



PARAMETRIC SIMULATION AND EXERGY ANALYSIS OF A 30W ETHANOL FUEL CELL: THEORITICAL APPROACH

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Abstract

Ethanol has the potential of being an abundant biofuel considering raw materials and indigenous technology available. Due to its oxidation

Keywords: Fuel cells, ethanol, simulation, Voltage loss, efficiency, exergy.

tendency, higher energy density, nontoxic and

INTRODUCTION

In the bid to rein in greenhouse effect through clean energy, advancement in fuel cell simulation and design has taken the topnotch in virtually all portable devices and is tending to be another key source of energy alongside the solar power source; mainly for domestic use. This advancement has remained constant in the quest to develop fuel cell (FC) that will meet economic and environmental lines. Fuel cell is an electrochemical devices that convert the chemical energy directly into electrical energy with high efficiency. Ethanol fuel cell has advantages over other fuel cells considering the availability of ethanol directly and the ease

venvironmental affability, etc., studies have accord and intensify preference and suitability in the use of ethanol in fuel cells. Hence, this work adopts a theoretical approach in the simulation and exergy analysis of a 30W ethanol fuel cell. While making empirically considerable assumptions on the layers' thicknesses and other parameters, the simulation considers 1atm. and 65°C operating condition. Fixed and standard parameters from literature were applied in the mathematical expressions and models describing the over-potentials, energy and power generation and, the efficiencies inherent of the simulation. Voltage

loss due to transport contributes about 80% of the 0.1211 V total over-potential that culminates to the 3.633W irreversible power. The exergy analysis of the simulated 95% Direct Ethanol Fuel Cell (DEFC) gave 89% cell efficiency for the generation of 3,050 kJ energy, 33.80 W ideal power and 30.28W useful power in a 90 seconds operation at a 1.1267V potential.

was to develop birthrate monitoring system. To achieve this aim, the study set as its objectives to; ascertain the birth record system of the understudied hospitals, develop a platform for birth information, design a module that computes birth statistics and to

integrate the birth information platform with the birth statistics module. The Rapid Application Development (RAD) was used to develop the study. The Object-Oriented Analysis and Design Methodology (OOAaD) was used to analyze and design this system. The Hyper-Preprocessor (PHP) and MYSQL were used as tools to implementing the system. The MYSQL was used to develop a centralized web-based database. Birth rate monitoring information system was developed. The system was tested and deployed. The result showed that using the proposed system makes data entry and information retrieval easier and simple compared to the existing system.

In the numerous means of production from agricultural waste. It has high energy conversion: about 80% and has wide spread applications due to its potentials for power generation (Abdulrazzak & Abdullah,

2021). The major drawback of microbial fuel cell that gave the leap for Ethanol fuel cell is the huge amount of catalysts required. These catalysts are not easily synthesized due to high time and resource demand hence are not readily available, commercially or preparatory (Santoro, et al., 2018). Considering the size of the electrical cells, fuel of high economic viability is very important in coupling a high performance FC. Fuel cells are applicable as sources of primary and backup power in buildings, vehicles, small electrical appliances, electronic gadgets, etc.; and are capable of producing more than 250W power. 'The FC energy density for such devices is increasing 3 to 10 times more quickly than the energy density of the lithium batteries currently in use.' (Abdullah *et al.*, 2014). When power is the target, energy and power densities at optimum conditions become more important features than efficiency.

