

Energy and Exergy analysis of Fuel Cells: A Review

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Abstract

In this paper, the fundamental overview of theoretical and practical aspects of thermodynamics analysis for mainly used fuel cells (FCs) are presented. The FC converts the chemical energy of fuel (normally hydrogen) directly into electrical energy resulting heat and liquid water as a waste products. In first part, governing equation of mass, energy, entropy and exergy are presented according to first law of thermodynamics (FLT) and second law of thermodynamics (SLT), more specifically energy and exergy analysis are covered for fuel cell system. Basic criteria of energy and exergy analysis of flowing and non-flowing system, energy and exergy efficiencies, analysis procedure and models of reference environment are discussed in detail. In the second part, electrochemical reactions and thermodynamics modeling of proton exchange membrane or polymer electrolyte membrane fuel cell (PEMFC), solid oxide fuel cell (SOFC), and molten carbonate fuel cell (MCFC) are presented.

Keywords: Energy, Exergy, Fuel cell, First law of thermodynamics (FLT), Second law of thermodynamics (SLT), Electrochemical, PEMFC, SOFC, MCFC.

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1. Introduction

Today the world is going to find the several ways in the progress of energy generation and conversion which have the key factor to increase the economy of a nation and play a vital role in interaction between nature and society. Since yet, fossil fuels have the main lead to provide the energy resulting environmental pollution and greenhouse emission, especially toxic gasses, such as CO_2 and CO cause the health hazard in urban areas. Hazards to health and environmental degradation due to pollutant air and dangerous non-treatable viruses have been encompassed both locally and globally. With the increasing energy demand of world, many global environmental issues are predicted due to the conventional technologies of production, transformation and use of energy. Conventional energy conversion technologies like power plants that use the fossil fuels such as coal, oil and natural gas, are the major source of acidic rain, global climate change, stratospheric ozone depletion, floods, landslides and so on. These conventional energy conversion technologies are continuously increasing the global warming and health issues. The main reason in developed industrial countries is the environment management mainly CO_2 which causing all the environmental impacts [1, 2, 3, 4]. Reducing emission of CO_2 suggested in Kyoto Protocol proposed mainly three preliminary actions:

1. Introduction of renewable energy resources,
2. New segregation technologies of CO_2 which require initial high investment cost,
3. Acceptation of low emission CO_2 technologies and advancement in high efficiency energy technologies.

In fact, the reduction of CO_2 , CO and other toxic gasses ultimately decrease the thermodynamic efficiency of the energy conversion systems. Intensifying fossil fuel prices, strict environment legislation and continuing consumption of fossil fuels demand urgently a modern highly efficient energy conversion technology with the aim of low carbon emission, cost effective, more efficiently operated and decreasing greenhouse gases to improve the quality of environmental system [5]. The adverse effects such as energy resources depletion, global warming and gradually increasing prices of fossil fuels now have been spurring to explore new beneficial and efficient energy resources to convert the chemical energy of fuels into electricity, building heating and cooling and thermal management of automotives and electronics.

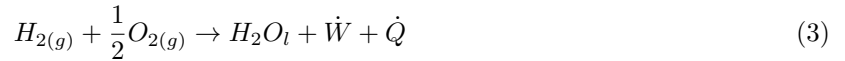
Since yet majority energy conversion technologies are consuming the fossil fuels, however fuel cell has stood itself with a most advanced promising technology which avoid combustion greenhouse gases, with due to directly converting the chemical energy of fuel into electricity through an electrochemical reaction resulting high efficiency, low emissions, and clean operation. Additionally, operating on versatile range of fuels, higher power rate, capability to produce energy both locally and globally, easy installation and operation have made the fuel cell a promising clean, efficient and economics energy conversion technology [6, 5]. Fuel cell, which is electrochemical device, has taken considerable attention in the sight of industrialist to replace the conventional fossil fuels driven energy conversion technologies towards fuel cells operated energy conversion technologies. This review paper covers the thermodynamics analysis based on energy and exergy point of view of three major types of fuel cells (i.e. PEMFC, SOFC and MCFC).

1.1. The fuel cell

The fuel cell converts the chemical energy of hydrogen from fuel directly into electrical energy and resulting emits the waste heat and liquid water. The following generalized electrochemical reactions occur between hydrogen and oxygen:

$$\sum_{rc} N_{rc} \text{reactants} \rightarrow \sum_{pr} N_{pr} \text{products} \quad (1)$$

$$\text{Fuel} + \text{Oxidant} \rightarrow \text{Electric Power} + \text{Waste Heat} + \text{Water} \quad (2)$$



Where \dot{Q} the waste heat rate is produced, \dot{W} is the electric power done, rc and pr are reactants and products respectively. Here $H_{2(g)}$ and $O_{2(g)}$ are chosen as a fuel and oxidant, respectively, to define the fundamental of fuel cell system. Fuel cell has capability in modern energy conversion tools to produce the electric power efficiently in a single step with no moving parts. All the components which convert chemical energy into electrical energy are compact in a single unit cell. Electrolyte is in contact with two electrodes; positive electrode (a cathode) and negative electrode (an anode). The classification of fuel cells are categorized according to the use of electrolyte and fuel is being used [7, 8];

1. Proton Exchange Membrane or Polymer Electrolyte Membrane Fuel Cell (PEMFC)
2. High Temperature PEMFC (HT- PEMFC)
3. Direct Methanol Fuel Cell (DMFC)
4. Molten Carbonate Fuel Cell (MCFC)
5. Phosphoric Acid Fuel Cell (PAFC)
6. Solid Oxide Fuel Cell (SOFC)
7. Alkaline Fuel Cell (AFC)

Table 1: Fuel Cells classifications [6]

Characteristics	Polymer Electrolyte	Alkaline	Phosphoric Acid	Molten Carbonate	Solid Oxide
FCs operating temperature	40 – 80°C	65 – 220°C	205°C	650°C	600 – 1000°C
Electrolyte	Hydrated polymeric ion Exchange membrane	Mobilized or immobilized potassium hydroxide in asbestos matrix	Immobilized liquid phosphoric acid in <i>Sic</i>	Immobilized liquid molten carbonate in <i>LiAlO₂</i>	Perovskites (ceramics)
Electrode	Carbon	Platinum	Carbon	Nickel and nickel oxide	Perovskite and perovskite/metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or nickel	Nickel, ceramic or steel
Charge carrier	H^+	OH^-	H^+	CO_3^+	O^-

The complete summary specifications of above fuel cells are presented in Table 1 [6]. The following are the power systems which can be powered by fuel cells operating at different ranges of input powers [9, 6, 10];

1. At power range of 1 – 10kW: Mobile phone, laptops, personal digital assistants (PDAs), portable electronics devices etc.
2. At power range of 1 – 100kW: Power automobiles, public transportation i.e. buses, cars, mini-trains, etc.
3. At power range of 1 – 1MW: Energy power system to provide electricity and cogeneration systems.

2. What is Energy and Exergy Analysis?

Energy and exergy are two basic fundamental terminologies associated to any thermodynamic system to determine its quantity and quality of the system performance. Energy, a measure of ability to do a useful work, which exists in variety of forms i.e chemical, mechanical, thermal, nuclear, electrical. Energy law states that *energy can neither be created nor destroyed but it can change from one form to another form*, by first law of thermodynamics (FLT) which is the conservation of energy. FLT describes the transformations of energy in other forms of any energy conversion system. FLT actually quantifies the amount of energies supplied are equal to amount of energies exited. In any energy conversion system, energy analysis deals the energy balance of all forms of energies at inlet and outlet of the system. Entering energy can be a single or multiple forms at the inlet of a specific device or overall the system but exciting energies come in form of products and wastes. Exergy analysis, the second part of thermodynamics analysis of energy conversion power systems, illustrates the quality of energies flow through the system. Energy analysis often misleads and does not provide the actual picture of system performance that how much the system approaches to ideality. Additionally, energy analysis does not identify and quantify those factors which cause of the thermodynamics losses inside the system resulting deviating the system from ideality. Energy analysis of has many shortcomings which do not indicate the inefficiencies within actual sections of the system. To overcome this limitations, exergy analysis based on the second law of thermodynamics (SLT) covers the many deficiencies of the energy conversion system that needed to be overcome. Exergy analysis measures the degradation of available energy and identifies the causes, locations and true magnitude of energy losses due to system inefficiencies. Exergy actually provides the available energy, availability, work capability, work potential, essergy and so on. To get the maximum work or energy potential from input energies it is necessary to operate the system undergoing different processes on reversible manners. However, in actual processes there are always losses which cause of the loss of work potential resulting the irreversibility in process. These losses are generally due to the irreversibilities in flow of energy in different processes. The exergy consumption is actually called the irreversibility, loss of work potential, dissipated work and dissipation or looseness.

