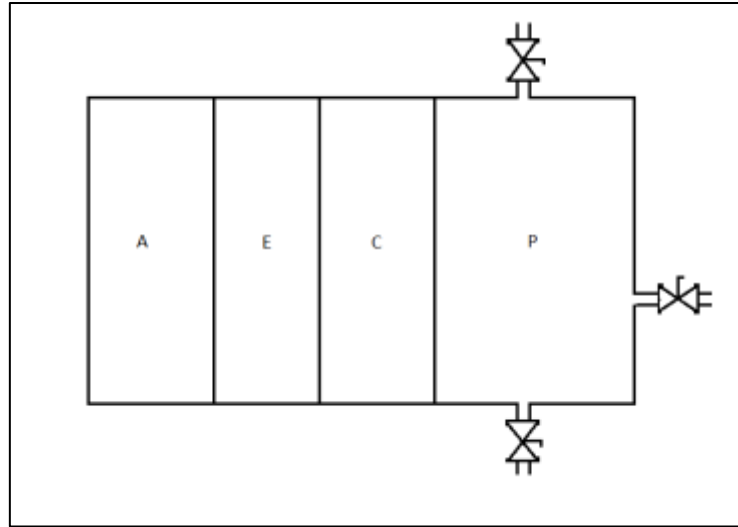


Figure 1: Sodium/carbon dioxide-oxygen gas mixture fuel cell (the sketch not to a scale).

The main components of the fuel cell sketched above are:

A (anode): Sodium as the fuel cell anode-side reactant in the liquid phase; sodium melting point = 97.8 °C and boiling point = 883 °C.

E (electrolyte): Sodium beta-alumina solid electrolyte (Na-BASE), $\text{Na-}\beta''\text{Al}_2\text{O}_3(\text{s})$.

C (cathode): Sputtered gold (Au) layer film on a thin microporous nickel foam layer. The cell cathode-side reactant: gas mixture of carbon dioxide and oxygen for example.

P (plenum): Cell cathode – side plenum for holding a gaseous reactant or a gaseous reactant mixture. Configured for a

reactant gas or gas-mixture flow parallel, or perpendicular to porous interface between the cathode and plenum as well as for the stagnant flow conditions.

The fuel cell system sketched in Figure 1, must be experimentally characterized with respect to its electrochemical performance for the initial investigation over the operational conditions of: Temperature range: 25 – 300 °C; the cell cathode-side reactant gas mixture pressure range: 1 – 5 bar; the reaction stoichiometric and non – stoichiometric compositions of carbon dioxide and oxygen gas mixture; and the cell geometric current density range: 10 – 100 $\text{mA} \cdot \text{cm}_{geom}^{-2}$.

2. FORMULATION

The overall cell reaction is:



$$\nu_{\text{Na}} = -2, \nu_{\text{CO}_{2(g)}} = -1, \nu_{\text{O}_{2(g)}} = -0.5, \nu_{\text{Na}_2\text{CO}_{3(s)}} = 1.$$

Per mole of reaction, Equation (2-1), occurring, the charge involved is: $nF = 2F \text{ coulombs}$; where F (called the Faraday constant) = 96487.00 [$\text{coulombs} \cdot (\text{g} - \text{equivalent})^{-1}$]. For the occurrence of the above reaction in the forward direction at the reference temperature of $T_0 = 298.15 \text{ K}$; the standard – state enthalpy and Gibbs – free energy changes are given as follows by Equation (2-2) and (2-3), respectively,

$$\Delta H_0^o = \Delta H_{f,\text{Na}_2\text{CO}_{3(s)},T_0}^o - \left(2\Delta H_{f,\text{Na}_{(l)},T_0}^o + \Delta H_{f,\text{CO}_{2(g)},T_0}^o + 0.5\Delta H_{f,\text{O}_{2(g)},T_0}^o \right) \quad (2-2)$$

$$\Delta G_0^o = \Delta G_{f,\text{Na}_2\text{CO}_{3(s)},T_0}^o - \left(2\Delta G_{f,\text{Na}_{(l)},T_0}^o + \Delta G_{f,\text{CO}_{2(g)},T_0}^o + 0.5\Delta G_{f,\text{O}_{2(g)},T_0}^o \right) \quad (2-3)$$

The Gibbs free energy change for occurrence of reaction (2-1) in the net forward direction with the chemical species in their respective standard states at the cell temperature, $T[\text{K}]$, is given as:

$$\Delta G_{\text{reaction},T}^o = \Delta H_0^o - (\Delta H_0^o - \Delta G_0^o) \left(\frac{T}{T_0} \right) \quad (2-4)$$

The cell standard open – circuit voltage at temperature, $T[\text{K}]$, is given by:

$$E_T^o = \frac{(-\Delta G_{\text{reaction},T}^o)}{nF} = \frac{(-\Delta H_0^o + (\Delta H_0^o - \Delta G_0^o) \frac{T}{T_0})}{nF} \quad (2-5)$$

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For the cell operation at $T[K]$ with the chemical species involved in it, not in their respective standard states, the Gibbs free energy change, $\Delta G_{reaction,T}$, is given by:

$$\Delta G_{reaction,T} = \Delta G_{reaction,T}^o + RT \ln \left[\prod_i a_i^{v_i} \right] \quad (2-6)$$

where $R = 8.314 \text{ (J} - \text{mol}^{-1} - \text{K}^{-1})$ = the universal – gas constant, $\hat{a}_i$ = activity of a chemical species i taking part in the cell reaction, Equation (2-1), and v_i = stoichiometric number of species i in the cell reaction, Equation (2-1); v_i is a negative value for a reactant species being consumed and a positive number value for a product species being generated. The term $\left[\prod_i a_i^{v_i} \right]$ represents the product of $[(\hat{a}_i^{v_i})]$ factor over all species (i) taking part in reaction,

Equation (2-1).