The world is faced with global warming, which is majorly brought about by the incomplete combustion of fossil fuels and the consequent emission of harmful gases (Marina, *et al.*, 2009), which are non-biodegradable. Nigeria is known to be one of the world's major petroleum producing countries (Oyegoke & Dabai, 2018). Though petroleum as fossil fuel, as well as other chemicals are important sources of power in cells, the use of bio-fuel is preferred due to the leverage on health and environmental friendliness. Studies have not denied the preference of hydrogen to other fuels as the most benign; however, to generate hydrogen requires a very complex and costly system. Though till date, methanol remains the fuel with very high electrochemical activity, its lethargic anode kinetics and high fuel crossover (Song & Tsiakaras, 2006) begot its relegation in fuel cell applications; hence the research reportage on the continuing quest for a better alternative has brought ethanol to the fore in recent applications and studies. Ethanol, as bio-fuel, is an alternative to fossil fuel having high octane number, high heating value and undergoes complete combustion in automobiles due to its high oxygen content, which leads to fewer emissions of poisonous gases (Balat, 2007). As an alcohol, it has comparable energy density to that of fossil fuels - gasoline and diesel (Abdullah *et al.*, 2014). It is preferred for its oxidation tendency, higher energy density, nontoxicity, lower crossover rate and environmental friendliness (Songa, *et al.*, 2005; Zakaria, Kamarudin, & Timmiati, 2016). It is also readily and naturally available and abundant.

While Nigeria was aiming at 1.27 billion litres (335 million gallons) of ethanol for the year 2011 (Agboola & Agboola, 2011), the world production stood at 22.5 billion gallons (Renewable Fuel Association, 2018). The Nigerian urban and rural areas are typical of heavy biomasses, waste constituents, and plant parts and product inherent for ethanol production. Traditionally, in energy generation, biomass and waste constitute 74% while oil, natural gas and hydropower consist of 13%, 12%, and 1%, respectively (Oyegoke T. , Dabai, Muhammed, & Jibril, 2017).

Ethanol is a biofuel chiefly gotten via biochemical process of fermentation and biodegradation of agro-allied products: palm-wine, food crops, plant parts, biomasses and even municipal waste. Advent of ethanol heralds an era of renewable and clean energy fuel with relative equivalent performance and efficiency (Berg, Nyman, Erlandsson, Johansson, and Matic, 2015; Saisirirat and Joommanee, 2018) with other energy sources hence the arrival of the Direct Ethanol Fuel Cell (DEFC).

There is yet no fuel cell that has met the optimum parameter (conditions and materials) for an ideal fuel cell in terms of operating temperature and pressure, electrolyte and membrane type, cell structure, the exchangeable ions and the reactants in the electrolyte; hence fuel cells are classified based on these parameters. Each and every operating condition and material consideration for a fuel cell has its demerits, this results in the numerous considerations in simulations, models and designs based on availability and convenience. To conserve, hence reduce losses, simulations for power generation needs a lot of loss control and performance improvement. Therefore, use of thin materials implies lighter product with reduced losses due to resistivity and improved conductivity for performance enhancement.

Low ethanol permeability and high conductivity are primary features of a suitable electrolyte membrane for DEFCs. Amidst SiC ceramic membrane (Back-Sub & Young-Hoon, 2016); and polybenzimidazole (PBI), poly (vinyl alcohol) (PVA) and sulfonated poly-ether ether ketone (SPEEK) (Zakaria, Kamarudin, & Timmiati, 2016), research has reported anion exchange membrane (AEM) as more suitable in DEFC design and setup (Song & Tsiakaras, 2006; Back-Sub & Young-Hoon, 2016). The preference of electrocatalyst is measured by the lowest possible onset potential: DHE - dynamic hydrogen reference electrode (Sousa Jr, *et al.*, 2008). Song &

Tsiakaras, (2006) reported DHE 85 for PtSn/C at the same condition where PtRu/C and Pt gave 200 and 380 respectively.

In every FC design as in DEFC, voltage losses have remained a limitation. Voltage losses: Polarization or over potential include **activation** loss due to charge transfer reactions at electrodes, loss due to fuel crossover from anode to cathode, Ohmic loss due to materials' conductivity, concentration loss due to transfer resistance and reactant availability at reaction sites, and other traces of losses. Fuel cross over to the cathode reduces the amount of ethanol available for power generation. Energy leakage due to poor material contact and the energy loss due to heat in materials of poor conductivity reduces the quantity of useful energy. Transfer resistances like pore blockage and flooding limit the amount of the reactant (EtOH/O₂) needed at the reaction sites to generate the expected energy.