3. Fundamental governing equations of thermodynamic analysis

The general relation of a quantity carrying energy through the system may be expressed as follows [11]:

$$Input + Generation - Output - Consumption = Accumulation \quad (4)$$

Here, the input and output are energy quantities entering and leaving through an energy conversion system boundaries, respectively. Generation and consumption are referred to the quantities which are produced and consumed inside the system volume, respectively. Finally the accumulation refers to the developed of a quantity either positive or negative inside the system [5]. The above equation 4 can be written individually for the mass, energy, entropy, and exergy as well. The mass and energy equations are associated with energy conservation law i.e. FLT which means that it can be degraded but not consumed or generated. The equation 4 for mass and energy can be as follows:

$$\text{Mass Input} - \text{Mass Output} = \text{Mass Accumulation} \quad (5)$$

$$\text{Energy Input} - \text{Energy Output} = \text{Energy Accumulation} \quad (6)$$

The entropy and exergy quantities are associated with SLT with are due the irreversibilities occurred during a process which cannot be consumed, can be examined as follows:

$$\text{Entropy Input} + \text{Entropy Generation} - \text{Entropy Output} = \text{Entropy Accumulation} \quad (7)$$

$$\text{Exergy Input} - \text{Exergy Output} - \text{Exergy Consumption} = \text{Exergy Accumulation} \quad (8)$$

It can be seen from Equations 7 and 8 that exergy is consumed due to irreversibilities and exergy consumption is proportional to entropy creation. The difference between energy and exergy can be demonstrated from Equations 6 and 8 that energy is conserved while exergy can be consumed which is measure of energy quality or work potential.

4. Energy and exergy balance of thermodynamics systems

In thermodynamics, generally there are two type of systems are considered: closed system (non-flow) and open system (flow). Further, the closed system and open system are also called control mass and control volume system, respectively. In control mass systems, generally there is no interaction of mass only heat and work can transfer in or out through the system boundaries. Contrarily, in control volume systems mass, heat and work can transfer through the system boundaries. The mathematical formulation of physical interpretations of conservative quantities mass and energy and non-conservative quantities entropy and exergy can be written for a control volume, non-steady flow process between time interval of t_1 and t_2 as follows:

$$\sum_i m_i - \sum_o m_o = \Delta m \quad (9)$$

Here, m_i and m_o are representing the mass flow in and out across the system boundaries. For mass flow m within a control volume of time interval t_1 to t_2 :

$$m = \int_{t_1}^{t_2} \left[\oint (\rho V_n dA) \right] dt \quad (10)$$

Here, the ρ is density of matter flowing across the dA in time interval of t_1 and t_2 . V_n is the normal velocity vector at the surface of dA of the matter m .

For one dimensional flow, along which the velocity and mass do not vary position over the control surface:

$$m = \int_{t_1}^{t_2} (\rho V_n A) dt \quad (11)$$

The quantity m of Equation 9 in the control volume can be expressed in generalized form as following;

$$m = \int \rho dV \quad (12)$$

4.1. FLT Balances

From FLT, the energy balance for a control volume can be expressed as follows:

$$\sum_i (e + Pv)_i m_i - \sum_o (e + Pv)_o m_o + (Q)_{1,2} - (W)_{1,2} = \Delta E \quad (13)$$

The specific energy e is given as follows:

$$e = u + ke + pe \quad (14)$$

Here, u , ke , and pe are internal energy, kinetic energy and potential energy, respectively. The Equation 13 becomes as following, by substituting e :

$$\sum_i (u + ke + pe + Pv)_i m_i - \sum_o (u + ke + pe + Pv)_o m_o + (Q)_{1,2} - (W)_{1,2} = \Delta E \quad (15)$$

From the definition of enthalpy $h = u + Pv$, the Equation 15 would be:

$$\sum_i (h + ke + pe)_i m_i - \sum_o (h + ke + pe)_o m_o + (Q)_{1,2} - (W)_{1,2} = \Delta E \quad (16)$$

Neglecting the terms ke and pe for non moving system the final form of energy equation as follows:

$$\sum_i h_i m_i - \sum_o h_o m_o + (Q)_{1,2} - (W)_{1,2} = \Delta E \quad (17)$$

It is assumed that for a closed surface, the heat transfer and temperature are constant. If the temperature varies in time interval of t_1 to t_2 :

$$(Q)_{1,2} = \int_{t_1}^{t_2} \left[\oint (q dA) \right] dt \quad (18)$$

and

$$E = \int \rho e dV \quad (19)$$

In form of molar flow, molar enthalpy, at same temperature T and pressure p during the reaction process, the energy balance from FLT as follows [12, 13, 14, 15]:

$$\tilde{G} \sum_i \tilde{h}_i m_i - \tilde{G} \sum_o \tilde{h}_o m_o + (Q)_{1,2} - (W)_{1,2} = \Delta E \quad (20)$$

For steady state process of the system the Equation 20 can be written as:

$$\tilde{G} (\sum_i \tilde{h}_i m_i - \sum_o \tilde{h}_o m_o) + Q + W = 0 \quad (21)$$

Here, \tilde{G} and \tilde{h} are the molar flow and molar enthalpy respectively. The molar enthalpy of reactants and products, respectively, at the inlet and out can be written as [12, 13, 14, 15];

$$\tilde{h}_i = \tilde{h}_{rc} = \frac{1}{N_f} \sum_{rc} N_{rc} \tilde{h}_{rc} = \tilde{h}_f + \frac{\tilde{G}_{ox}}{\tilde{G}_f} \tilde{h}_{ox} \quad (22)$$

and

$$\tilde{h}_o = \tilde{h}_{pr} = \frac{1}{N_f} \sum_{pr} N_{pr} \tilde{h}_{pr} = \frac{\tilde{G}_{pr}}{\tilde{G}_f} \tilde{h}_{pr} \quad (23)$$

Here, f is fuel, ox is oxidant, pr is products, rs is reactants, i and o are inlet and outlet of system boundaries.

4.2. SLT Balances

Principle of non-conservation, the SLT balances the entropy and exergy for a non-steady flow process during time interval of t_1 to t_2 the, as follows [12, 13, 14, 15]:

$$\sum_i s_i m_i - \sum_o s_o m_o + \left(\frac{Q}{T}\right)_{1,2} + S_{g,1,2} = \Delta S \quad (24)$$

and

$$\sum_i ex_i m_i - \sum_o ex_o m_o + (Ex_Q)_{1,2} - (Ex_W)_{1,2} - (W_{net})_{1,2} - I_{1,2} = \Delta Ex \quad (25)$$

Here, for varying temperature, the heat transfer can be as follows:

$$\left(\frac{Q}{T}\right)_{1,2} = \int_{t_1}^{t_2} \left[\oint (q/T) dA \right] dt \quad (26)$$

and

$$S = \int \rho s dV \quad (27)$$

Where, $(Ex_Q)_{1,2}$, $(W_{net})_{1,2}$ and $I_{1,2}$ can be given as follows:

$$(Ex_Q)_{1,2} = \int_{t_1}^{t_2} \left[\oint (1 - T_o/T) dA \right] dt \quad (28)$$

$$(W_{net})_{1,2} = W_{1,2} - P_o(V_2 - V_1) \quad (29)$$

$$I_{1,2} = T_o S_{g,1,2} \quad (30)$$

and

$$Ex = \int \rho \xi dV \quad (31)$$

In terms of molar flow \tilde{G} and molar entropy \tilde{s} , the Equation 24 can be written as:

$$\tilde{G} \sum_i s_i m_i - \tilde{G} \sum_o s_o m_o + \left(\frac{Q}{T} \right)_{1,2} + S_g = \Delta S \quad (32)$$

For steady-state system, the Equation 30 can be written as follows [12, 13, 14, 15]:

$$\tilde{G} \left(\sum_i s_i m_i - \sum_o s_o m_o \right) + \left(\frac{Q}{T} \right) + S_g = 0 \quad (33)$$

Here, the molar entropy of reactants and products, respectively, at the inlet and out can be written as;

$$\tilde{s}_i = \tilde{s}_{rc} = \frac{1}{N_f} \sum_{rc} N_{rc} \tilde{s}_{rc} = \tilde{s}_f + \frac{\tilde{G}_{ox}}{\tilde{G}_f} \tilde{s}_{ox} \quad (34)$$

and

$$\tilde{h}_o = \tilde{s}_{pr} = \frac{1}{N_f} \sum_{pr} N_{pr} \tilde{s}_{pr} = \frac{\tilde{G}_{pr}}{\tilde{G}_f} \tilde{s}_{pr} \quad (35)$$

Now dividing the Equation 21 and 32 by molar flow of fuel, \tilde{G} and we know the Gibbs molar potential is $\tilde{g} = \tilde{h} - T\tilde{s}$. The equation becomes as follows:

$$\tilde{q}_o = T(\tilde{s}_o - \tilde{s}_i) + T\tilde{s}_g \quad (36)$$

and

$$\tilde{w}_o = \tilde{g}_i - \tilde{g}_o + T\tilde{s}_g \quad (37)$$

Here, $\tilde{s}_g = \tilde{S}_g/\tilde{G}$ molar specific entropy generation, $\tilde{w}_g = W/\tilde{G}$ molar specific work, and $\tilde{q}_g = Q/\tilde{G}$ molar specific heat.

