Temperature and voltage responses of a molten carbonate fuel cell in the presence of a hydrogen fuel leakage

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Abstract. A two dimensional (2-D), dynamic model of a molten carbonate fuel cell (MCFC) was developed using COMSOL Multi-physics. The model was used to investigate the dynamic behaviour of the MCFC in the presence of hydrogen fuel leakage. A leakage was modelled as a known outflow velocity at the anode gas channel. The effects of leakage velocity and the leakage location were investigated. The simulations show that anode electrode temperature increases as the leakage velocity increases. The voltage generated is shown to decrease at the start of the leakage occurrence due to loss of hydrogen gas. Later the voltage increases as the anode temperature increases. The results also show that the changes of temperature and voltage are more significant if a leakage occurs nearer to the inlet compared to that at the outlet of anode gas channel.

1. Introduction
Fossil fuels have been the main energy source for centuries. However, due to the issues of environmental pollution and scarcity of the fossil fuels, the demand for greener energy sources is increasing. A molten carbonate fuel cell (MCFC) appears to be one of the strong energy alternatives in this respect.

A MCFC stack consists of a number of anode and cathode electrodes which are separated by an electrolyte as shown in the figure 1.

| Separator Plate |
|-----------------|
| Anode Gas Channel |
| Anode Plate |
| Electrolyte |
| Cathode Plate |
| Cathode Gas Channel |
| Separator Plate |

Figure 1. Schematic of a typical MCFC.

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At the cathode electrode, the following reaction occurs,
\[
\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3
\]
(R1)

At the anode electrode, hydrogen gas is used as a fuel,
\[
H_2 + CO_2 \rightarrow H_2O + CO_2 + 2e^- 
\]
(R2)

The overall reaction can be written as,
\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O 
\]
(R3)

which produces water as a by-product.

As hydrogen is a flammable gas which could cause explosion, it is important to take precautionary measures to prevent the hydrogen leakage. If the leakage does occur, it is important to ensure that the leakage can be detected as early as possible.

From the literature conducted, there is a limited amount of work which has been done on the hydrogen leakage detection. From the study of Ashraf Khorasani et al. [1], the location of the leakage in the fuel cell could be determined based on the data received from the voltage-time graphs of the stack under hydrogen sudden stop condition. The authors suggested an approximate expression for the cells voltage loss due to a decrease in partial pressure of anode and cathode reactants. Tian et al.[2] presented data of a failed fuel stack due to the internal gas leakage. With the help of statistical analysis tools, it enables the detection of failed cells inside the fuel cell stack in two different cases, namely anode/cathode crossover and anode/cooling compartment leak. Voltage and the pressure readings of the cell were analysed to detect the cell with leakages. Husar, Serra and Kunusch [3] reported that cross-over in polymer membrane fuel cell resulted in unexpected changes in system variables such as temperature, pressure and voltage. Kim et al.[4] predicted the hydrogen dispersion in a residential fuel cell systems by using computational fluid dynamics (CFD) simulations. A three dimensional geometric model of the system was constructed and the flow pattern and hydrogen concentration in the residential fuel cell system was studied.

The objective of the current work is to investigate the performance changes of a MCFC in the presence of hydrogen leakages. The result is helpful in developing a model-based hydrogen leakage detection method in future.

2. Model development

2.1. Governing equations

The governing equations of the MCFC model are as follows:

For the gases in the channels, Navier–Stokes equation is used,
\[
\frac{\partial \rho}{\partial t} + \nabla (\rho \mathbf{u}) = 0 
\]
(1)

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \mu \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) - \frac{2}{3} \left( \mu (\nabla \mathbf{u}) \right) 
\]
(2)

where \( \rho \), \( \mu \) and \( \mathbf{u} \) are the gas density, dynamic viscosity and velocity vector respectively.

For the gas phase momentum conservation of porous anode and cathode electrodes is described by Darcy equation,
\[
\frac{\rho}{\varepsilon_p} \left( \frac{\partial \mathbf{u}}{\partial t} + \frac{\mathbf{u} \cdot \nabla \mathbf{u}}{\varepsilon_p} \right) = \nabla \cdot \left( -p \mathbf{I} + \frac{\mu}{\varepsilon_p} \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) - \frac{2\mu}{3\varepsilon_p} (\nabla \cdot \mathbf{u}) \mathbf{I} \right) - \frac{\mu u}{\kappa} 
\]
(3)