However, in simulation model, these losses can be managed depending on the amount of expected power, materials (electrode, diffusion layer and, catalyst and electrolyte membrane) used, as well as the cell operating condition. These losses define the systems irreversibility. It is noteworthy that FC models, simulations, designs and the consequent manufacture is tailored towards electrical power generation for electrical appliances. The performance of any FC is mirrored by the simulated efficiencies. The efficiencies that can be simulated in a FC model and design encompass the thermodynamic efficiency (reversible efficiency, ϵ_{th}), the ideal electrochemical efficiency (ϵ_{elect}), and the cell efficiency (ϵ_{cell}) among other efficiencies and performance measures.

The extensive theoretical and empirical studies on DEFC is geared towards hastening and strengthening its application in portable electronic devices. Amidst other shared merits of the DEFC, it is typical of fuel replacement, rapid starting, low operating temperature and comparative high current density. Chiefly, literature has reported virtually on mathematical modeling, current and potentials of DEFC. In the recent past, few works have considered simulation and exergy analysis in fuel cells. Studying the possible configuration of hybrid power plants, Abdulrazzak & Abdullah, (2021) considered theoretical simulation and exergy analysis. In a bid to improve reactant usage for higher efficiency, Mert, Toprak, & Depci, (2019) looked at the simulation and exergy of several proton exchange membrane (PEM) FC flow channels. The high temperature enhancement of FC performance have gotten wide reportage over a decade now. The

simulation and exergy of high temperature membrane fuel cell has been studied (Haghighi & Sharifhassan, 2016), although, this work did not give empirical concern to the fuel and its chemistry. Works on the exergy analysis of alcohol fuel cell has been very scanty with much interest given to Methanol amidst the few studies reported. The literature has no report or study on the simulation and exergy of a DEFC for a specific power generation. This work therefore considered the empirical chemistry of ethanol as a direct fuel for a parametric simulation and exergy analysis of a 30W fuel cell. The simulation would expose parameters, besides standard values, that can sway the power generation and the over-potential with respect to the available materials and the target power output.

SIMULATION

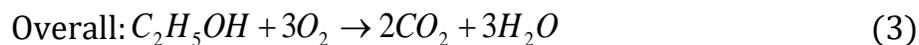
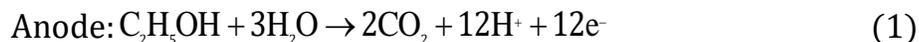
The Simulation Considerations

Low feed concentration has been reported as a key parameters to mitigate ethanol crossover via reducing the electro-osmotic drag of ethanol and as well limit the current density, and vice versa (Zakaria, Kamarudin, & Timmiati, 2016), hence 0.003 – 0.005mol/cm³ and 0.03 – 0.05g/s were supposed optimum in this simulation.

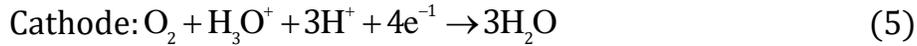
This simulation considered a 95% ethanol of density 0.789g/cm³ and molar mass 46.07g/mol. A 20% ethanol aqueous solution formed from 19ml 95% EtOH and 76ml distilled water. A 2cm³/s EtOH feed rate was used.

The actual efficiency and performance of DEFC is low attributive to the incomplete oxidation to CO₂ resulting from slow electro-oxidation (EOR) due to low operating temperature (Song and Tsiakaras, 2006; Abdullah, Kamarudin, Hasran, and Daud, 2014). To attain a near empirical simulation, a steady state complete conversion of ethanol to acetaldehyde (CH₃CHO) then to acetic acid (CH₃COOH) and CO₂ was assumed.

Ideally, the elementary equations for the complete ethanol oxidation is given as:



Therefore, the incomplete oxidation typical of acetic acid formation was considered as:



Considering that elementary reaction order cannot be fractional, anodic oxidation order of 1.0 and the ORR order of 0.75 were used.

Voltages between 0.5 and 0.6V at normal operating loads are typical for a real fuel cell and can reach 1.1 V at open circuit conditions. It follows that electrochemical efficiency can typically be approximated between 40 and 50% for open circuit conditions and reaching 90% (Mench, 2008).