For a closed system, the FLT and SLT balances can be written as follows:

$$0 = \Delta m = m_2 - m_1 \quad (38)$$

as for closed system, $m_i = m_o = 0$

$$(Q)_{1,2} - (W)_{1,2} = \Delta E = E_2 - E_1 \quad (39)$$

$$\left(\frac{Q}{T}\right)_{1,2} + S_{g,1,2} = \Delta S = S_2 - S_1 \quad (40)$$

and

$$(Ex_Q)_{1,2} - (Ex_W)_{1,2} - (W_{net})_{1,2} - I_{1,2} = \Delta Ex = Ex_2 - Ex_1 \quad (41)$$

5. Exergy of non-flow and flow Systems

A detail discussion of exergy balances of flow (open system) and non-flow (closed system) are presented individually as follows:

5.1. Exergy of non-flow system

The exergy of non-flow or closed system of mass m can be written as [16, 17, 18]:

$$Ex_{non-flow} = Ex_{pe} + Ex_{ke} + Ex_{ch} + Ex_{ph} = m(ex_{pe} + ex_{ke} + ex_{ch} + ex_{ph}) \quad (42)$$

where

$$Ex_{pe} = PE = g(z - z_o) \quad (43)$$

$$Ex_{ke} = KE = \frac{1}{2}(V^2 - V_o^2) \quad (44)$$

$$Ex_{ch} = \sum_j (\mu_{jo} - \mu_{joo}) N_j \quad (45)$$

$$Ex_{ph,non-flow} = (U - U_o) + P_o(V - V_o) - T_o(S - S_o) \quad (46)$$

Here, the right hand side of Equation 42 are representing potential, kinetic, chemical and physical components, respectively, of the non-flow exergy. Further, system has temperature, pressure, entropy, internal energy, volume and enthalpy as T , P , S , U , V , and H , respectively. The N_j is the number of moles of species j , μ_{jo} is chemical potential at environment state i.e. T_o and P_o of species j and μ_{joo} is the chemical potential of species of j in non-flow system taken at reference or dead environment in an equilibrium state.

5.2. Exergy of Flow system

The exergy of flow or open system is the summation of exergy of non-flow and exergy of flow work of the flowing stream across the system boundaries at reference pressure P_o :

$$Ex_{flow} = Ex_{non-flow} + (P - P_o)V \quad (47)$$

Here, the Ex_{flow} similarly can be expressed as in Equation 42

$$Ex_{flow} = Ex_{pe} + Ex_{ke} + Ex_{ch} + Ex_{ph} = m(ex_{pe} + ex_{ke} + ex_{ch} + ex_{ph}) \quad (48)$$

Where;

$$Ex_{pe} = PE = g(z - z_o) \quad (49)$$

$$Ex_{ke} = KE = \frac{1}{2}(V^2 - V_o^2) \quad (50)$$

$$Ex_{ch} = \sum_j (\mu_{jo} - \mu_{joo}) N_j \quad (51)$$

$$Ex_{ph,flow} = (H - H_o) - T_o(S - S_o) \quad (52)$$

Exergy transfer associated with heat transfer at location with temperature of T . For a control mass, at a dead state with its initial state, as it is heated or cooled causes the transfer of heat which resulting exergy transfer. So heat transfer by mass m is Q . For a control volume, the exergy associated with thermal energy Q at temperature T can be expressed for initial i and final states f as follows:

$$Ex_Q = \int_i^f \left(1 - \frac{T_o}{T}\right) \delta Q \quad (53)$$

Here, δQ is amount of heat transfer during the time interval. During heat transfer, entropy transfers equal to the amount of Q/T and exergy transfers equal to the amount of $(1 - T/T_o)$. From Equation 53 it can be identified that thermal exergy is minimum amount of heat energy needed for a control mass and reference environment to accomplish the system from its dead state to final state.

Introducing the dimensionless factor called *exergetic temperature factor* for terms $(1 - T/T_o)$ denoted by τ [18, 16]:

$$\tau = 1 - \frac{T}{T_o} \quad (54)$$

For a constant temperature, the thermal exergy associate with heat transfer can be as follows:

$$Ex_Q = \left(1 - \frac{T_o}{T}\right) Q = \tau Q \quad (55)$$

For a control surface, the thermal exergy can be written as:

$$Ex_Q = \int \left[q \left(1 - \frac{T_o}{T}\right) dA \right] \quad (56)$$

Here, q is heat flux, the heat transfer per unit area on the control surface with a temperature T .

Exergy which is the maximum useful work potential of the system, can be expressed as follows [19]:

$$W_{net} = \begin{cases} W - W_{sur} & \text{for boundary work} \\ W & \text{for other forms of work} \end{cases} \quad (57)$$

Here, a boundary work, the net work due to change of volume, thus can be defined as follows for a time interval of t_1 to t_2 :

$$(W_{net})_{1,2} = W_{1,2} - P_o(V_2 - V_1) \quad (58)$$

Where, P_o is reference pressure due to the environment exerted against the work done by the system during process while $W_{1,2}$ work by changing the volume of system. It can be clearly revealed that exergy exerted by shaft work and electric work is equal to the work W or energy itself.

The exergy of mass of varying fluid properties can be defined as:

$$Ex_m = mEx_{flow} = \int_{t_1}^{t_2} \int_A Ex_{flow} \rho V_n dA_c dt \quad (59)$$

During the flow process, there are always irreversibilities which are due to frictional effects, sudden contraction or expansion, heat losses due to finite temperature gradient, non-equilibrium compression and expansion processes, mixing and chemical reactions which causes to increase of entropy generation. Any phenomenon which generates the entropy resulting the *exergy consumption* or *exergy destruction*, which is less than exergy accumulation is expressed as follows:

$$I = T_o S_g \geq 0 \quad (60)$$

The Equation 60 is called Gouy-Stodola relation. Hence the exergy destroyed or accumulation is proportional to entropy generation or creation. Further, exergy destroyed is positive quantity which is greater than 0 for actual processes and equal to 0 for reversible processes. Overall, the exergy destroyed in any thermodynamic system is actually the loss of useful work potential, also called *irreversibility* or *lost work* [19].

Note, for an adiabatic system the exergy transfers by thermal energy Ex_Q and for closed system the exergy transfers by mass Ex_m is zero. Additionally, for isolated system (no interaction of mass, heat and work) the total exergy Ex is zero.

6. Energy and exergy efficiencies and procedure analysis

6.1. Energy and exergy efficiencies

In any thermodynamic system, efficiency is an key factor regarding making a decision for any input resource utilization. Efficiency can be defined as *the quality level of something to extracts from the something else waste of, or with minimum utilization energy resources for of time and cost, or degree of improvement or effectiveness to perform a task.*

In general, to quantify the level of achievement efficiencies are determined by the ratio of two non-dimensionless parameters. Efficiencies are generally expressed on the basis of FLT and SLT. From FLT, ratios of energies are defined for those systems whose primary purpose is the transformation or conversion

of energies. According to FLT analysis, a process or cycle has best or maximum efficiency has if the input or provided energy equals to the output or recoverable energy with minimum losses or no energy losses. However, the efficiencies carried out using FLT analysis approach have some limitation or misleading. These do not approach the measure of ideality of the system.

To measure the actual approach of the system processes how is accomplished towards the ideality, the SLT efficiency analysis approach is used. SLT efficiency analysis displays the how much maximum efficiency is obtained or ideality can be achieved for a reversible process. From SLT, it is noted that entropy is created due to irreversibilities only in non-ideal or irreversible processes called *increase of entropy principle*. The maximum efficiency is achieved when the entropy is conserved for a process.

Hfele [20] discussed a meaningful quantity negentropy to measure the efficiency, which is defined as *negentropy destruction and entropy generation are equal to each other which are due to the irreversibilities*. Like the entropy, negentropy is conserved and maximum efficiency is achieved in such a process in which it is conserved. Negentropy is the measure of the order so the degradation of the order means there is the consumption or destruction of negentropy. Moreover, negentropy is further described as the ability to perform work. So the maximum efficiency is only possible if sum of all the input energies, to perform a process or cycle, must do an equal amount of work and should be equal to sum of all energies attained after the completion of process or cycle.

Exergy, like negentropy, has the ability to perform maximum work and consequently maximum efficiency is only possible when all the exergy is conserved. Gaggioli [21] calls the exergy efficiency is a *true* or *real* efficiency, as it considers the non-ideality of the process. Ibrahim and Rosen [16] expressed the general forms of energy and exergy efficiencies for a steady-state process as follows:

$$\eta = \frac{\text{Output Energy}}{\text{Input Energy}} = 1 - \frac{\text{Energy Loss}}{\text{Input Energy}} \quad (61)$$

$$\psi = \frac{\text{Output Exergy}}{\text{Input Exergy}} = \frac{\text{Exergy Loss plus Consumption}}{\text{Input Exergy}} \quad (62)$$

The other two forms of exergy efficiency for steadily operating devices can be as follows:

$$\text{Rational Efficiency} = \frac{\text{Total Exergy Recovered}}{\text{Total Exergy Supplied}} = 1 - \frac{\text{Exergy Destruction}}{\text{Total Exergy Supplied}} \quad (63)$$

and

$$\text{Task Efficiency} = \frac{\text{Theoretical Minimum Input Exergy}}{\text{Actual Input Exergy}} \quad (64)$$

Generally, exergy efficiencies reveal the clear picture of energy contents of the system as per its exergy contents and separate the inefficiencies associated with irreversibilities. Furthermore, exergy efficiencies measure the potential needed for improvement.