It is well known that:

$$\Delta G_{reaction,T} = [-nFE_T] \quad (2-7)$$

$$\text{Therefore, } E_T = \left(\frac{-\Delta G_{reaction,T}}{nF} \right)$$

Inserting the information from Equation (2-6) into the above equation and simplifying,

$$E_T = \left(\frac{-\Delta G_{reaction,T}^o}{nF} \right) - \left(\frac{RT}{nF} \right) \ln \left[\prod_i a_i^{v_i} \right] \quad (2-8)$$

Or

$$E_T = E_T^o - \left(\frac{RT}{nF} \right) \ln \left[\prod_i a_i^{v_i} \right] \quad (2-9)$$

where $\hat{a}_i$ = activity of a species i to account for its non – ideal thermodynamic behavior. For the chemical species taking part in the overall cell reaction, Equation (2-1),

$\hat{a}_{Na(s \text{ or } l)} = 1$, $\hat{a}_{Na_2CO_3(s)} = 1$ (pure chemical species); for a species i in a gas phase mixture

$$\hat{a}_{i(g)} = \left(\hat{\phi}_i \frac{p_i}{p^o} \right) = \left(\frac{\hat{\phi}_i y_i P}{p^o} \right) \quad (2-10)$$

Here p_i , y_i = partial pressure and mole fraction of a species i , respectively; P, P^o = gas mixture pressure and standard-state pressure of P^o (= 1 bar); and $\hat{\phi}_i = \hat{\phi}_i(T, y_i, P)$, fugacity coefficient of a gas species i to account for its non-ideal gas behavior. For a gaseous species i in a gas mixture following ideal gas behavior at the mixture temperature and pressure conditions, $\hat{\phi}_i = 1$. Then

$$\hat{a}_{i(ideal \text{ gas})} = \left(\frac{y_i P}{p^o} \right) \quad (2-11)$$

Generally, activity of a chemical species i in a solid homogenous phase mixture is given as:

$$a_i = a_{i(s)} = \gamma_{i(s)} \quad (2-12)$$

where x_i = mole fraction of a species i in the solid-phase mixture and $\gamma_{i(s)} = \gamma_{i(s)}(x_i, T)$ = activity coefficient of a species i in a solid phase mixture to account for its non-ideal behavior. For the ideal solid phase mixture behavior, $\gamma_{i(s)} = 1.0$. For a pure solid-state species, i , $\gamma_{i(s)} = 1.0$. It is also noted that $\gamma_{i(s)}$ is a weak function of pressure.

Activity of a chemical species i in a liquid phase mixture following non-ideal solution behavior is given as:

$$a_i = a_{i(l)} = \gamma_{i(l)} \left(\frac{f_i}{f_i^0} \right), \quad (2-13)$$

where x_i = mole fraction of a species i in a liquid solution mixture; $\gamma_{i(l)} = [\gamma_{i(l)}(T, x_i)]$ = activity coefficient of a species i in a liquid-phase solution mixture to account for its non-ideal energetic interaction behavior in a non-ideal solution mixture; generally, it is a weak function of pressure.

$$\left(\frac{f_i}{f_i^0} \right) = \left(\frac{\text{pure liquid } i \text{ fugacity at the liquid mixture temperature and pressure}}{\text{pure liquid } i \text{ fugacity at the liquid mixture temperature and pressure of } (P^o=1 \text{ bar})} \right) \quad (2-14)$$

This $\left(\frac{f_i}{f_i^0} \right)$ is given by:

$$\frac{f_i}{f_i^0} = e^{\left(\frac{\int_{P^0}^P V_{i(l)} dP}{RT} \right)} \quad (2-15)$$

The exponential in Equation (2-15) is known as a Poynting factor. $V_{i(l)}$ = the liquid-phase molar volume of species i; it is a very weak function of pressure at temperatures well below the critical state temperature, $T_{c,i}$, of a species i. With $V_{i(l)}$ at $P^0 = 1$ bar and mixture temperature, Eq. (2-15), leads to:

$$\left(\frac{f_i}{f_i^0} \right) = e^{\left(\frac{V_{i(l)}(P-P^0)}{RT} \right)} \quad (2-16)$$

From Equations (2-13) and (2-16), the following equation is obtained:

$$\hat{a}_i = \gamma_{i(l)} x_i e^{\left(\frac{V_{i(l)}(P-P^0)}{RT} \right)} \quad (2-17)$$

Except for high pressures, the exponential term is close to unity. Then, Equation (2-17) becomes:

$$a_i = a_{i(l)} = \gamma_{i(l)} x_i \quad (2-18)$$

If the liquid-phase mixture composition is in terms of molar concentrations; then, the activity of a species i is given by:

$$\hat{a}_{i(l)} = \left[\frac{\gamma_{i,c} \cdot c_i}{c_{i(l)}^0} \right] \quad (2-19)$$

where $c_{i(l)}$ = molar concentration of species i in a liquid-phase mixture and $c_{i(l)}^0$ = molar concentration = $[1 \text{ mol} - (\text{liter})^{-1}]$ and $\gamma_{i,c}$ = activity co-efficient of a species i in a non-ideal solution mixture = $\gamma_{i,c}(T, c_{i(l)})$.