where \( \varepsilon_p \) and \( \kappa \) are the porosity and permeability of the porous media.
For the transport of concentrated gas species \( \omega_i \), it can be described as,
\[
\rho \frac{\partial \omega_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \rho \left( \mathbf{u} \cdot \nabla \right) \omega_i = \dot{R}_i
\]
(4)
\( \mathbf{J}_i \) is the mass flux, \( i \) relative to the average mass velocity. For the water gas shift (WGS) reaction, the equation that takes place in the anode is as follows [5],
\[
\dot{R}_{\text{WGS}} = k_{\text{WGS},f} \left( p_{\text{H}_2\text{O}} p_{\text{CO}} - p_{\text{H}_2} p_{\text{CO}_2} / K_{p,\text{WGS}} \right)
\]
(5)
\[
k_{\text{WGS},f} = 0.0171 \exp \left( - \frac{103191}{R_T T} \right)
\]
(6)
\[
K_{p,\text{WGS}} = \exp ( -0.2935 Z^3 + 0.635 Z^2 + 4.1788 Z + 0.3169 )
\]
(7)
and
\[
Z = \frac{1000}{T_g} - 1
\]
(8)

\( T_g \) is the gas phase temperature and \( p_i \) is the partial pressure of a gas species, \( i \).

For the cathode electrode, oxygen and carbon dioxide are consumed. Thus, the rates of consumption of the gas species are as follows,
\[
\dot{R}_{\text{O}_2} = -i_{\text{ct}} M_{\text{O}_2} / \left( 4 F \delta_{\text{ct}} \right)
\]
(9)
\[
\dot{R}_{\text{CO}_2} = -i_{\text{ct}} M_{\text{CO}_2} / \left( 2 F \delta_{\text{ct}} \right)
\]
(10)
where the supplied current density is denoted as \( i_{\text{ct}} \). The molecular weight of a gas species \( i \) is denoted as \( M_i \) and \( F \) and \( \delta \) are Faraday’s constant and thickness of an electrode respectively.

For the anode electrode, carbon dioxide and water vapour are produced and hydrogen gas is consumed. Thus, the rates of consumption of the gas species are as follows [6],
\[
\dot{R}_{\text{H}_2} = M_{\text{H}_2} \left[ \dot{R}_{\text{WGS}} - i_{\text{ct}} / (2 F \delta_{\text{an}}) \right]
\]
(11)
\[
\dot{R}_{\text{H}_2\text{O}} = M_{\text{H}_2\text{O}} \left[ i_{\text{ct}} / (2 F \delta_{\text{an}}) - \dot{R}_{\text{WGS}} \right]
\]
(12)
\[
\dot{R}_{\text{CO}_2} = M_{\text{CO}_2} \left[ \dot{R}_{\text{WGS}} + i_{\text{ct}} / (2 F \delta_{\text{an}}) \right]
\]
(13)

It is assumed that the electrodes of the MCFC are porous structures and thermal equilibrium. Hence, the heat transfer of the MCFC is governed by convection, conduction and radiation mechanisms. Although the effect of the thermal radiation is found to be negligible by Koh et al [7], it is still be consider in the present work with case study. Hence, the temperature of the fuel cell, \( T_p \) is calculated according to,
\[
\rho c_{\text{eff}} \frac{dT_p}{dt} + \rho c_{\text{eff}} \mathbf{u} \cdot \nabla T_p = \nabla \cdot \left( k_{\text{eff}} \nabla T_p \right) + \dot{Q}_{\text{Ohm}} + \dot{Q}_r + \dot{Q}_{\text{rad}}
\]
(14)
where \( c_{\text{eff}} \) and \( k_{\text{eff}} \) are the specific heat capacity and the thermal conductivity respectively.

The reaction heat source for the anode electrode,
\[
\dot{Q}_r = -\left[ \Delta H_{\text{WGS}} \dot{R}_{\text{WGS}} + \Delta H_{f,\text{H}_2\text{O}} M_{\text{H}_2\text{O}} \delta_{\text{ct}} / (2 F \delta_{\text{an}}) \right]
\]
(15)
whilst it is zero at the cathode electrode. The enthalpies of reaction for water-gas shift and water formation are denoted as \( \Delta H_{\text{WGS}} \) and \( \Delta H_{f,\text{H}_2\text{O}} \) respectively.