All current densities considered for the over-potentials were obtained from the polarization curve (Fig. 2). The linear region of the curve showed current density ranging 1.1 - 1.3 A/cm² typical for ohmic losses, $i = 0.06A/cm^2$ current density was obtained from the activation region. Anodic and cathodic charge transfer coefficients adopted were 0.089 and 1.00 respectively (Saisirirat and Joommanee, 2018; Andreadis, Podias and Tsiakara 2008; Andreadis and Tsiakara 2006; Jeng and Chen, 2002).

Nafion 112: 51µm and ≈ 60µm thick in wet state (Mench, 2008), graphite plate (GP) were chosen as the cell membrane and the current collector respectively. Anode and cathode diffusion and catalyst layer were assumed to be of equal dimension and that electro oxidation occurs in the middle of the CL. A 250µm DL thickness of 20% polytetraflouroethelyne (PTFE) and 2×10^4 S/m conductance was considered. A 30mΩ.cm² contact resistance for a Landing to channel ratio of 3:1 was adopted. Due to the low operating temperature and rapid diffusion, anodic polarization was assumed negligible.

At the cell **operating condition**, the humidified air is generated at 80°C, 1atm and would enter the cell at 65°C, 1atm. Characteristic values of m and n from several fitted polarization curves for a Polymer Electrode Fuel Cell (PEFC) fall around 3×10^{-5} V and 8.00 cm²/A respectively (Mench, 2008). The current density that compels reactant mass transport at the electrodes for a typical operating condition of a PEFC ranges 1.0 – 1.55A/cm² for mild to steep loss (Weber & Delacourt, 2020; Mench, 2008).

The Simulation Assumptions

At the cathode, considering voltage loss due to oxygen concentration, exchange current density (i) was constant and transfer resistance for the

oxygen reduction reaction negligible. A relative humidity of the humidified air carrying and charging the oxygen was unity. All likely chemical energies in the reaction went into electrical work, hence there is no heat transfer and no entropy change.

Over-potential due to electrical short circuits, mixed-potential due to EtOH crossover, ionic and electronic transfer, etc. can be managed via design consideration and material selection, hence were negligible.

The Simulation Calculations

A 0.01627 mol/cm^3 reference concentration was calculated for the 95% ethanol stock and a 0.0034 mol/cm^3 feed concentration was considered from the 20% ethanol feed. The process flow diagram, showed a 95mL reservoir of 20% ethanol charged at the Cell operating temperature (65°C) and $2 \text{ cm}^3/\text{s}$; therefore, 0.0068 mol/s of ethanol was charged into the cell channels.

The cell stoichiometry showed the release of $4e^-$ from the oxidation of 1 mole EtOH, giving a $0.0272e^-$ release for 0.0068 moles fed. The Cell open circuit current from Faradays second law relation for a 0.0068 mol/s feed and 0.0272 electron charge released was calculated as 17.846A ; taking $F = 96485\text{C}$:

$$I_o = i_o A = NnF = 0.0068 \times 0.0272 \times 96485 = 17.846\text{A} \quad (7)$$

Current and power losses in FCs depends on the application of resistivity concept; practically, the thinnest materials are considered. Thus, a cell of 0.41cm componential thickness, 10cm height and 5cm width will give 50cm^2 2D contact surface available for current flow. Therefore, the anodic reference exchange current was 0.3569Acm^2 :

$$i_{o,ref} = 17.846\text{A}/50\text{cm}^2 = 0.3569\text{A.cm}^{-2} \quad (8)$$

With $C_{ref,EtOH} = 0.01629 \text{ mol/cm}^3$ and $C_{F,EtOH} = 0.0034 \text{ mol/cm}^3$; considering the elementary reaction order 1.0, the exchange current density: 0.0744Acm^2 was calculated;

Activation Loss: Predicting low polarization, the Butler–Volmer (BV) facile kinetic model was applied:

$$\eta_a = \frac{i}{i_o} \frac{RT}{(\alpha_a + \alpha_c)F} = \frac{i}{i_o} \frac{RT}{nF} \quad (9)$$

