

# Thermodynamic Study of a Molten Carbonate Fuel Cell (MCFC) System

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**Abstract:** *In the present work, thermodynamic analysis of a molten carbonate fuel cell (MCFC) is considered. Accordingly, a thermodynamic model is developed to understand performance of the cell at different operating conditions. The effect of operating parameters like working temperature, fuel utilization, current density, gas constituents etc. on the performance of the basic MCFC are studied to understand the behaviour of the cell. It is noticed that the cell voltage shows a strong dependence on the operating temperature. The actual cell voltage is less than the reversible cell voltage because of the losses occurs in a cell which is taken constant in the present analysis. Result shows that an operating temperature of 650°C offers an optimization for better performance and cell life.*

**Keywords -** MCFC, Analysis, Fuel utilization, Cell temperature, Cell voltage, Cell power.

## I. INTRODUCTION

From the perspective of energy security and environmental sustainability, highly effective uses for fossil fuels in the energy industries are desirable. In this context, fuel cell certainly has an important role to play. A fuel cell is a device that generates electricity through a set of chemical reactions that take place within it while continuous supplies of fuel and oxidants are made to its electrodes. Now a day, fuel cell is a technology that is being developed and its various forms have received worldwide acceptance and interest. This is because of its high energy conversion efficiency, low emission capability. It can also utilize fuels like hydrogen which is readily available and produce water as the only by-product thus being very environment friendly. As an introduction to fuel cells, it is studied for two important reasons: firstly, it is an emerging technology that needs to be understood, thus enabling the continuation of R & D and the eventual rollout of commercialization. Secondly, fuel cells are studied to understand how the presence of fuel cells will change current application of energy dependent devices. In the present work, therefore, a thermodynamic model of a molten carbonate fuel cell (MCFC) system is developed for a systematic study of the system.

For understanding the modelling of the MCFC, some related research works are reviewed. According to Roberto Bove et al. (2004) biogas recovery is an environmentally friendly and cost-effective practice that is getting consensus in both the scientific and industrial community, as the growing numbers of projects demonstrate. The use of fuel cells as energy conversion systems increases the conversion efficiency, as well as the environmental benefits. Molten carbonate fuel cells (MCFC) operate at a temperature of about 650°C, thus presenting high fuel flexibility, compared to low temperature fuel cells. Aim of the present study is to compare the performance of an MCFC single cell, fuelled with different biogas types as well as methane. The biogases considered are derived from steam gasification in an entrained flow gasifier and steam gasification in a dual interconnect fluidized bed gasifier. The performances are evaluated for different fuel utilization and current densities. Freni S. et al. (1996) investigated the use of water/ethanol mixture as an alternative fuel for molten carbonate fuel cells. Some thermodynamic calculations have been carried out by a mathematical model to determine the energy and mass balances for a water/ethanol fuelled molten carbonate fuel cell. G. De Simon et al. (2003) presented a molten carbonate fuel cell (MCFC) power plant steady-state simulation. A simulation is obtained with the preliminary input specification to get to the base case and a sensitivity analysis is conducted, in order to find the process parameters whose change improves the global efficiency. Huisheng Zhang et al. (2005) presented the dynamic models for the molten carbonate fuel cell (MCFC)-gas turbine hybrid cycle. This paper analyzed the performance of various components in the hybrid power plant, such as the compressor, turbine, recuperator, generator, fuel cell stack, etc. According to Franco Cotana et al. [5], Molten Carbonate Fuel Cells (MCFC) operate at temperatures ranging from 600 to 700°C; high temperatures allow to obtain low internal losses with large benefits in terms of generated electric power. A new geometry for small sized MCFCs is proposed in their paper. Lunghi P. et al. (2004) provides information about a standard molten carbonate fuel cell stack, it has been a source of the knowledge of the ideal number of fuel cells to be used in a stack and the number of stacks needed to optimize the system and the flow rate that will not cause choking of flow or starve the system. It is found from the above literature that MCFC is the best candidate for stationary power generation and in most cases fuelled by natural gas or biogas. It operates at high temperature (more than 650°C) and neither need costly catalysts and external reformers when running on natural gas. MCFC is generally fuelled by pure H<sub>2</sub> as they need CO<sub>2</sub> input. Therefore, the objective of the present work is to develop a thermodynamic model of a MCFC in order to understand their thermodynamic operations i.e. how operating conditions affect the performance of the cell. The effect of different operating parameters like working temperature, fuel utilization, current density, gas constituents etc. on the performance of the basic MCFC are studied to properly to understand the behavior of the cell.