6.2. Energy and exergy procedure analysis

A generalized procedure for analyzing energy and exergy analysis of thermodynamic system comprises the following steps:

- Subdivide the system into different sections as per the components comprising the whole system for easy understanding and detail depth analysis.
- Apply fundamental governing equations i.e. mass and energy balances on the subsections and determine basic quantities e.g. heat and work and properties e.g. temperature and pressure.
- Describe the nature of the process and select the reference environment model.
- Perform exergy balance and determine the exergy destruction of each component of the system.
- As per the reference environment, calculate the energy and exergy quantities.
- Calculate the efficiencies as per the desired efficiency model.
- Perform the interpretation of required results and give discussion and recommendation relating issues of system design, operating parameters and system modifications etc.

7. Reference environment and models

In SLT analysis, generally exergy is evaluated with respect to a reference environment. The intensive properties of reference environment is used as model or reference to determine the ideality of the process. The selected reference environment is stable both in thermal and chemical equilibrium relative to its own parameters. The reference environment acts as sink and is a infinite internally reversible system which means that its intensive properties such as temperature T_o , pressure P_o , chemical potential μ_{joo} do not change and remain constant. Exergy of reference environment and system under analysis is zero when it is on totally equilibrium with reference environment.

However, it is observed that the theoretical characteristics of natural environment are varying both in temporal and spatial coordinates as for the reference environment. As natural environment does not remain in equilibrium because of its variation in intensive properties, thus exergy is not zero. Consequently, different models have been presented for the reference environment to achieve the minimum deviation between theoretical and actual natural environment.

7.1. Models for reference environment

Several reference environment models presented by different researchers are following:

1. **Natural-Environment-Subsystem Model:** Firstly presented by Baehr and Schmidt [22]. Extension was presented by Gaggioli and Petit [23] and Rodriguez [24]. The pressure P_o and Temperature T_o are presented in this model are chosen 25°C and 1atm respectively. The Table 2 presents the natural-environment-subsystem model.
2. **Reference-Substance Models:** Presented by Szargut [25] in which a reference substance is selected and assigned zero exergy value. Then further proposed by Sussman [26, 27], who arbitrary selected the reference substance.
3. **Equilibrium Models:** Proposed by Ahrendts [28] and selected equilibrium composition of all the materials, present in atmosphere, oceans and layer of earth's crust at a given temperature.

Table 2: Reference–Environment Model [16]

$T_o = 298.15K$	
$P_o = 1atm$	
At T_o and P_o , the composition of saturated air as follows;	
Elements	Mole Fraction
N_2	0.7567
O_2	0.2035
H_2O	0.0303
Ar	0.0091
CO_2	0.0003
H_2	0.0001

4. **Constrained-Equilibrium Models:** Modified by further by Ahrendts [28]. Excluded the formation of nitric acid (HNO_3) and its composition in equilibrium model.
5. **Process-Dependent Models:** Presented by Bosnjakovic [29] and considered only that components which participate in the process at stable equilibrium.

8. Energy and exergy analysis of PEMFC

Proton Exchange Membrane or Polymer Electrolyte Membrane Fuel Cell (PEMFC) is very promising electrochemical energy conversion device for light duty application, maximum temperature of $90^\circ C$, for auto-mobiles, buildings, electronics rechargeable batteries etc.[30]. It has become an eye catching energy conversion device for efficient and eco-friendly because of its maximum conversion of chemical energy into electricity energy without any emission gases and moving parts. The fuel, pure hydrogen, is feed from the anode side plate of the cell and comes in contact with proton exchange membrane thin plastic sheet, coated with active catalysts of metal alloy namely platinum, the catalysts split the hydrogen into electron and proton (hydrogen ions). The electron are passed through a electric circuit where it produced electricity before going directly towards cathode side plate of fuel cell to make a closed loop. At cathode side plate, the oxygen is fed which reacts to defused electron and proton together resulting produced pure 99.9% and heat. A schematic of working principle of PEMFC is shown in Figure 1. The protons transport in PEMFC are classified two categorizes; (i) *Grothuss mechanism* and (ii) *vehicle mechanism*, the difference is shown in Figure 2. PEMFC is provide an alternative source of energy especially replacement of internal combustion engine is transport vehicles.

In last five years there are a few studies have been reported on PEMFC with different hybrid applications. Nguyen et, al. [33] performed the exergy analysis of PEMFC with heat recovery system for preheating of air of standalone solar-hydrogen system to increase the performance of PEMFC. HOMER and TRNSYS softwares coupled with MATLAB were used for modeling of PEMFC heat recovery system and compared with external heater. Rahimi et, al. [34] carried out a significant study of a wind-hydrogen hybrid system comprises of wind turbine, electrolysis, and PEMFC to produce the hydrogen via electrolysis. Gandiglio et, al. [35] performed the design and optimization study of a micro-cogeneration system based on PEMFC having capacity of $1kWe$. Fuel cell stack, with an average temperature of $62^\circ C$, and heat recovery system was analyzed under mass and energy balance and efficiencies were obtained. Ratlamwala et, al. [31] presented parametric study on the concept of flow channels in PEMFC for operating parameters and obtained an

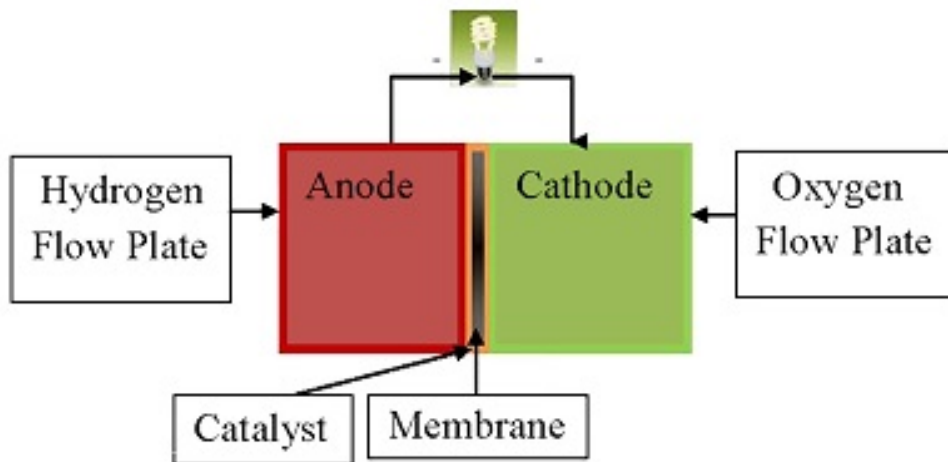
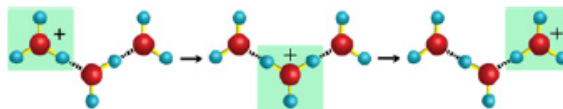


Figure 1: Schematic diagram of a PEMFC. [31]

Grotthuss mechanism



vehicle mechanism

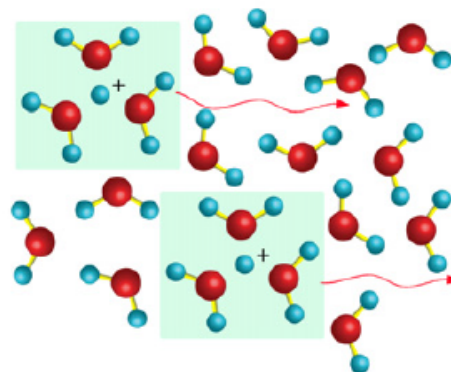
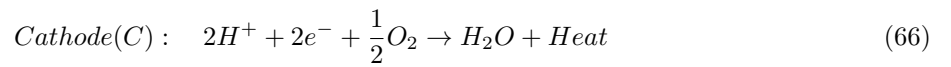


Figure 2: Schematic representation of protons mechanism in PEMFC. [32]

increase of efficiency from 33.8% to 47.7% and from 2.6 to 282.5W increase in output power. Mert et, al. [36] performed a comprehensive parametric investigation of a PEMFC for transportation system through energy and exergy analysis. Thermodynamics analysis was performed for compressor, humidifiers, pressure regulator, cooling system and fuel cell stack. Authors predicated the improvement in exergy efficiency of 8% with the increase of temperature and pressure, humidity about 10%. Ni et, al. [37] carried out the energy and exergy analysis of a PEM electrolyzer plant for hydrogen production. Authors found that energy efficiency decreased by increasing temperature, lowering current density, reducing electrolyte thickness and increasing the electrode catalytic activity. Caliskan et, al. [38] carried out energy, exergy and sustainability analysis of various energy conversion systems such as geothermal, wind energy turbine, solar PV panels, inverter, electrolyzer, hydrogen storage system, PEMFC and battery systems. Zafar and Dincer [39] conducted the analysis of a hybrid renewable energy system consisting of wind turbine, PV and fuel cell to provide power and heat to residential application. Further energy and exergy efficiencies were calculated for the overall system. Ahmadi et, al. [40] conducted a parametric study of hybrid hydrogen production system via ocean thermal energy conversion system coupled with solar-enhanced PEM electrolyzer. The system was comprised of turbine, evaporator, condenser, pump, solar collector, and PEM electrolyzer. Hydrogen production, exergy efficiency of each component, and exergy destruction were calculated. Fukuhara et al. [32] carried out the preparation of PEMFC with nanomatrix channel to investigate the activation energy of proton conductivity. Recently, Taner [41, 42, 43] conducted the experimental study of PEMFC and investigated the effective parameters and optimized the water conditions. Further, author performed the energy and exergy analysis of PEMFC in terms of pressure and voltage parameters, and reported the energy and exergy efficiencies of 47.6% and 50.4%, respectively.