Heat transfer by thermal radiation (\( Q_{\text{rad}} \)) is described as,
\[
Q_{\text{rad}} = \sigma_B \varepsilon_s (T_s^4 - T_{\text{sur}}^4)
\]
(16)
where \( \sigma_B \) is the Stefan-Boltzmann constant, \( T_s, T_{\text{sur}} \) and \( \varepsilon_s \) are cell separator temperature, surrounding temperature and emissivity of the separator plates, respectively.
The Ohmic heat source $Q_{\text{Ohm}}$ is defined as,
\[ Q_{\text{Ohm}} = V_{\text{cell}}i_{\text{cell}}/\delta_k \] (17)
where $\delta_k$ is the thickness of anode, cathode electrodes or current collector.

The temperature of the gas domain in the gas phase is governed by the following equations,
\[ \rho c_{p,g}\frac{\partial T_g}{\partial t} + \rho c_{p,g}u \cdot \nabla T_g = \nabla \cdot (k_g \nabla T_g) + \dot{Q}_r \] (18)
where $\dot{Q}_r = -\left( \Delta H_{\text{WGS}} \dot{R}_{\text{WGS}} \right)$ for the anode gas phase and $\dot{Q}_r = 0$ for the cathode gas phase.

The impact of electrochemical dynamics of cell voltage is accounted for in the MCFC model. The voltage of the MCFC can be calculated via [8]:
\[ V_{\text{cell}} = E_{\text{eq}} - i_{\text{cell}} (\eta_{\text{act}} + \eta_{\text{conc}} + \eta_{\text{Ohm}}) \] (19)
where $E_{\text{eq}}$ is calculated by Nernst equation and the voltage losses due to activation, concentration and Ohmic overpotentials are calculated as follows,
\[ \eta_{\text{act}} = 2.27 \times 10^{-9} \exp \left( \frac{6435}{T_p} \right) P_{H_2}^{0.42} P_{CO_2}^{-0.17} P_{H_2O}^{-1} \] (20)
\[ \eta_{\text{conc}} = 7.505 \times 10^{-10} \exp \left( \frac{9298}{T_p} \right) P_{O_2}^{0.43} P_{CO_2}^{-0.80} \] (21)
\[ \eta_{\text{Ohm}} = 0.5 \times 10^{-4} \exp \left[ -3016 \left( 1/T_p - 1/923 \right) \right] \] (22)
Detailed discussion on the modeling can be found in [9].

2.2. Computational domain
A number of leakages are introduced at the separator of the anode gas channels as shown in figure 2.

![Figure 2. Computational domain of the MCFC.](image)

2.3. Leakage modelling and boundary / operating conditions
The leakage modelling is carried in two stages. The first stage is to assume no leakage in the fuel cell. The above-mentioned governing equations are solved to obtain the steady-state solution. The leakage domains A, B and C are assumed to be a porous media with a low porosity ($\varepsilon_p \approx 10^{-5}$) and the boundary conditions of the leakages are described as walls. The second stage involves solving the transient governing equations (1) to (22). The initial conditions are taken from the previously obtained steady-state solution. This is important because it improves the convergence of the transient solution. The leakage domains A, B and C are now treated as part of the gas channel ($\varepsilon_p = 1$). The boundary condition of the leakage is prescribed by a known flow velocity. The leakage is not prescribed by atmospheric pressure because it avoids the need to generate a high number of meshes around a small leakage region.
The inputs of the model [10] are summarized in table 1.

| Input                                      | Values                                      |
|--------------------------------------------|---------------------------------------------|
| Anode gas velocity (m/s)                   | 1.24                                        |
| Cathode gas velocity (m/s)                 | 3.73                                        |
| Molar fraction in the anode gas channel,   |                                             |
| $H_2$:CO$_2$:H$_2$O                        | 0.4:0.4:0.2                                 |
| Molar fraction in the cathode gas channel, |                                             |
| $O_2$:CO$_2$:N$_2$                         | 0.148:0.296:0.556                           |
| Inlet gas temperature at the anode and     |                                             |
| cathode gas channel (K)                    | 873                                         |
| Current density demand (A/m$^2$)           | 1400                                        |
| MCFC length (m)                            | 0.14                                        |
| Anode / cathode gas channel width (m)      | 0.0016                                      |
| Emissivity of the separator plate          | 0.286                                       |

3. Results and discussions
Two case studies are conducted using the current model. These include: The effects of leakage flow rates and the locations of leakage.

3.1. The effects of leakage flow rates
In the first case study, a leakage is assumed to occur at the middle of the MCFC, i.e. leakage B as in figure 2. Figure 3 shows the velocity magnitude of the anode gas channel for the case when the leakage velocity is 1.5m/s. It can be observed that upon entering the gas channel, the velocity increases due to the entrance effect. The anode gas velocity remains constant before it encounters the leakage. The velocity is reduced after it passes by leakage as a portion of the gas is lost to the environment through the leakage.