$\gamma_{i,c}$ is a very weak function of pressure. For the ideal solution behavior, $\gamma_{i,c} = 1$, and Equation (2-19) leads to:

$$\hat{a}_{i(l)} = \frac{c_{i(l)}}{c_{i(l)}^0} \quad (2-20)$$

Application of Equation (2-9) to the overall cell reaction, Equation (2-1) leads to:

$$E_T = E_T^0 - \left(\frac{RT}{2F} \right) \ln \left[a_{Na}^{-2} \times (\hat{a}_{CO_2(g)})^{-1} \times (\hat{a}_{O_2(g)})^{-0.5} \times (a_{Na_2CO_3(s)})^1 \right]$$

Here, $a_{Na} = 1$, $a_{Na_2CO_3(s)} = 1$; then, the above equation becomes:

$$E_T = E_T^0 - \left(\frac{RT}{2F} \right) \ln \left[\frac{1}{\hat{a}_{CO_2(g)} \cdot \hat{a}_{O_2(g)}^{0.5}} \right], \quad (2-21)$$

$$\text{where } \hat{a}_{CO_2(g)} = \left(\frac{\hat{\phi}_{CO_2(g)} \cdot y_{CO_2(g)} \cdot P}{P^0} \right) = \left[\hat{\phi}_{CO_2(g)} \cdot y_{CO_2(g)} \cdot \left(\frac{P}{P^0} \right) \right],$$

$$\hat{a}_{O_2(g)} = \left[\hat{\phi}_{O_2(g)} \cdot y_{O_2(g)} \cdot \frac{P}{P^0} \right]. \text{ Inserting this information into Equation (2-21) and simplifying, the following expression is obtained.}$$

$$E_T = E_T^0 - \left(\frac{RT}{2F} \right) \ln \left[\frac{1}{\left(\hat{\phi}_{CO_2(g)} \cdot y_{CO_2(g)} \cdot \sqrt{\hat{\phi}_{O_2(g)}} \right) \left(y_{CO_2(g)} \cdot y_{O_2(g)} \right) \left(\frac{P}{P^0} \right)^{1.5}} \right] \quad (2-22)$$

For the gas mixture of $CO_2(g)$ and $O_2(g)$ for the cell cathode-side pressure of 5 bar or less, it is assumed that $\hat{\phi}_{CO_2(g)} = \hat{\phi}_{O_2(g)} = 1$. Equation (2-22), then, leads to:

$$E_T = E_T^0 - \left(\frac{RT}{2F} \right) \ln \left[\frac{1}{y_{CO_2(g)} \cdot y_{O_2(g)}^{0.5} \cdot \left(\frac{P}{P^0} \right)^{1.5}} \right] \quad (2-23)$$

Further simplification of Equation (2-23) leads to:

$$E_T = E_T^0 + 1.5 \left(\frac{RT}{2F} \right) \ln \left(\frac{P}{P^0} \right) + \left(\frac{RT}{2F} \right) \left[\ln y_{CO_2} + 0.5 \ln y_{O_2(g)} \right], (volt) \quad (2-24)$$

where $F = 96487 \text{ coulombs per } g - \text{equivalent}$.

For the case of the cell operation as a batch reactor with respect to the cathode side reactant mixture of $CO_2(g)$ and $O_2(g)$ initially fed to the cell plenum in batch-form; it is interesting to relate the changes in the moles of species taking part in the overall cell

reaction, Equation (2-1), and also, relate the species mole fractions to a simple variable, ξ (called the reaction extent). The reaction extent, ξ , of the reaction, Equation (2-1), is a measure of progress of its occurrence towards right. A definition of $d\xi$ is given by the following equation for the reaction, Equation (2-1):

$$\frac{dn_{Na}}{V_{Na}} = \frac{dn_{CO_2(g)}}{V_{CO_2(g)}} = \frac{dn_{O_2(g)}}{V_{O_2(g)}} = \frac{dn_{Na_2CO_3(s)}}{V_{Na_2CO_3(s)}} = \dots = \frac{dn_i}{V_i} = \dots = d\xi \quad (2-25)$$

For any species i taking part in the overall cell reaction;

$$dn_i = v_i \cdot d\xi \quad (i = Na_{(s \text{ or } l)}, CO_2(g), O_2(g) \text{ and } Na_2CO_3(s)). \quad (2-26)$$

Corresponding to the initial amounts, ' $\xi' = 0$, and ' $\xi' = \xi$ ' corresponding to an arbitrary extent of the reaction, Equation (2.1).

Integrating, (2-26)

$$\int_{n_{i,0}}^{n_i} dn_i = \int_0^{\xi} v_i d\xi \quad (2-27)$$

$$(n_i - n_{i,0}) = v_i \xi \quad (2-28)$$

$$\text{Therefore, } n_i = (n_{i,0} + v_i \xi), \text{ (moles) of species } i. \quad (2-29)$$

For $Na_{(s)} \text{ or } (l)$ and $Na_2CO_3(s)$,

$$n_{Na_{(s)} \text{ or } (l)} = (n_{Na_{(s),0}} - 2\xi), \text{ (moles)}, \quad (2-30)$$

$$n_{Na_2CO_3(s)} = n_{Na_2CO_3(s),0} + \xi = 0 + \xi = \xi, \text{ (moles)}, \quad (2-31)$$

$$n_{CO_2(g)} = n_{CO_2(g),0} - \xi, \text{ (moles)}, \text{ and} \quad (2-32)$$

$$n_{O_2(g)} = n_{O_2(g),0} - 0.5\xi, \text{ (moles)}. \quad (2-33)$$

At the reaction extent level of ξ , total gas mixture moles in the plenum,

$$n_{total(gas)} = (n_{CO_2(g)} + n_{O_2(g)}) = (n_{CO_2(g),0} + n_{O_2(g),0} - 1.5\xi), \text{ (moles)} \quad (2-34)$$

Or,

$$n_{total(g)} = (n_{total(g),0} - 1.5\xi), \text{ (moles)} \quad (2-35)$$

where

$$n_{total(g),0} = (n_{CO_2(g),0} + n_{O_2(g),0}) = \left(\begin{array}{c} \text{sum of the gaseous reactant species} \\ \text{in the initial} \\ \text{feed mixture in the cell plenum} \end{array} \right), \text{ (moles)} \quad (2-36)$$