8.1. Electro-Chemical analysis of PEMFC

The electro-chemical reactions inside the PEMFC can be expressed as follows:



Ref. [31] presented the following relations to calculate the molar fractions of hydrogen and oxygen at anode and cathode, respectively:

$$X_{H_2} = \frac{1 - \chi_{H_2O,A}}{1 + \frac{\chi_A}{2} \times \left[1 + \frac{\varsigma_A}{\varsigma_A - 1}\right]} \quad (68)$$

and

$$X_{O_2} = \frac{1 - \chi_{H_2O,C}}{1 + \frac{\chi_C}{2} \times \left[1 + \frac{\varsigma_C}{\varsigma_C - 1}\right]} \quad (69)$$

Water molar fractions at anode and cathode can be calculated using saturation pressure P_{sat} as follows:

$$X_{H_2O,A} = \frac{P_{sat}}{P_A} \quad (70)$$

and

$$X_{H_2O,C} = \frac{P_{sat}}{P_C} \quad (71)$$

Further, P_{sat} of fuel cell based of hydrogen temperature can be obtained as:

$$P_{sat} = 10^{(-2.1794+0.02953 \times T - 9.1837 \times 10^{-5} \times T^2 + 1.4454 \times 10^{-7} \times T^3)} \quad (72)$$

The electrical power is known as follows:

$$P = V \times I \quad (73)$$

$$P_{PEMFC} = V_{PEMFC} \times j \quad (74)$$

Here, V_{PEMFC} is the input voltage and j is the current density. To avoid the effect of area, j is presented as follows:

$$j = \frac{I}{A} \quad (75)$$

8.2. PEMFC Cell Voltage

The overall PEMFC voltage can be expressed as difference of reversible and irreversible cell voltage.

$$V_{PEMFC} = V_{rev} - V_{irrev} \quad (76)$$

8.2.1. Reversible cell voltage

The reversible (maximum) voltage can be produced without irreversibilities. The reversible cell voltage can be obtained using famous Nernst Equation, as follows:

$$V_{rev} = \frac{-\Delta G^\circ}{n_e F} + \frac{RT_{FC}}{n_e F} \ln \left(\frac{P_{H_2} \sqrt{P_{O_2}}}{P_{H_2O}^{sat}} \right) \quad (77)$$

Here, ΔG° is the Gibbs free energy change, n_e is the number of electrons transferring in electrochemical reaction ($= 2$), F is the Faraday constant, R is the universal gas constant ($= 8.314 J mol^{-1} K^{-1}$), T_{FC} is the operating temperature of PEMFC, P_{H_2} and P_{O_2} are the partial pressures of H_2 and O_2 , respectively and $P_{H_2O}^{sat}$ is saturation pressure of water vapor.

Where, the partial pressures of H_2 and O_2 can be calculated as [36, 44]:

$$P_{H_2} = \left(\frac{1}{2} P_{H_2O}^{sat} \right) \left[\frac{1}{\exp \left(\frac{1.653j}{T_{FC}^{1.3334}} \right) \cdot \chi_{H_2O}} - 1 \right] \quad (78)$$

and

$$P_{O_2} = P \left[1 - \chi_{H_2O} - \chi_{N_2} \exp \left(\frac{0.291j}{T_{FC}^{0.832}} \right) \right] \quad (79)$$

Here, χ_{H_2O} and χ_{N_2} are the molar fraction of water and nitrogen, P is the operating pressure of fuel cell, j is current density. Further, water molar fractions at anode and cathode can be calculated using P_{sat} , as follows:

$$\chi_{H_2O}^{sat} = \frac{P_{H_2O}^{sat}}{P} \quad (80)$$

The molar fraction of nitrogen in the air stream is calculated by the ratio of difference of molar fraction nitrogen in and out to log mean average of molar fraction nitrogen in and out of humidified air.

$$\chi_{N_2} = \frac{\chi_{N_2,in} - \chi_{N_2,out}}{\ln(\chi_{N_2,in}/\chi_{N_2,out})} \quad (81)$$

where,

$$\chi_{N_2,in} = 0.79 (1 - \chi_{H_2O}^{sat}) \quad (82)$$

and

$$\chi_{N_2,out} = \frac{1 - \chi_{H_2O}^{sat}}{1 + ((\lambda_{air} - 1)/\lambda_{air}) \left(\frac{0.21}{0.79} \right)} \quad (83)$$

where, λ_{air} is the stoichiometric rate of air, $\chi_{N_2,in}$ and $\chi_{N_2,out}$ are the molar fraction of nitrogen at the inlet and outlet respectively.

The saturation water vapor pressure can be expressed from following empirical relation [45, 46]:

$$\log_{10} (P_{H_2O}^{sat}) = -2.1794 + 0.02953t - 9.1837 \times 10^{-5}t^2 + 1.4454 \times 10^{-7}t^3 \quad (84)$$

where t is fuel cell operating temperature and Celsius can be calculated as;

$$t = T_{FC} - 273.15 \quad (85)$$

8.2.2. Irreversible cell voltage

The irreversible voltage loss or overpotential are due to irreversibilities which are composed of activation η_{act} , ohmic η_{ohm} , and concentration η_{conc} over voltage losses. As follows:

$$V_{irrev} = \eta_{act} + \eta_{ohm} + \eta_{conc} \quad (86)$$

1 Activation cell voltage loss: It is caused by layers of catalyst during the electrochemical reaction, kinetics of charge, transformation of electron and proton across the electrode-electrolyte [47].

$$\eta_{act} = \eta_{act}^A + \eta_{act}^C \quad (87)$$

Here, η_{act}^A and η_{act}^C are the activation overvoltage loss on the anode and cathode catalyst layers.

The Stefan-Maxwell relation can express the activation overpotential as follows:

$$\eta_{act} = - \left[-0.948 + \xi T_{FC} + 0.000076 T_{FC} (\ln(I)) - 0.000193 T_{FC} (\ln(C_{O_2,conc})) \right] \quad (88)$$

Here, I is current flowing through the PEM fuel cell, $C_{O_2,conc}$ is the oxygen concentration at cathode-membrane interface and ξ can be calculated as follows:

$$\xi = 0.00286 + 0.0002 \ln(A_{FC}) + 0.000043 \ln(C_{H_2,conc}) \quad (89)$$

Here, $C_{H_2,conc}$ and A_{FC} are the hydrogen concentration at cathode-membrane interface and active fuel cell area, respectively. Hnery's presented the concentrations of hydrogen and oxygen as follows [48]:

$$C_{H_2,conc} = 9.174 \times 10^{-7} P_{H_2} \exp\left(\frac{-77}{T_{FC}}\right) \quad (90)$$

and

$$C_{O_2,conc} = 1.97 \times 10^{-7} P_{O_2} \exp\left(\frac{498}{T_{FC}}\right) \quad (91)$$

2 Ohmic cell voltage loss: These are the losses of electric resistance in fuel cell. It is due to shifting of electron towards the bipolar plates, ionic and electronic resistance is anode and cathode electrode, ionic resistance in polymer membrane [49]. Ohmic overpotential is obtained from following relation:

$$\eta_{ohm} = \eta_{bp}^A + \eta_{bp}^C + \eta_e^A + \eta_e^C + \eta_{mem} \quad (92)$$

Here, the η_{bp}^A and η_{bp}^C are the ohmic losses of anode and cathode bipolar plates, respectively. The η_e^A and η_e^C are the ohmic losses of backing layers of anode and cathode respectively, and η_{mem} is the electrolyte membrane overvoltage losses. According to Ohmic's law, the ohmic overpotential losses can be expressed as [50]:

$$\eta_{ohm} = IR_{int} \quad (93)$$

Here, I is current flowing in the fuel cell and R_{int} is the total internal resistance. A general relation of internal resistance presented by [50]:

$$R_{int} = \frac{\gamma_{mem} L}{A_{FC}} \quad (94)$$

Where, γ_{mem} is the membrane resistivity. For Nafion membrane resistivity, an empirical relation is following:

$$\gamma_{mem} = \frac{181.6 \left[1 + 0.03j + 0.062 \left(\frac{T_{FC}}{303} \right)^2 j^{2.5} \right]}{[\zeta - 0.634 - 3j] \exp[4.18 (T_{FC} - 303/T_{FC})]} \quad (95)$$

where, ζ is the water content of membrane.