## II. DESCRIPTION OF THE PHYSICAL PROBLEM

In Fig.1, the schematic of an MCFC system considered for present work is shown. The molten LiNa carbonate which is stabilized in a matrix (LiAlO<sub>2</sub>) is considered. Nickel as anode and nickel oxide as cathode is considered in the cell. They are adequate to promote reaction at the high operating temperatures in MCFC. Noble metals are not required. An advantage of the MCFC is the possibility to allow for internal reforming due to the high operating temperatures (600-700°C). The high temperatures improve the oxygen reduction kinetics dramatically eliminating the need for very high loadings of precious-metal catalysts. The fuel constituents which are fed to the anode compartment are CH<sub>4</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and oxidant constituents which are fed to the cathode compartment are O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub> whereas CO<sub>2</sub> is separately supplied to the cathode compartment.

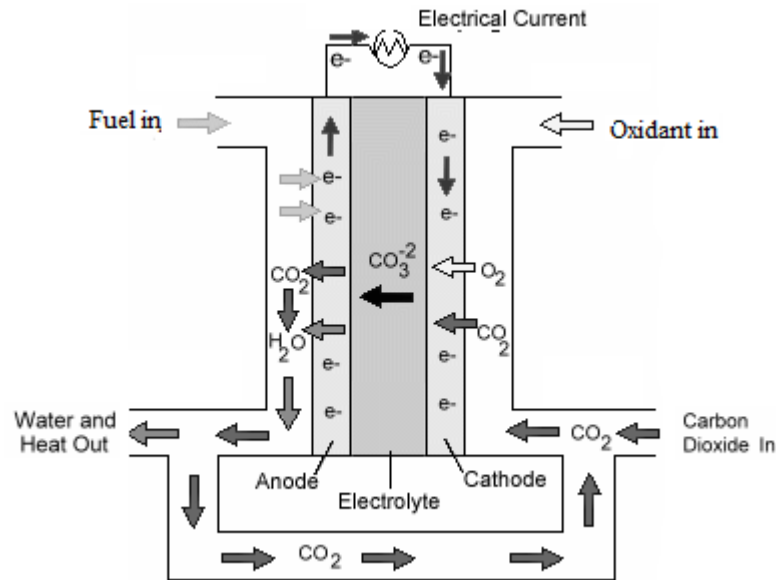


Fig 1: Schematic of a molten carbonate fuel cell system.

### III. MATHEMATICAL ANALYSIS

The performance of a fuel cell depends on electrochemical reaction.  $H_2$ ,  $CO$ ,  $CH_4$  undergoes anodic oxidation. In actuality insignificant direct oxidation of the  $CO$  and  $CH_4$  may occur. It is common practice to assume that  $H_2$ , the more readily oxidized fuel, is produced by  $CO$  and  $CH_4$  reacting, at equilibrium, with  $H_2O$  through the water gas shift and steam reforming reactions, respectively. The  $H_2$  calculated to be produced from  $CO$  and  $CH_4$ , along with any  $H_2$  in the fuel supply steam, is referred to as equivalent  $H_2$ . The temperature and catalyst of present MCFC provide the proper environment for the water gas shift reaction to produce  $H_2$  and  $CO_2$  from  $CO$  and  $H_2O$ . In an internal reforming (IR) MCFC, the reforming reaction to produce  $H_2$  and  $CO_2$  from  $CH_4$  and  $H_2O$  can occur if a reforming catalyst is placed in proximity to the anode to promote the reaction. It is fortunate that converting  $CO$  and  $CH_4$  to equivalent  $H_2$ , then reacting within the cell simplifies analysis while accurately predicting the electrochemical behaviour of the fuel cell.