Carbon dioxide and oxygen mole fractions, at the reaction extent of ξ , are given as:

$$y_{CO_2(g)} = \frac{n_{CO_2(g)}}{n_{total(g)}} = \frac{n_{CO_2(g),0} - \xi}{n_{total(g),0} - 1.5\xi}, \quad (2-37)$$

$$\text{and } y_{O_2(g)} = \frac{n_{O_2(g)}}{n_{total(g)}} = \frac{n_{O_2(g),0} - 0.5\xi}{n_{total(g),0} - 1.5\xi} \quad (2-38)$$

Equations (2-37) and (2-38) can also be expressed as:

$$y_{CO_2(g)} = \left[\frac{y_{CO_2(g),0} - \left(\frac{\xi}{n_{total(g),0}} \right)}{1 - 1.5 \left(\frac{\xi}{n_{total(g),0}} \right)} \right] \quad (2-39)$$

$$y_{O_2(g)} = \left[\frac{y_{O_2(g),0} - 0.5 \left(\frac{\xi}{n_{total(g),0}} \right)}{1 - 1.5 \left(\frac{\xi}{n_{total(g),0}} \right)} \right] \quad (2-40)$$

Now, a modified reaction extent, ξ_{mod} , is defined as:

$$\xi_{mod} = \left(\frac{\xi}{n_{total(g),0}} \right) \quad (2-41)$$

Equations (2-39) and (2-40) reduce to the following forms,

$$y_{CO_2(g)} = \frac{y_{CO_2(g),0}^{-\xi_{mod}}}{1-1.5\xi_{mod}}, \quad (2-42)$$

$$y_{O_2(g)} = \frac{y_{O_2(g),0}^{-0.5\xi_{mod}}}{1-1.5\xi_{mod}}. \quad (2-43)$$

Putting, for $n_{total(g),0} = 1 \text{ mole of } (CO_{2(g)} \text{ and } O_{2(g)})$ in initial mixture,

$$\xi_{mod} = \xi.$$

Inserting the information for $y_{CO_2(g)}$ and $y_{O_2(g)}$ from Equations (2-42) and (2-43), respectively into Equation (2-24) and simplifying leads to:

$$E_T = E_T^0 + 1.5 \left(\frac{RT}{2F} \right) \ln \left(\frac{P}{P^0} \right) + \left(\frac{RT}{2F} \right) \ln \left[\frac{(y_{CO_2(g),0}^{-\xi_{mod}})(y_{O_2(g),0}^{-0.5\xi_{mod}})^{0.5}}{(1-1.5\xi_{mod})^{1.5}} \right], (volt) \quad (2-44)$$

It is here noted that the expression within the square brackets, [], is a function only of ξ_{mod} . For the application of Equation (2-44) at any cell temperature and pressure conditions, the modified reaction extent, ξ_{mod} , must be such that it is less than $y_{CO_2(g),0}$; as well as $(0.5\xi_{mod})$ less than $y_{O_2(g),0}$ and $(1.5\xi_{mod})$ less than 1.

Sodium ionic conductivity in the solid electrolyte, sodium beta-alumina solid electrolyte (Na-BASE), $Na - \beta''Al_2O_{3(s)}$, at a temperature, $T[K]$, is given by:

$$\sigma_{Na^+,T} = \sigma_{Na^+,T_0} \cdot \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (2-45)$$

where σ_{Na^+,T_0} = sodium ionic conductivity at a reference temperature $T_0 = 298.15 \text{ K}$, $\left(\frac{1}{ohm \cdot cm} = \frac{S}{cm} \right)$; E = activation energy for the ionic transport through the electrolyte, $(J \cdot mol^{-1})$; and R = the universal gas constant = $8.314, (J \cdot mol^{-1} \cdot K^{-1})$.

Using the supplemental information from Figure S2 [8], σ_{Na^+,T_0} and $\left(\frac{E}{R} \right)$ were determined. Their values are $\sigma_{Na^+,T_0} = 3.540 \times 10^{-3} (ohm^{-1} \cdot cm^{-1}) = 3.540 \text{ mS} \cdot cm^{-1}$ and $\left(\frac{E}{R} \right) = 1248.88K$.

The cell-voltage loss due to the resistance to the sodium-ion transport through the solid electrolyte sodium-beta alumina ($Na - \beta''Al_2O_{3(s)}$) separator between the cell electrodes, during the cell discharge period, is given as:

$$(\Delta V)_{drop-electro-sep} = \left(\frac{i_{geom} \times l_{electro-sep}}{\sigma_{Na^+,T}} \right), (volt) \quad (2-46)$$

where $l_{electro-sep}$ = thickness of the solid electrolyte.

It has been stated that the cell electrode activation overpotential (i.e., the cell electrode polarization voltage loss is negligibly small (i.e., less than 0.050 volt depending on the cell operational temperature and geometric current density [8]). For the analytic work being reported in this paper, it is further assumed that the porous cell cathode is thin enough that the resistance to the mass transfer of chemical species carbon dioxide/oxygen gas from the cathode-side plenum to the highly active reaction sites for the overall cell reaction, Equation (2-1), is negligible.

It has been mentioned [9] that a practical successful electrode should be free of species diffusional mass control. Also, it is assumed that sodium ion transport in the cathode and its reaction with the gaseous species oxygen and carbon dioxide is such that the solid reaction product is formed on the external surface of the cathode facing towards the cathode-side plenum, P.