- 3** Concentration cell voltage loss: This loss arises because of mass transfer limitation between the reactants and products at higher current densities, and it is acted both of anode and cathode electrode surface.

$$\eta_{conc} = \eta_{conc}^A + \eta_{conc}^C \quad (96)$$

Where η_{conc}^A and η_{conc}^C the concentration overpotential at the anode and cathode, respectively, and can be expressed as [51]:

$$\eta_{conc,A} = \frac{R_u T_{FC}}{n_e F} \ln \left[\frac{1 - j/j_{l,H_2}}{1 + j/j_{l,H_2O}} \right] \quad (97)$$

and

$$\eta_{conc,C} = \frac{R_u T_{FC}}{n_e F} \ln \left[\frac{1}{1 + j/j_{l,O_2}} \right] \quad (98)$$

Here, R_u is the universal gas constant and j_l is the limiting current density explained from maximum current density, and j is the current density. The relation of limiting current density for H_2 , O_2 , and H_2O are expressed by following relations:

$$j_{l,H_2} = \frac{n_e D_{eff,H_2}}{R_u T \delta_A} \times p_{H_2} \quad (99)$$

$$j_{l,O_2} = \frac{n_e F D_{eff,O_2}}{R_u T \delta_C} \times p_{O_2} \quad (100)$$

and

$$j_{H_2O} = \frac{n_e F D_{eff,H_2O}}{R_u T \delta_A} \times p_{H_2O} \quad (101)$$

Where, δ_A and δ_C are the thickness of anode and cathode, respectively. The D_{eff,H_2} , D_{eff,O_2} , D_{eff,H_2O} are the effective gas diffusion factor for H_2 , O_2 , and H_2O , respectively. The D_{eff,H_2O} can be obtained from Knudsen diffusion and binary diffusion coefficient as follows:

$$\frac{1}{D_{eff,H_2}} = \frac{\varepsilon}{\tau} \left[\frac{1}{D_{H_2,k}} + \frac{1}{D_{H_2,H_2O}} \right] \quad (102)$$

$$\frac{1}{D_{eff,O_2}} = \frac{\varepsilon}{\tau} \left[\frac{1}{D_{O_2,k}} + \frac{1}{D_{O_2,N_2}} \right] \quad (103)$$

and

$$\frac{1}{D_{eff,H_2O}} = \frac{\varepsilon}{\tau} \left[\frac{1}{D_{H_2O,k}} + \frac{1}{D_{H_2,H_2O}} \right] \quad (104)$$

Here, ε and τ are the porosity and tortuosity of the respective electrode materials, respectively. Further, $D_{H_2,k}$, D_{eff,O_2} , and $D_{H_2O,k}$ are the Knudsen diffusion coefficients for H_2 , O_2 , and H_2O , respectively. The D_{O_2,N_2} and D_{H_2,H_2O} are the binary diffusion coefficients whose values are determined by following relations [52]:

$$D_{O_2,N_2} = \frac{0.00143T^{1.75}}{M_{O_2,N_2}^{0.5} [\nu_{O_2}^{0.33} + \nu_{N_2}^{0.33}]^2 p} \quad (105)$$

and

$$D_{H_2,H_2O} = \frac{0.00143T^{1.75}}{M_{H_2,H_2O}^{0.5} [\nu_{H_2}^{0.33} + \nu_{H_2O}^{0.33}]^2 p} \quad (106)$$

where, ν_{H_2} , ν_{O_2} , and ν_{H_2O} are the Fuller diffusion volume coefficients of H_2 , O_2 , and H_2O , respectively. The M_{H_2,H_2O} and M_{O_2,N_2} are the molecular weights and whose values can be obtained as follows:

$$M_{H_2,H_2O} = \frac{2}{(1/M_{H_2}) + (1/M_{H_2O})} \quad (107)$$

and

$$M_{O_2,N_2} = \frac{2}{(1/M_{O_2}) + (1/M_{N_2})} \quad (108)$$

The Knudsen diffusion coefficient can be expressed in terms of the mean free path of the gas and average pore radius. The Knudsen coefficient are obtained for H_2 , O_2 , and H_2O as follows [51]:

$$D_{H_2,k} = 97r_{por} \left(\frac{T}{M_{H_2}} \right)^{0.5} \quad (109)$$

$$D_{O_2,k} = 97r_{por} \left(\frac{T}{M_{O_2}} \right)^{0.5} \quad (110)$$

and

$$D_{H_2O,k} = 97r_{por} \left(\frac{T}{M_{H_2O}} \right)^{0.5} \quad (111)$$

Here, r_{por} is the average pore radius.

The power of PEM stack can be calculated by multiplying the number o fuel cells to the power of a single fuel cell;

$$V_{PEMFC,Stack} = N_{PEMFC} \times V_{PEMFC} \quad (112)$$

and

$$P_{PEMFC,Stack} = V_{PEMFC,Stack} \times j \quad (113)$$

According to Faraday's Law, the amount of hydrogen produced in electrolysis for each fuel cell [53]:

$$\dot{n}_{H_2,in}^{PEMFC} - \dot{n}_{H_2,out}^{PEMFC} = -\frac{jA}{2F} \quad (114)$$

$$\dot{n}_{H_2}^{PEMFC} = \frac{jA}{2F} \quad (115)$$

So, the hydrogen produced in PEM stack;

$$\dot{n}_{H_2,in} - \dot{n}_{H_2,out} = -\frac{N_{PEMFC}jA}{2F} \quad (116)$$

$$\dot{n}_{H_2} = \frac{N_{PEMFC}jA}{2F} = \dot{n}_{H_2O,reacted} \quad (117)$$

Here, $\dot{n}_{H_2O,reacted}$ is rate of H_2O reacted at the in reaction process. Similarly, the molar flow of oxygen and water at anode side-electrolyte interface for each cell can be calculated as follows:

$$\dot{n}_{O_2,out}^{PEMFC} = \frac{jA}{4F} \quad (118)$$

$$\dot{n}_{H_2O,out}^{PEMFC} = \dot{n}_{H_2O,in}^{PEMFC} - \frac{jA}{2F} \quad (119)$$

For, PEM stack it would be;

$$\dot{n}_{O_2,out} = \frac{N_{PEMFC}jA}{4F} \quad (120)$$

$$\dot{n}_{H_2O,out} = \dot{n}_{H_2O,in} - \frac{N_{PEMFC}jA}{2F} \quad (121)$$

The relation between current density and hydrogen consumed can be expressed as [54]:

$$H_{2,cons} = 2O_{2,cons} = \frac{N_{PEMFC}A_{PEMFC}I}{2F} \quad (122)$$

$$2O_{2,cons} = \frac{P_{PEMFC,Stack}}{4F \times V_{FC,Stack}} \quad (123)$$

8.3. PEMFC thermal modeling

The total energy in PEMFC can be calculated as following;

$$\Delta H = \Delta G + T\Delta S \quad (124)$$

Here, ΔG and $T\Delta S$ are the electric energy (change of Gibb's free energy) and thermal energy demand, respectively. From JANAF table [55], the values of G , H , and S of corresponding H_2 , O_2 , and H_2O can be taken.

The energy efficiency of PEMFC system can be formulated using following relation [54]:

$$\eta_{en,PEMFC} = \frac{HHV_{H_2} \times \dot{n}_{H_2}}{Q_{elec} + Q_{heat,PEM} + Q_{heat,H_2O}} \quad (125)$$

Where, HHV_{H_2} and \dot{n}_{H_2} high heating value and molar flow rate of H_2 , respectively. The Q_{elec} and $Q_{heat,PEM}$ are the rate of input of electric and thermal energy, respectively. The Q_{heat,H_2O} is the rate of input thermal energy for heating the water. The Q_{elec} , $Q_{heat,PEM}$ and Q_{heat,H_2O} can be obtained as follows:

$$Q_{elec} = P_{PEMFC,Stack} = V_{PEMFC,Stack} \times j \quad (126)$$

$$Q_{heat,H_2O} = \frac{j}{2F} \left(H_{H_2O}^T - H_{H_2O}^{T_o} \right) \quad (127)$$

Here, $H_{H_2O}^T$ and $H_{H_2O}^{T_o}$ are the enthalpies of water at temperature T and T_o , respectively.

$$Q_{heat,PEM} = [T\Delta S - S_g] \dot{n}_{H_2O,reacted} = \frac{j}{2F} [T\Delta S - S_g] \quad (128)$$

Here, the S_g is entropy generation due to irreversibilities or overpotentials. It can be formulated as follows [37]:

$$S_g = n_e F (V_{irrev}) = n_e F (\eta_{act} + \eta_{ohm} + \eta_{conc}) \quad (129)$$

- For $S_g \geq T\Delta S$, the heat generated due to irreversibilities is greater than or equal to provided heat input. So, in this case no external source of heat ($Q_{heat,PEM} = 0$) is needed to PEM electrolysis.
- For $S_g < T\Delta S$, the heat generated is less than the input provided thermal energy. So, external heat is required and which can be calculated by Equation 128.

The total exergy of PEMFC can be calculated by following exergy balance [54]:

$$Ex_{in} = Ex_{out} + Ex_{loss} \quad (130)$$

$$Ex_{loss} = Ex_{dis} + Ex_{des} \quad (131)$$

Here, Ex_{in} and Ex_{out} are representing the exergy rate of in and out, respectively. While Ex_{dis} and Ex_{des} are the exergy dissipation (exergy of stream transfer towards the environment) and exergy destruction (due to irreversibilities), respectively.

The exergy efficiency PEMFC can be represented by given relation:

$$\eta_{ex,PEMFC} = \frac{Ex_{out}}{Ex_{in}} = \frac{Ex_{H_2} \times \dot{n}_{H_2}}{Ex_{elec} + Ex_{heat,PEM} + Ex_{heat,H_2O}} \quad (132)$$

Here,

$$Ex_{elec} = P_{PEMFC,Stack} = V_{PEMFC,Stack} \times j \quad (133)$$

$$Ex_{heat,PEM} = Q_{heat,PEM} \left(1 - \frac{T_o}{T_{FC}} \right) \quad (134)$$

Where, T_o and T_{FC} are temperature of reference environment and fuel cell, respectively.

$$Ex_{heat,H_2O} = Q_{heat,H_2O} \left(1 - \frac{T_o}{T_{source}} \right) \quad (135)$$

Here, T_{source} is the temperature of heat source.