The electrochemical reactions occurring in MCFC can be written as (Hirschenhofer et al., 1998)

At the anode:



At the cathode:



Overall cell reaction:



Besides the reaction involving  $H_2$  and  $O_2$  to produce  $H_2O$ , the equation shows a transfer of  $CO_2$  from the cathode gas stream to the anode gas stream, with one mole  $CO_2$  transferred along with two Faradays of charge or two gram moles of electrons. The reversible potential for an MCFC, taking into account the transfer of  $CO_2$ , is given by the equation (Hirschenhofer et al., 1998)

$$E = E^\circ - (RT/nF) \ln (p_{H_2O} / p_{H_2} \times (p_{O_2})^{0.5}) + (RT/nF) \ln (p_{CO_2,c} / p_{CO_2,a}) \quad (4)$$

Where the subscripts  $a$  and  $c$  refer to the anode and cathode gas compartments, respectively.

When the partial pressures of  $CO_2$  are identical at the anode and cathode, and the electrolyte is invariant, the cell potential depends only on the partial pressures of  $H_2$ ,  $O_2$ , and  $H_2O$ . Typically, the  $CO_2$  partial pressures are different in the two electrode compartments and the cell potential is affected accordingly, as shown in Eq.4. It is usual practice in an MCFC system that the  $CO_2$  generated at the anode be recycled to the cathode where it is consumed. This will require some type of device. The present work considers a  $CO_2$  transfer device to transfer the  $CO_2$  from the anode exit gas to the cathode inlet gas.

Steam reforming reaction:

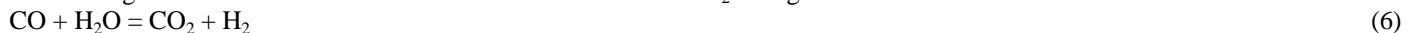
In an internal reforming (IR) MCFC, the reforming reaction to produce  $H_2$  and  $CO_2$  from  $CH_4$  and  $H_2O$  can occur if a reforming catalyst is placed in proximity to the anode to promote the reaction. The steam reforming reaction is given as



The Eq.5 occurs simultaneously with the electrochemical oxidation of hydrogen in the anode compartment.

Water gas shift reaction:

The water gas shift reaction involves the conversion of  $CO$  into  $CO_2$  using steam as an oxidant.



The temperature and catalyst of present MCFC provide the proper environment for the water gas shift reaction to provide  $H_2$  and  $CO_2$  from  $CO$  and  $H_2O$ . The equilibrium constant of the shift reaction

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad (7)$$

The equation (7) can be equilibrate by introducing a variable  $x$ , to represent the extent of the reaction to proceed to the right and rewriting the equation as:

$$K = \frac{[CO_2 + x][H_2 + x]}{[CO - x][H_2O - x]} \quad (8)$$

The Eq.8 can be written as

$$K[CO - x][H_2O - x] = [CO_2 + x][H_2 + x] \quad (9)$$

The Eq. 9 can be arrange and solved as the standard quadratic form as

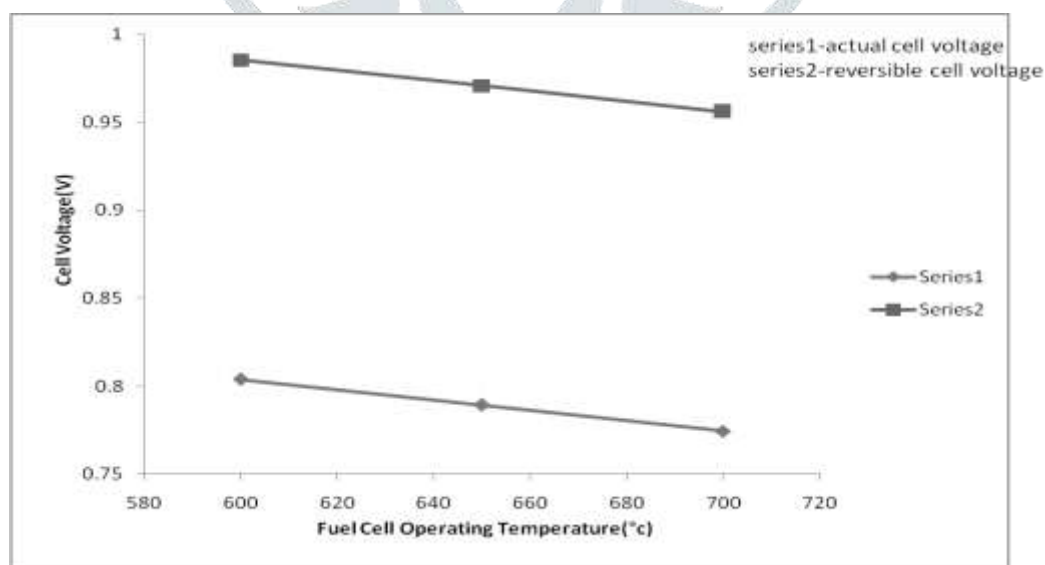
$$(1 - K)x^2 + \{[CO_2] + [H_2] + K([CO] + [H_2O])\}x + \{[CO_2] + [H_2] - K([CO] + [H_2O])\} = 0 \quad (10)$$