The reactant species molar consumption rates, corresponding to a fixed value of the geometric current density, $i_{geom}, (amp \cdot cm_{geom}^{-2})$; according to the occurrence of reaction, Equation (2-1), are given as follows:

$$\dot{n}_{Na} = \left(\frac{i_{geom}}{F} \right), (mol \cdot s^{-1} \cdot cm^{-2}) \quad (2-47)$$

$$\dot{n}_{CO_2(g)} = \left(\frac{i_{geom}}{2F} \right), (mol \cdot s^{-1} \cdot cm^{-2}) \quad (2-48)$$

$$\dot{n}_{O_2(g)} = \left(\frac{i_{geom}}{4F} \right), (mol \cdot s^{-1} \cdot cm^{-2}) \quad (2-49)$$

Also, the generation rate of solid product, $Na_2CO_{3(s)}$, from the cell reaction, is given by:

$$\dot{n}_{Na_2CO_{3(s)}} = \left(\frac{i_{geom}}{2F} \right), (mol \cdot s^{-1} \cdot cm^{-2}) \quad (2-50)$$

For the case of relatively thin cathode electrode (e.g., $10\mu m$ thickness), the cell voltage drop associated with the sodium ion transport to the external surface of the cathode is expected to be negligibly small; of the order of $10mV$ or less depending on the cell operational temperature and the magnitude of the cell geometric current density. For this situation, the cell operational voltage available at a fixed geometric current density, i_{geom} , is:

$$E_{T,operational} = E_T - [|(\Delta V)_{drop-electro-sep}| + |(\Delta V)_{drop-electro-cath}|] \quad (2-51)$$

where $|(\Delta V)_{drop-electro-cath}|$ = (voltage loss for sodium ion transport from the electrolyte separator to the exterior surface of the cell cathode facing the cathode-side plenum. Here, for the assumption of a thin, porous cathode electrode, $|(\Delta V)_{drop-electro-cath}|$ is being set equal to zero. Consequently, $E_{T,operational} = E_T - [|(\Delta V)_{drop-electro-sep}|]$ (2-52)

The cell electric power, $\dot{P}$, is given as

$$\dot{P} = (E_{T,operational}) \times i_{geom} [W \cdot cm^{-2}] \quad (2-53)$$

The cell electric efficiency, η_{cell} , defined as:

$$\eta_{cell} = \frac{E_{T,operational}}{E_T} = \frac{E_T - \sum_j |(\Delta V)_{drop,j}|}{E_T} \quad (2-54)$$

Or,

$$\eta_{cell} = 1 - \left(\frac{\sum_j |(\Delta V)_{drop,j}|}{E_T} \right) \quad (2-55)$$

where the $(\sum_j)$ = (sum of the voltage losses, during the cell operation to deliver electric power to an electric circuit external to the cell, due to the cell electrode reaction polarization, ohmic resistance associated with the electron and ion transport in the interior cell components as well as with the electron transport in the cell anode and cathode current collectors. For the work presented in this paper, η_{cell} is given by

$$\eta_{cell} = 1 - \left(\frac{|(\Delta V)_{drop-electro-sep}|}{E_T} \right) \quad (2-56)$$

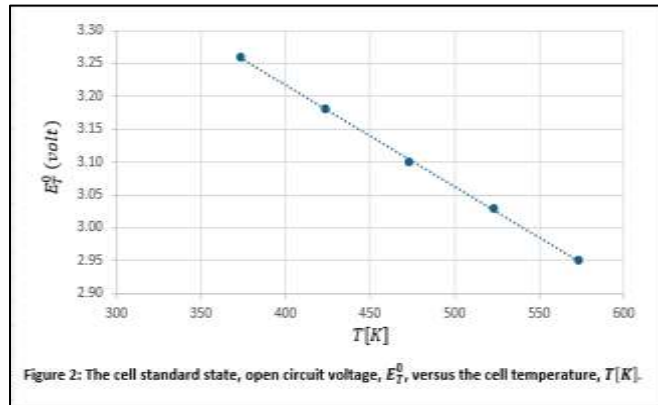
We focused our analysis on the overall cell reaction, Equation (2-1); where the mixture of carbon dioxide and oxygen was assumed to be dry. For the situation of this mixture being moistened with water vapor; there is likelihood for the occurrence of the reaction:



The standard-state Gibbs free energy change of this reaction, $\Delta G_0^o = (-265.208 \text{ kJ} \cdot \text{mol}^{-1})$ whereas that for the reaction, Equation (2-1), is $(-650.081 \text{ kJ} \cdot \text{mol}^{-1})$ at $T_0 = 298.15K$. ΔG_0^o for the reaction, Equation (2-1), is lower (i.e., more negative) than that for the reaction, Equation (2-57), by the factor of 2.45. So, it is envisioned that the reaction, Equation (2-1), occurrence would predominate over the reaction, Equation (2-57).

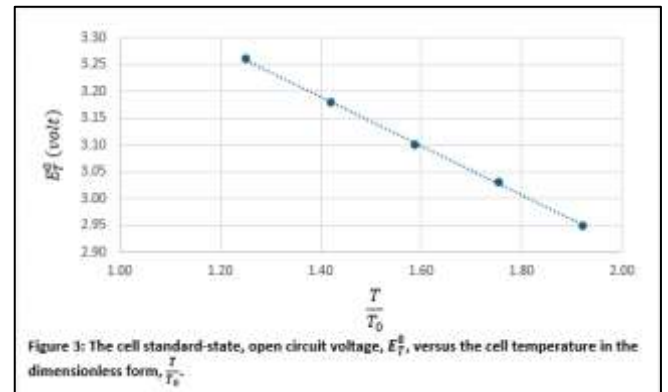
3. COMPUTED DATA AND DISCUSSION

The data calculated from the formulation given in section 2 is presented in this section in the form of plots.