The Ex_{H_2} is exergy of the hydrogen and it can be calculated as following, neglecting the kinetic and potential exergies terms:

$$Ex_{H_2} = (Ex_{ch} + Ex_{ph})_{H_2} \quad (136)$$

The physical and chemical exergies can be formulated by [54]:

$$Ex_{ph,H_2} = c_p T_o \left[\frac{T_{H_2}}{T_o} - 1 - \ln \left(\frac{T_{H_2}}{T_o} \right) + \left(\frac{P_{H_2}}{P_o} \right)^{\frac{\kappa-1}{\kappa}} \right] \quad (137)$$

and

$$Ex_{ch,H_2} = \Sigma \chi_{H_2} Ex_{o,ch,H_2} + \tilde{R}_{H_2} T_o \Sigma \chi_{H_2} \ln \chi_{H_2} \quad (138)$$

Where, c_p is specific heat of H_2 , \tilde{R}_{H_2} is the gas constant of H_2 , T_{H_2} and P_{H_2} are the outlet temperature and pressure of H_2 , respectively, κ is adiabatic constant, and Ex_{o,ch,H_2} is the standard chemical exergy of H_2 .

9. Energy and exergy analysis of SOFC

The solid oxide fuel cells (SOFCs) are normally used for high temperatures approximately 800°C-1000°C for stationary applications in industry and utility. In SOFC usually doped zirconia is used as a electrolyte which becomes easily conductive to oxide ions. The temperature at the exhaust of SOFC is around 500°C-850°C, which can be further cogeneration application or for other thermal power energy conversion cycles [56]. The fuel is provided at the anode electrode or fuel electrode and air is provided at cathode electrode or air electrode. The oxygen ions are formed at cathode, through a solid electrolyte, and react with CO and H_2 , contained in fuel, and produce electricity by electron movement. The reaction process of formation of CO and H_2 from natural gas or any other hydrocarbon fuels called, reforming or steam reforming, occurs internally in the generator. The fuel cells are packed making a generator building block are packed serial and parallel arrangements electrically connected to each other.

The technology of SOFC has made itself a promising and reliable technology with several advance features such as with safe and high capability to fuel contaminants and high temperature production. During electrochemical reactions, SOFC does not require expensive catalysts and allows directs fuel processing. The stability of the electrolyte is very resistive that there is no liquid phase exist in the solid oxide electrolyte, and losses like electrolyte migration, catalyst wetting and electrode flooding are prevented. In spite of the ability of producing electricity from SOFC, there are many other industrial applications combination

with SOFC. A review on SOFC applications for power generation systems combined with SOFC has been reviewed by Choudhury et al. [57].

9.1. SOFC reformer modeling

The electrochemical reactions (reforming and shifting) occur in stack of each cell of SOFC at the anode section. It is supposed that the reforming and shifting reactions are in chemical equilibrium. The positive feature of SOFC is to utilize the carbon monoxide and hydrogen as a fuel simultaneously. Due to direct internal reforming methane and carbon monoxide can be used as a fuel in anode compartment of fuel cell and compressed air is supplied at the cathodes side which is acting as an oxidant. The following electrochemical reactions occur inside the stack:

- Reforming (Steam reforming)



- Shifting (Water-gas shift)



- Electrochemical



So, the net chemical reaction inside the fuel cell follows as:



The equilibrium reactions of the internal reforming and shifting of water inside the SOFC are following [58]:

- Reforming (Steam reforming)



- Shifting (Water-gas shift)



- Electrochemical (Total)



Here, x , y , z are representing the molar rates during reforming, shifting and total reactions, respectively. The molar rates of flowing gases through the SOFC can be determined from following [51]:

Table 3: Equilibrium Constants values [59]

Sr.No.	Reforming	Shifting
A	-2.6312×10^{-11}	5.47×10^{-12}
B	1.2406×10^{-17}	-2.547×10^{-8}
C	-2.2523×10^{-4}	4.6374×10^{-5}
D	0.195027	-3.915×10^{-2}
E	-66.139488	13.209723

$$(\dot{n}_{CH_4})^{out} = (\dot{n}_{CH_4})^{in} - x \quad (146)$$

$$(\dot{n}_{H_2O})^{out} = (\dot{n}_{H_2O})^{in} - x - y + z \quad (147)$$

$$(\dot{n}_{H_2})^{out} = (\dot{n}_{H_2})^{in} + 3x + y + z \quad (148)$$

$$(\dot{n}_{CO})^{out} = (\dot{n}_{CO})^{in} + x - z \quad (149)$$

$$(\dot{n}_{CO_2})^{out} = (\dot{n}_{CO_2})^{in} + y \quad (150)$$

$$(\dot{n}_{tot})^{out} = (\dot{n}_{tot})^{in} + 2x \quad (151)$$

From above equations, the partial pressures of gases occurring at anode and cathode electrodes can be obtained as:

$$p_i = \frac{\dot{n}_i}{\dot{n}_{tot}} p_{tot} \quad (152)$$

The constants in equilibrium reactions in terms of partial pressures or concentration of the species determine the amount of component, composition and final temperature of equilibrium of reforming and shifting reactions. The equilibrium constants for reforming and shifting reactions can be obtained as follows:

$$K_{p,r} = \frac{p_{CO} \times p_{H_2}^3}{p_{CH_4} \times p_{H_2O}} \quad (153)$$

and

$$K_{p,s} = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} \quad (154)$$

The equilibrium constants can be determined from the concentrations of partial pressures. The following of temperature dependent polynomial equation can be used to obtained the equilibrium constants;

$$\log(K_p) = AT^4 + BT^3 + CT^2 + DT + E \quad (155)$$

The values of equilibrium constants are provided in Table 3

In terms of molar compositions, the equilibrium constant can be expressed as follows:

$$K_{p,r} = \frac{y_{eq,H_2}^3 \times y_{eq,CO}}{y_{eq,CH_4} \times y_{eq,H_2O}} \times \left(\frac{p}{p_o} \right)^2 \quad (156)$$

and

$$K_{p,s} = \frac{y_{eq,H_2} \times y_{eq,CO_2}}{y_{eq,CO} \times y_{eq,H_2O}} \quad (157)$$

Here, $y_{eq,i}$ is equilibrium molar concentration of the species, which is ratio of the total number of moles of the species to total number of moles at the equilibrium, as follows:

$$y_{eq,i} = \frac{\dot{n}_{tot,i}}{\dot{n}_{tot}} \quad (158)$$

From the Equations 156 to 158 and chemical reactions, the following relations can be obtained as:

$$K_{p,r} = \frac{[(\dot{n}_{H_2})^{in} + 3x + y - z]^3 \times [(\dot{n}_{CO})^{in} + x - y]}{[(\dot{n}_{CH_4})^{in} - x] \times [(\dot{n}_{H_2O})^{in} - x - y + z]} \times \frac{p_{SOFC}^2}{[(\dot{n}_{tot})^{in} + 2x]^2} \quad (159)$$

$$K_{p,s} = \frac{[(\dot{n}_{CO_2})^{in} + y] \times [(\dot{n}_{H_2})^{in} + 3x + y - z]}{[(\dot{n}_{CO})^{in} + x - y] \times [(\dot{n}_{H_2O})^{in} - x - y + z]} \quad (160)$$

and

$$U_f = \frac{z}{3x + y} \Rightarrow z = U_f \times (3x + y) \quad (161)$$

Here, U_f is fuel utilization ratio or factor, defined as the ratio of the concentrated or reacted hydrogen number of moles to total provided number of moles of hydrogen at input. Mathematically, can be expressed as [60]:

$$U_f = \frac{Fuel_{consumed}}{Fuel_{supplied}} = \frac{H_{2,consumed}}{H_{2,supplied}} = \frac{H_{2,in} - H_{2,out}}{H_{2,supplied}} = \frac{z}{3x + y} \quad (162)$$

and for air utilization ratio or factor U_o from following [61]:

$$U_o = \frac{Air_{consumed}}{Air_{supplied}} = \frac{O_{2,consumed}}{O_{2,supplied}} = \frac{O_{2,in} - O_{2,out}}{O_{2,supplied}} = \frac{z/2}{\dot{n}_{O_2}} \quad (163)$$

The equilibrium constant in reforming and shifting reactions can be evaluated through Gibbs free energy of reactions method [62] as follows:

$$K_{p,r} = \exp \left[\frac{\Delta \tilde{g}_r^\circ}{RT_{SOFC,stack}} \right] \quad (164)$$

and

$$K_{p,s} = \exp \left[\frac{\Delta \tilde{g}_s^\circ}{RT_{SOFC,stack}} \right] \quad (165)$$

Here, R is the gas constant and $T_{SOFC,stack}$ is the stack temperature of SOFC. The free energy of reactions Gibbs function is evaluated by the different of standards free energies of reactant and products, as follows:

$$\Delta \tilde{g}_{r,s}^\circ = \Sigma n \Delta \tilde{g}_{products}^\circ - \Sigma n \Delta \tilde{g}_{reactants}^\circ \quad (166)$$

The n is representing the number of moles and constants values of reforming and shifting reactions can be found in JANAF tables [55].