### IV. RESULTS AND DISCUSSION

In the present work, thermodynamic analysis of a MCFC is considered for a systematic study of the system. Based on the input data the output results are tabulated in the Table 1.

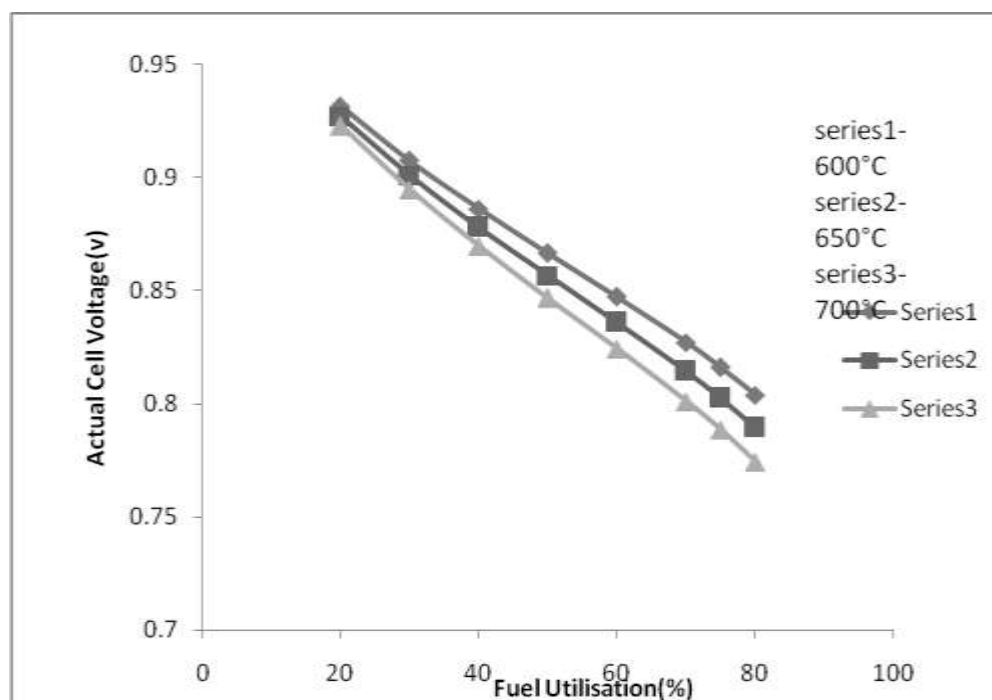
Table 1: Base Case Performance of the fuel cell

Performance Parameter	Value
<b>Input</b> (Hirschenhofer et al., 1998)	
Operating temperature (°C)	650
Operating pressure (atm.)	1
Mass flow rate of fuel (kg/h)	500
Fuel composition (%)	
CH <sub>4</sub>	20
CO <sub>2</sub>	20
H <sub>2</sub> O	60
In oxidant air	70
Utilization of fuel	80
Utilization of oxidant	50
Current density (Ma/cm <sup>2</sup> )	150
Number of cell in a stack	280
<b>Output</b>	
Air required (kg-mole)	172.444977
Composition of the spent fuel (%)	
CH <sub>4</sub>	1.538461
CO	3.500266
CO <sub>2</sub>	47.268967
H <sub>2</sub>	6.038197
H <sub>2</sub> O	41.654114
Composition of spent oxidant (%)	
CO <sub>2</sub>	16.847031
H <sub>2</sub> O	0.922845
N <sub>2</sub>	72.175728
O <sub>2</sub>	10.054399
Total current flowing (amp.)	2014.206909
Nernst cell voltage (V)	0.970825
Actual cell voltage (V)	0.789325
Power generated from the fuel cell stack (MW)	1.589864
Total number of cell	1008
Total number of stack	4
Actual efficiency of the cell (%)	43.223976
Ideal efficiency of the cell (%)	64.617607