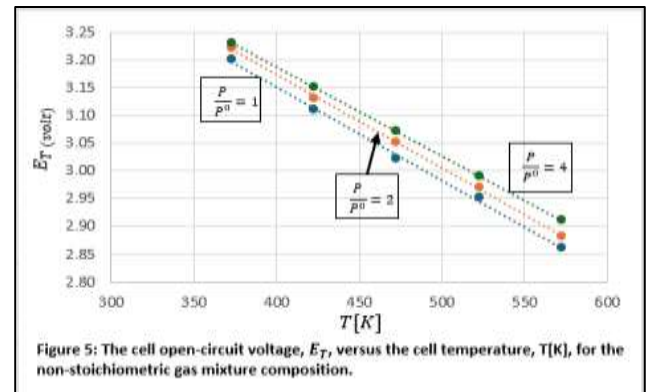
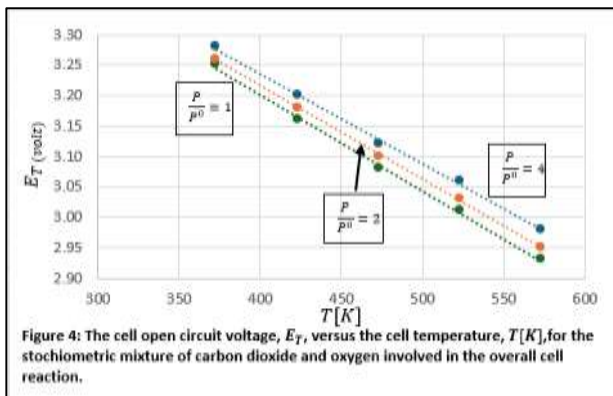


The open-circuit cell voltage decreases from 3.26 to 2.95 volt for the cell temperature increase from 373.15 to 573.15K. One observes a linear relation between the cell voltage decrease and the cell temperature increase. Figures 4 and 5

Figures 2 and 3 shows the standard-state, open-circuit cell voltage calculated using Equation (2-5) as a function of the cell temperature.



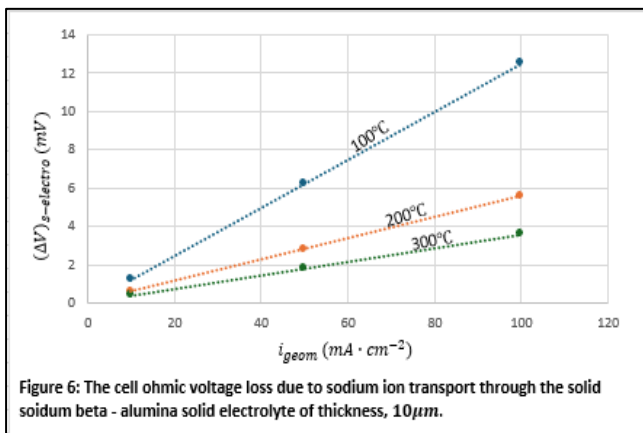
show the effect of the cell Cathode-side reactant gas mixture composition on the open-circuit cell voltage, E_T , as a function of temperature at $\frac{P}{P_0} = 1, 2 \text{ and } 3$.



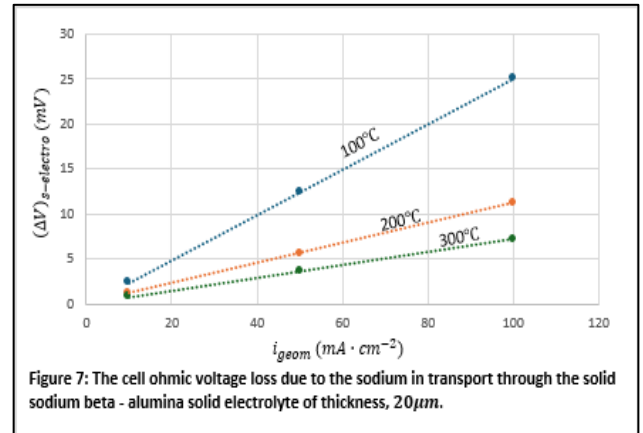
In figure 4, a decrease in E_T with an increase in the cell temperature is observed at a $\left(\frac{P}{P_0}\right)$ value at the cell Cathode-side stoichiometric reactant gas mixture of carbon dioxide and oxygen (carbon dioxide mole fraction = $\frac{2}{3}$ and oxygen mole fraction = $\frac{1}{3}$). Also, at a cell temperature; E_T increases with an increase in $\left(\frac{P}{P_0}\right)$ value; however, the increase in E_T is small; for example, the increase of $\cong 0.03 \text{ volt}$ for the $\left(\frac{P}{P_0}\right)$ increase from 1 to 4 at 100°C ($\cong 373.15\text{K}$). Figure 5 shows the similar relation between E_T and $\left(T \text{ and } \frac{P}{P_0}\right)$ for the cell cathode-side non-stoichiometric reactant gas mixture (e.g., carbon dioxide mole fraction $y_{\text{CO}_2(g)} =$

0.1053, oxygen mole fraction $y_{\text{O}_2(g)} = 0.0526$ and nitrogen mole fraction $y_{\text{N}_2(g)} = 1 - (y_{\text{CO}_2(g)} + y_{\text{O}_2(g)})$). Comparison of the data presented in Figure 4 and 5 informs us that the open circuit cell voltage is slightly lower for the cathode-side non-stoichiometric reactant gas mixture at any $\left(\text{temperature}, \frac{P}{P_0}\right)$ pair; for example, lower by about 0.05 volt at $T = 200^\circ\text{C}$ and $\frac{P}{P_0} = 2$.