9.2. Electrochemical modeling of SOFC

The electric power from the SOFC can be obtained from following relations, which is related to stack cell voltage and flowing current:

$$P_{SOFC,Stack} = N_{SOFC}V_{SOFC}I \quad (167)$$

Here, the I can be obtained as [60]:

$$I = N_{SOFC}jA_{SOFC} = 2Fz = n_eU_f n_{H_2,eq} F \quad (168)$$

and z is [63]:

$$z = \frac{jA_{SOFC}N_{SOFC}}{n_eF} \quad (169)$$

Here, j is the current density, A_{SOFC} is the active surface of SOFC, N_{SOFC} are the total number of fuel cells in stack, n_e is number of electron of hydrogen per mole that reacts in the electrochemical reactions, and F is the Faraday's constant ($9.649 \times 10^7 C/kmol$).

Further, the V_{SOFC} are the operating voltage on SOFC which is difference of reversible voltage V_{rev} and V_{irrev} , discussed in previous section.

Energy and exergy efficiencies of SOFC fuel cell can be obtained as follows:

$$\eta_{en,SOFC} = \frac{P_{SOFC,Stack}}{\dot{n}_f \times LHV_f} \quad (170)$$

and

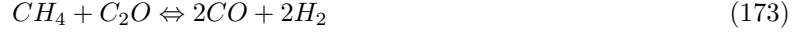
$$\eta_{ex,SOFC} = \frac{P_{SOFC,Stack}}{Ex_f + Ex_{air}} \quad (171)$$

10. Energy and exergy analysis of MCFC

The molten carbonate fuel cell (MCFC) is the advancement in fuel cell technology. Due to its high temperature over 600°C , there is no need of external reforming. Thus, the MCFC has the tendency of internal reforming to generate hydrogen. Along with this, the MCFC allows the recovery of waste heat which is further can be used for cogeneration power distribution systems for stationary applications. A molten-carbonate electrolyte of salt mixture is used in MCFC with ceramic matrix solid electrolyte. MCFC has the high efficiency than other fuel cells around 60% and in hybrid system sometimes efficiency reaches around 80%. There are some challenges such as corrosion, short life time, low oxygen reduction rate, and high cost. However, the diversity of various input fuels like gases from coal gasification, natural gas and biogases [64].

10.1. MCFC reformer modeling

The steam reforming (mixture of steam and methane) reactions occur in the reformer and required enriched fuel, hydrogen, leave for electrochemical reactions at the anode of the fuel cell. The reactions occurring in the reformer sections are mainly endothermic, expect of water–gas shifting reaction, and heat produced from hot flue gases. The following reactions are occurred in the reactor [64, 65]:



and



The corresponding kinetic parameters of rate equations are as follows [66]:

$$r_1 = \frac{k_1}{p_{H_2}^{2.5}} \left[\frac{p_{CH_4} p_{H_2O} - (p_{H_2}^3 p_{CO} / K_1)}{(DEN)^2} \right] \quad (175)$$

$$r_2 = \frac{k_2}{p_{H_2}} \left[\frac{p_{CO} p_{H_2O} - (p_{H_2} p_{CO_2} / K_2)}{(DEN)^2} \right] \quad (176)$$

$$r_3 = \frac{k_3}{p_{H_2}^{3.5}} \left[\frac{p_{CH_4} p_{H_2O}^2 - (p_{H_2}^4 p_{CO_2} / K_3)}{(DEN)^2} \right] \quad (177)$$

Where, p_j is the partial pressure of the species j in the mixture and;

$$DEN = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \quad (178)$$

The rate constant (k_i), equilibrium constant (K_i) adsorption constant (K_j) are obtained as follows [65, 66]:

$$k_i = A(k_i) \exp \left[-\frac{E_{act,i}}{R_u T} \right], \text{ for } i = 1, 2, 3 \quad (179)$$

$$K_i = A(K_i) \exp \left[-\frac{\Delta G_i^\circ}{R_u T} \right], \text{ for } i = 1, 2, 3 \quad (180)$$

$$K_j = A(K_j) \exp \left[-\frac{\Delta H_j^\circ}{R_u T} \right], \text{ for } j = CH_4, H_2O, CO, H_2 \quad (181)$$

Here, $E_{act,i}$ is the activation energy of species i in the mixture and $A(k_i)$ and $A(K_j)$ can be calculated by Arrhenius equation and Van't Hoff equation as follows:

$$A(k_i) = k_{i,T} \exp \left(\frac{E_i}{RT} \right) \quad (182)$$

and

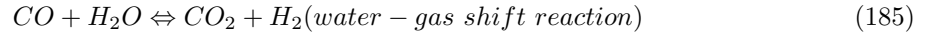
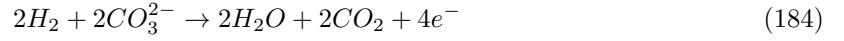
$$A(K_j) = k_{j,T} \exp\left(\frac{\Delta H_j}{RT}\right) \quad (183)$$

The kinetic parameters of above relations and heat transfer relations inside the reformer can be obtained from Ref.[66]

10.2. MCFC stack modeling

The fundamental principle of MCFC is to produce electricity through electrochemical reactions. The fuel, (hydrogen, water, unconsumed methane, carbon dioxide, and carbon monoxide) is supplied at the inlet of anode side. Produced hydrogen in the reformer reacts with carbonate ions CO_3^{2-} , passing through the membrane, and produce water, carbon dioxide and electrons. These electrons further flow in an external circuit and then enter to the cathode side of the fuel cell. At the cathode, the electrons react with the oxygen from the air and recycle stream of carbon dioxide at the outlet. In electrochemical reaction, the water–gas shifting reaction occur at the anode due the presence of carbon monoxide. The electrochemical reactions inside the stack are following [67]:

- At Anode:



- At Cathode:



- Overall Reaction



The equilibrium constant for water–gas shift (WGS) reaction is obtained as follow [67]:

$$K_{WGS} = \exp\left(\frac{4276}{T} - 3.961\right) \quad (188)$$

Where, T is temperature of MCFC stack in Kelvin. In terms of partial pressures, the equilibrium constant of WGS can be expressed as follows [67]:

$$K_{WGS} = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} \quad (189)$$

Here, there two different ways have been reported to find out the equilibrium by Xu et, al. [66] and Mamaghani et, al. [65, 67].

The Mamaghani et, al. [65, 67] reported the following relations assuming x and y are the molar flow rates of CO and H_2O participating in electrochemical and WGS reactions, respectively:

$$K_{WGS} = \frac{[\dot{n}_{CO_2,in} + x + y] \times [\dot{n}_{H_2,in} + x - y]}{[\dot{n}_{CO,in} - x] \times [\dot{n}_{H_2O,in} - x + y]} \quad (190)$$

$$y = U_f[\dot{n}_{H_2,out} + x] \quad (191)$$

$$U_f = \frac{Fuel_{consumed}}{Fuel_{supplied}} = \frac{\dot{n}_{H_2,in} - \dot{n}_{H_2,out}}{\dot{n}_{H_2,in}} \quad (192)$$

With the information of MCFC stack temperature, the equilibrium constant can be found from Equation 188 and from molar flow rates (x and y) can be calculated simultaneously from Equations 190 and 191.

10.3. Electrochemical modeling of MCFC

The electric output power of MCFC stack can be obtained similarly SOFC by multiplying the number of fuel cells with output power of a single cell, as following:

$$P_{MCFC} = V_{MCFC,Stack} I \quad (193)$$

Here, I and $V_{MCFC,Stack}$ can be obtained as follows [65]:

$$V_{MCFC,Stack} = N_{MCFC} V_{MCFC} \quad (194)$$

$$I = j A_{MCFC} = 2Fy \quad (195)$$

The energy and exergy efficiencies of the MCFC can be obtained from following relations [11]:

$$\eta_{en,MCFC} = \frac{P_{MCFC}}{\sum_{i=1}^N \dot{n}_i^{A,in} h_i^{A,in} + \sum_{i=1}^N \dot{n}_i^{C,in} h_i^{C,in}} \quad (196)$$

and

$$\eta_{ex,MCFC} = \frac{P_{MCFC}}{\sum_{i=1}^N \dot{n}_i^{A,in} ex_i^{A,in} + \sum_{i=1}^N \dot{n}_i^{C,in} ex_i^{C,in}} \quad (197)$$

11. Conclusions

This paper focuses on the fundamental concepts of theoretical and practical aspects of thermodynamics balances of energy and exergy analysis of the basic types of fuel cell systems. Fundamental principles of FLT and SLT for non-flow and flow systems, energy, exergy definitions and analysis procedure, reference environments selection and models have been discussed. A detail theoretical analysis of electrochemical and thermal modeling of the PEMFC, SOFC, and MCFC have been elaborated with respect to energy and exergy modeling. Energy, exergy efficiencies and step by step analysis procedure of respective to each type

of fuel cell have been also reviewed in this paper which further help to improve the thermal performance of fuel cell based hybrid thermal systems.

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