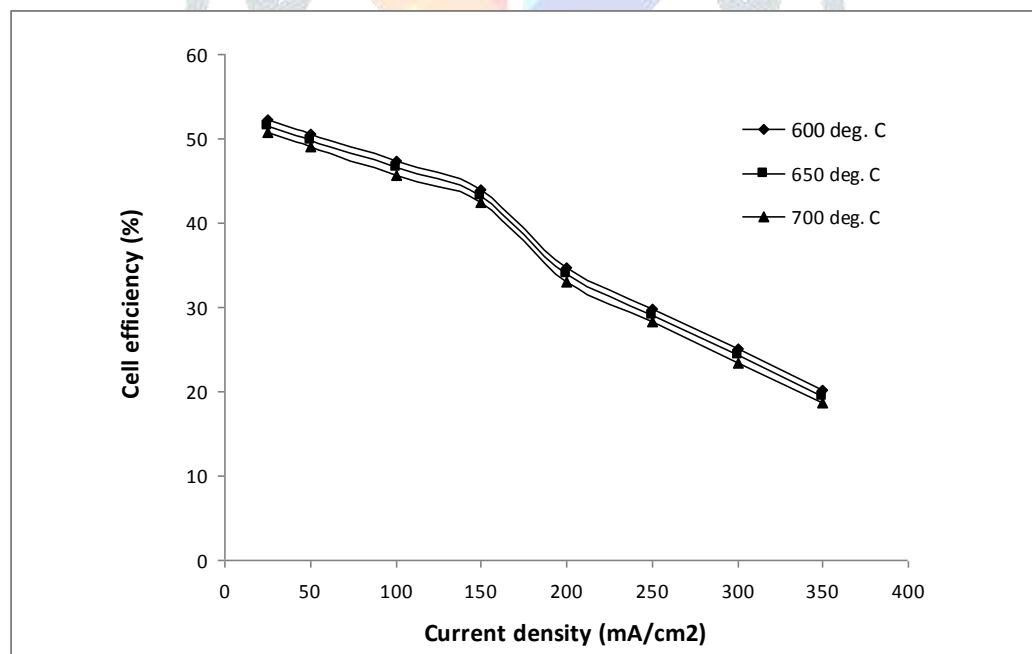
**Fig 2:** Variation of cell voltage with fuel cell operating temperature at current density 150mA/cm<sup>2</sup> fuel utilization 80%, oxidant utilization 50%, operating pressure 1 atm.

In **Fig. 2**, it is seen that the cell voltage of MCFC shows a strong dependence on temperature. The reversible potential decreases linearly with increasing temperature. The actual cell voltage is less than the reversible cell voltage because of the losses occurs in a cell which is taken constant for a range of current density. It is seen from the Nernst equation that as the temperature increases the Cell voltage decreases.



**Fig 3:** Variation of cell voltage with fuel cell temperature at current density  $150\text{mA}/\text{cm}^2$  oxidant utilization 50%, operating pressure 1 atm at three different temperature.