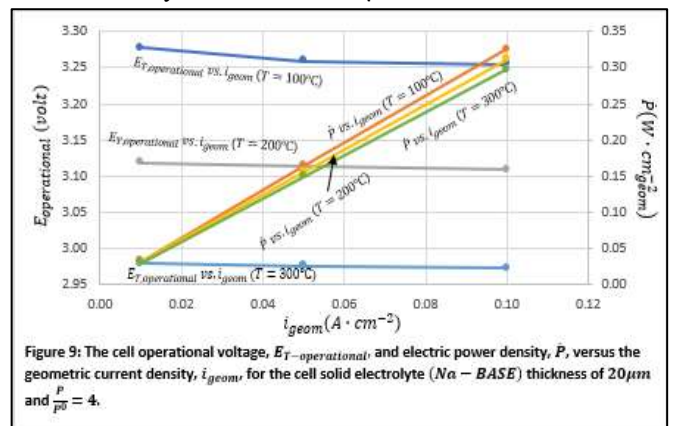
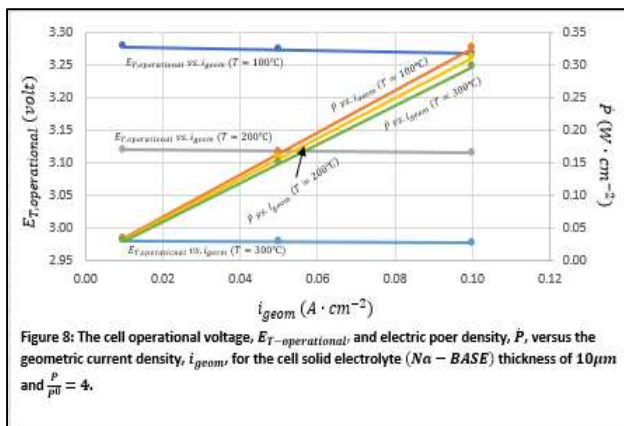
Figures 6 and 7 show the ohmic voltage loss associated with the sodium ion transport through the cell solid electrolyte of thickness 10 and $20\mu\text{m}$, respectively, as a function the cell geometric current density ranging from 10 to $100 \text{ mA} \cdot \text{cm}^{-2}_{\text{geom}}$ at three different cell temperatures: 100, 200 and 300°C



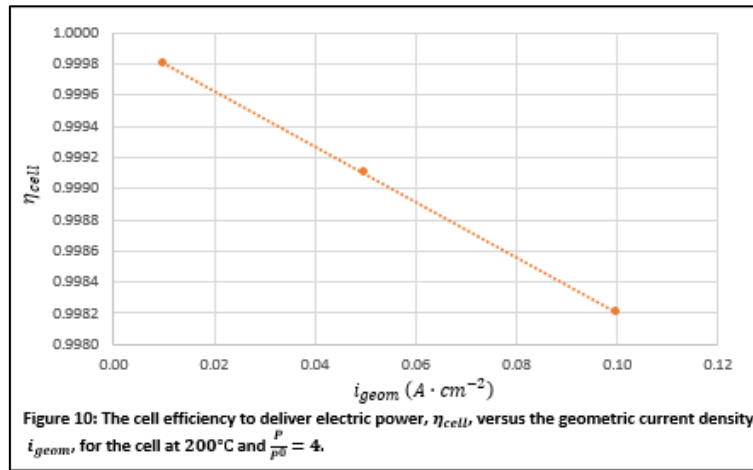
At each cell temperature and solid electrolyte thickness, an increase in the ohmic cell voltage loss with an increase in the cell geometric current density is observed in the plots in Figures 6 and 7 as expressed by Equation (2-46). Also, the ohmic voltage loss through the solid electrolyte decreases with an increase in the cell temperature at each cell-geometric current density. This is because of an increase in the sodium-ion ionic conductivity in the cell solid electrolyte as expressed by Equation (2-45). Comparison current density of $50 \text{ mA} \cdot \text{cm}^{-2}_{\text{geom}}$ shows the cell voltage loss of 2.8 and 5.6 volt , respectively, for the solid electrolyte thickness of 10 and $20\mu\text{m}$.



Figures 8 and 9 show the cell operational voltage, $E_{T\text{-operational}}$, and electric power density, $\dot{P}$, as a function of the cell geometric current density, i_{geom} , for the cell solid electrolyte thickness of 10 and $20\mu\text{m}$, respectively, with the cell at $\frac{P}{P_0} = 4$ and three different temperatures of 100, 200, and 300°C . At any cell geometric current density, a slight decrease in the cell operational voltage is observed with an increase in the cell temperature. For example, at the cell geometric current density of $0.05 \text{ A} \cdot \text{cm}^{-2}_{\text{geom}}$ ($50 \text{ mA} \cdot \text{cm}^{-2}_{\text{geom}}$), the arithmetic-average operational cell voltage decrease is approximately 0.15 volt as seen in Figure 8 over the cell temperature ranging from 200 to 300°C for the cell solid electrolyte thickness of $10\mu\text{m}$.



Also, at a cell temperature, there is a slight decrease in the cell operational voltage with an increase in the cell geometric current density from 0.01 to $0.10 \text{ A} \cdot \text{cm}_{geom}^{-2}$. For example, at 200°C , the decrease in the operational cell voltage is approximately equal to 3 mV over current range of 0.01 to $0.10 \text{ A} \cdot \text{cm}_{geom}^{-2}$. At each cell temperature, the electric power density, $\dot{P}$, increases with an increase in the cell geometric current density. The cell, with its solid electrolyte thickness of $20 \mu\text{m}$, shows the similar behavior with regard to the cell operational voltage and electric power density as presented in figure 9.