![Figure 3. Velocity magnitude of the anode gas channel of the MCFC](image_url)

Figure 4 shows the temperature of anode electrode at the outlet. It shows that as the anode temperature increases leakage velocity increases. This is because a larger leakage velocity causes the in-channel gas flow to decrease. A lower channel gas temperature is unable to dissipate heat quickly which causes an increase of the anode temperature.

Figure 5 shows the changes of the voltage of MCFC when the leakage occurs. It can be observed that there is a voltage drop initially due to the lower electrochemical reaction owing to the smaller convective mass flux at the electrodes. After a while, the voltages increase. The graph shows...
that the voltage becomes higher if the leakage velocity increases. This observation is due to the increasing electrode temperature which causes the reduction in the polarization voltage, i.e. activation, concentration and Ohmic polarizations. The changes of these polarizations are shown in figure 6 to figure 8. These graphs show that as the electrode temperature increases, the overpotentials decrease. The overpotentials drop more noticeably as the leakage velocity increases from 0.5 m/s to 1.5 m/s. From equation (19), the voltage generated increases as the overpotentials decrease. Among the three overpotentials, activation overpotential is relatively small compared to the other two. Figure 6 and figure 7 show that the change of overpotential decreases gradually as the temperature increases. On the other hand, a drastic drop can be observed for the activation overpotential at the onset of leakage at $t = 0$ s. The decrease is more pronounced for a higher leakage which is due to the decrease of gas pressure at the anode.

![Figure 4](image1.png)

**Figure 4.** The temperature of the anode electrode at the outlet of the gas channel for the case of middle leakage

![Figure 5](image2.png)

**Figure 5.** The voltage generated by the MCFC during various leakage conditions for the case of middle leakage
Figure 6. The concentration overpotential of the MCFC during various leakage conditions for the case of middle leakage

Figure 7. The activation overpotential of the MCFC during various leakage conditions for the case of middle leakage

Figure 8. The Ohmic overpotential of the MCFC during various leakage conditions for the case of middle leakage
3.2. The effects of leakage locations
The model was used to study the effects of leakage locations on the performances of the MCFC. Figures 9 and 10 show the anode electrode temperatures at the outlet for the cases of front and end leakages. By comparing figures 4, 9 and 10, it can be seen that the temperature rise is larger as the leakage is nearer to the inlet. This is because gas loss from the front leakage will result in smaller gas velocity in majority of the gas channel. On the other hand, much smaller temperature rise is observed as it is nearer to the outlet as lower gas velocity is available only at a small section of the gas channel after the leakage.

The voltages generated by both front and end leakages are also compared as shown in figure 11. It can be observed that the changes of voltage by end leakage are insignificant. By comparing figure 5 and figure 11, it can be concluded that front leakage will cause a noticeable change in voltage reading compared to the mid and end leakage conditions. The results can be used to develop a model-based hydrogen leakage detection system. Data collected from sensors will be used to compare with the simulation data. If the difference of both data is within a predefined tolerance, alarm will be triggered to inform the presence of hydrogen leakage from a MCFC.

![Figure 9](image)

**Figure 9.** The temperature of the anode electrode at the outlet of the gas channel for the cases of front leakage

![Figure 10](image)

**Figure 10.** The temperature of the anode electrode at the outlet of the gas channel for the case of end leakage
4. Conclusions
In the current study, a dynamic model of a MCFC was developed. The model was used to investigate the dynamic performance of the MCFC in the presence of hydrogen gas leakage. The study indicates that when a leakage occurs, the in-channel anode gas velocity will decrease. This in turn causes the anode electrode temperature to increase. The increase of anode electrode temperature is proportional to the leakage velocity. The simulation also shows that when a leakage occurs, the MCFC voltage decreases initially due to a lower electrochemical reaction rate. After that, the voltage increases due to the electrode temperature rise which encourages a higher reaction rate. In addition, it has been shown that a leakage location has a noticeable effect on the temperature and voltage of a MCFC. For the same leakage flow rate, a leakage nearer to the inlet of the gas channel results in larger temperature / voltage increase compared to that at the end of the gas channel. This is because the gas velocity in the majority section of the gas channel becomes smaller after it passes by the leakage in the former case. The current result is useful to develop a model-based hydrogen leakage detection system.

5. References
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