In **Fig. 3**, it is seen that as the fuel utilization increases the cell voltage decreases very rapidly. At higher temperature the decrease in cell voltage is more. The mole fraction of  $\text{H}_2$ ,  $\text{CO}$  in the fuel gas decreases as the utilization of the fuel increases and the mole fraction of  $\text{CO}_2$  at the anode outlet and  $\text{H}_2\text{O}$  shows the opposite trend. At the cathode, the mole fractions of  $\text{O}_2$  and  $\text{CO}_2$  decrease with an increase in utilization because they are both consumed in the electrochemical reaction. An analysis of the data in the figure indicates that a change in the utilization from 20 to 80% will cause a decrease in the reversible potential of about 0.1375 V, or roughly 0.00229 V/% utilization. These results show that MCFCs operating at high utilization will suffer a large voltage loss because of the magnitude of the Nernst term. The above graph implies that MCFCs should be operated at low reactant gas utilization to maintain voltage levels, but doing this means inefficient fuel use. So a compromise must be made to optimize overall performance. Typical utilizations are 75-85% of the fuel and 50% of the oxidant.



**Fig 4:** Variation of Cell Voltage with current density at fuel utilization 80%, oxidant utilization 50%, operating pressure 1 atm at three different temperatures.

In the above **Fig. 4**, it is seen that as the cell voltage of the MCFC system fed by mixture of methane,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  decreases with increasing current density. This decrease in potential depends on the reduction of  $\text{H}_2$  available at the anode from the reforming reaction which is influenced by cell temperature. At current density more than  $150\text{mA}/\text{cm}^2$ , the ohmic loss increases so the cell voltage decreases very sharply. At higher operating temperature the cell voltage is decreased due to the Nernst term. Cell operating at a lower current density and higher voltage (higher efficiency, lower operating cost) might be more suitable for stationary power plant operation.

## V. CONCLUSION

The present work developed a thermodynamic model for a systematic performance study and to understand the thermodynamic behaviour of a MCFC. It is noticed that the cell voltage shows a strong dependence on temperature and the reversible potential decreases linearly with



increasing temperature. It is also seen that as the fuel utilization increases, the cell voltage decreases. The cell efficiency decreases with an increase in cell operating temperature. Result shows that an operating temperature of 650<sup>0</sup>C offers an optimization of better performance and life. Finally, it is noticed that operating at a lower current density, but higher voltage might be more effective (higher efficiency, lower operating cost).

#### REFERENCES

- [1] Roberto, B., Piero, L., Alessio, L. and Nigel, M. S. 2004. Biogas as Fuel for a Fuel Cell System: Investigations and First Experimental Results for a Molten Carbonate Fuel Cell. *Journal of Fuel Cell Science and Technology*, 1(1): 21–24.
- [2] Freni, S., Maggio, G., and Cavailaro, S. 1996. Ethanol steam reforming in a molten carbonate fuel cell: a thermodynamic approach. *Journal of Power Sources*, 62 (1): 67-73.
- [3] Simon, G. De, Parodi, F., Fermeglia, M., and Taccani, R. 2003. Simulation of process for electrical energy production based on molten carbonate fuel cells. *Journal of Power Sources*, 115: 210–218.
- [4] Zhang, H., Weng, S. and Su, M. 2005. Dynamic Modeling on the Hybrid Molten Carbonate Fuel Cell–Gas Turbine Bottoming Cycle”. *Journal of Fuel Cell Science and Technology*, 2(2): 94–98.
- [5] Cotana, F., Rossi, F., and Nicolini A. 2004. A New Geometry High Performance Small Power MCFC. *Journal of Fuel Cell Science and Technology*, 1(1): 25–29.
- [6] Lunghi, P., Bove, R., and Desideri, U. 2004. LCA of a molten carbonate fuel cell system. *Journal of Power Sources*, 137: 239–247.
- [7] Lusardi, M., Bosio, B. and Arato, E. 2004. An example of innovative application in fuel cell system development: CO<sub>2</sub> segregation using Molten Carbonate fuel cell. *Journal of Power Sources*, 131: 351–360.
- [8] Lunghi, P., Bove, R. and Desideri, U. 2003. Analysis and optimization of hybrid MCFC gas turbine plants. *Journal of Power Sources*, 118: 108–117.
- [9] Byoung, S. K., Joon-Ho, K. and Hee C. L. 2002. Effect of system configuration and operating condition on MCFC system efficiency. *Journal of power Sources*, 108: 232–238.
- [10] Hirschenhofer, J.H., Stauffer, D.B., Engleman, R.R., and Klett, M.G. 1998. *Fuel cell handbook*, Fourth Edition, DOE/FETC-99/1076, U.S. Department of Energy.