4. CONCLUDING REMARKS IN BRIEF

In accordance with our intent to utilize carbon dioxide gas (a global warming gas) as one of the fuel cell reactants to generate electric power; the formulation based on the overall cell reaction,

$2\text{Na} + \text{CO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} = \text{Na}_2\text{CO}_{3(s)}$, has been developed and presented in Section 2. The formulation can be used, for example, to predict the following:

- The standard-state, open-circuit cell voltage as a function of the cell temperature.
- The open-circuit cell voltage as a function of the cell temperature with the cell cathode-electrode side reactive gas mixture of carbon dioxide and oxygen; the gas mixture may be in the ideal or non-ideal thermodynamic state.
- The cell operational voltage and electric power density as a function of the cell geometric current density.
- Electric power delivery efficiency of the cell as a function of the cell geometric current density.

Some computed data examples are given below:

- The standard-state, open-circuit cell voltage decreases from 3.26 to 2.95 volt for the cell temperature increase from 100 to 300°C .
- For the cell cathode-side stoichiometric reactant gas mixture of carbon dioxide and oxygen at $\frac{P}{p_0} = 2$, the open-circuit cell voltage decreases from 3.26 to

Figure 10 shows the cell efficiency, $\eta_{cell} = \frac{E_{T\text{-operational}}}{E_T}$, to deliver electric power to an external electrical circuit as a function of the cell geometric current density, i_{geom} , at 200°C and $\left(\frac{P}{p_0}\right) = 4$ for the cell with its solid electrolyte thickness of $10 \mu\text{m}$. It is quite obvious that the electric power delivery efficiency ranges from 99.98 to 99.80% over the cell geometric current density ranges from 0.01 to $0.10 \text{ A} \cdot \text{cm}_{geom}^{-2}$.

2.95 volt with increase in the cell temperature from 100 to 300°C . Similar open-circuit cell voltage behavior is observed for a non-stoichiometric reactant gas mixture.

- At a given cell temperature and pressure, e.g., 200°C and $\frac{P}{p_0} = 4$ for the cell having the solid electrolyte, sodium beta-alumina solid electrolyte ($\text{Na} - \text{BASE}; \text{Na} - \beta'' - \text{Al}_2\text{O}_3$) of $10 \mu\text{m}$ thickness, the operational cell voltage change is small, i.e., 3 mV for the cell geometric current density range of 10 to $100 \text{ mA} \cdot \text{cm}_{geom}^{-2}$.
- For the cell, with the solid electrolyte thickness of $10 \mu\text{m}$, at 200°C and $\frac{P}{p_0} = 4$, the electric power density increases from 3.12×10^{-2} to $3.11 \times 10^{-1} \text{ W} \cdot \text{cm}_{geom}^{-2}$ with an increase in the geometric current density from 10 to $100 \text{ mA} \cdot \text{cm}_{geom}^{-2}$.
- For the cell, having the solid electrolyte of $10 \mu\text{m}$ thickness, at $\frac{P}{p_0} = 4$ and 200°C ; the electric power delivery efficiency ranges from 99.98 to 99.80% over the cell geometric current density increase from 10 to $100 \text{ mA} \cdot \text{cm}_{geom}^{-2}$.

REFERENCES

- S.S. Sandhu. A Thermodynamic Simulation of A Hydrogen/Oxygen Fuel Cell Involving Nonideal

- Gas Flows. Proceedings of the Symposium on Fuel Cells. (Editors: R.E. White and A.J. Appleby) The Electrochemical Society, Inc., Pennington, NJ.; Vol. 89, No. 14, pp. 191-215 (year 1989).
2. S.S. Sandhu and J.P. Fellner. A Heat and Mass Transfer Analysis for An Ideal Hydrogen/Oxygen Fuel Cell. Proceedings of the 25th Intersociety Energy Conversion Engineering Conference (Editors: P.A. Nelson, M.W. Schertz and R.H. Hill) American Institute of Chemical Engineers, New York; Vol. 3, pp. 131-136 (year 1990).
3. S.S. Sandhu, R.O. Crowther, S.C. Krishnan and J.P. Fellner. Direct Methanol Polymer Electrolyte Fuel Cell Modeling: Reversible Open-Circuit Voltage and Species Flux Equations. Journal of Electrochimica Acta (The Journal of the International Society of Electrochemistry) Vol. 48 (Issue number: 14-16), pp. 2295-2303 (year 2003).
4. S.S. Sandhu and J.P. Fellner. Performance/design formulation for a solid polymer acid electrolyte hydrogen/air fuel cell. Journal of Power Sources, Vol. 164, pp. 365-371 (year 2006).
5. S.S. Sandhu and J.P. Fellner. Model Formulation and Simulation of a Solid-State Lithium-Based Cell. International Journal of Electrochimica Acta 88 (year 2013), pp. 495-506. (<http://dx.doi.org/10.1016/i.electacta.2012.10.110>).
6. S.S. Sandhu. Shrinking Core Model Formulation for the Electrochemical Performance Analysis of a Lithium Carbon Monofluoride Cell. RA Journal of Applied Research, Vol. 09, Issue: 03 (March-2023). DOI: 10.47791/rajar/v9i3.02.
7. S.S. Sandhu. A High Temperature Lithium-Aluminum Alloy/Oxygen or Air Fuel Cell. RA Journal of Applied Research, Vol. 11, Issue: 01 (January-2025), pp. 01-07. DOI: 10.47191/rajar/v11i1.01.
8. K. Sugano, et al. Sodium-air Fuel cell for high-energy density and low-cost electric power. July 9, p. 10.1962 (June 18, 2025).
9. A.J. Appleby and F.R. Foulkes. Fuel Cell Handbook, p. 244 (year 1989). Van Nostrand Reinhold, New York, USA.
10. J.M. Smith, H.C. Van Ness and M.M. Abbot. Introduction to Chemical Engineering Thermodynamics. Pp. 498, 499. (2005, 7th edition); The McGraw-Hill Companies, New York, USA.