Taking $i = 0.06\text{A/cm}^2$ and 0.089 and 1.00 anodic and cathodic charge transfer coefficients respectively, 0.0216V was lost due to activation:

$$\eta_a = \frac{i}{i_o} \frac{RT}{nF} = \frac{0.06 \times 8.314 \times 338}{0.0744 \times 1.089 \times 96485} = 0.0216$$

Ohmic (Conduction) Loss is chiefly due to Current flow, hence is based on the concept and law of resistivity. Reducing Ohmic losses entails applying the thinnest and highest possible conductivity material components (electrolyte, catalyst and diffusion materials) in the cell design and manufacture.

Ohms Law:
$$V = IR = iAR = iA(l/\sigma A) \tag{10}$$

Thus:
$$\eta_r = iA \sum_{j=1}^n l_j / \sigma_j A = \eta_{\text{ionic}} + \eta_{\text{elect}} + \eta_{\text{contact}} \tag{11}$$

$$\eta_r = iA \left\{ \left(\frac{l_a}{\iota_a \sigma_a A} + \frac{l_e}{\sigma_e A} + \frac{l_c}{\iota_c \sigma_c A} \right) + \left(\frac{l_{GP}}{\sigma_{GP} A} + \frac{l_{DL}}{\sigma_{DL} A} + \frac{l_{CL}}{2\sigma_{CL} A} \right) + \frac{R_{GBP}}{A_L} + \frac{R_L}{A_L} \right\} \tag{12}$$

Having a cell of 0.41cm thickness and 10cm height, 4.1cm² active area would be available for Ohmic loss. In a demonstrative estimation, Mench, (2008) reported that thin electrolytes support high current densities. Therefore, for a 1.10A/cm² when electro oxidation occurred at the middle of the CL, taking respectively 30% and 40% anode and cathode ionomer (ι) equivalents, 9.70x10⁻⁶V was lost due to ion conductivity for a 59 μ m thick wet Nafion® 112 (Mench, 2008):

Ionic **Loss:**

$$\eta_{\text{ionic}} = i \left(\frac{l_a}{\iota_a \sigma_e} + \frac{l_e}{\sigma_e} + \frac{l_c}{\iota_c \sigma_e} \right) = 1.10 \left(\frac{2.5 \times 10^{-6}}{0.3 \times 5} + \frac{59 \times 10^{-6}}{10} + \frac{2.5 \times 10^{-6}}{0.4 \times 5} \right) = 9.6984 \times 10^{-6} \text{V} \tag{13}$$

The flexibility of the woven-carbon-cloth DL makes for its durability hence its preference to the bristle nonwoven-paper DL that can barely withstand mechanical strain (Mench, 2008). Hence 7.84x10⁻⁷V was lost due to electron mobility in the 0.025cm thick DL of 20% polytetraflouroethelyne (PTFE) of 2 x 10⁴ S/m conductance:

Electronic **Loss:**

$$\eta_{\text{elect}} = i \left(\frac{l_{GP}}{\sigma_{GP}} + \frac{l_{DL}}{\sigma_{DL}} + \frac{l_{CL}}{2\sigma_{CL}} \right) = 1.10 \left(\frac{4 \times 10^{-3}}{2 \times 10^4} + \frac{25 \times 10^{-5}}{2 \times 10^4} + \frac{5 \times 10^{-6}}{2 \times 5} \right) = 7.84 \times 10^{-7} \text{V} \tag{14}$$

For a 3:1 Landing to Channel ratio: $A_{GP} = 0.75A = 0.75 \times 4.1 = 3.075 \text{cm}^2$ and for the DL-CL contact surface area which is equal the 2D surface area of either the DL or the CL: $A_L = 5 \times 10 = 50 \text{cm}^2$:

Contact

Loss:

$$\eta_{\text{contact}} = iA \left(\frac{R_{\text{GP}}}{A_{\text{GP}}} + \frac{R_{\text{L}}}{A_{\text{L}}} \right) = 1.10 \times 4.1 \left(\frac{30 \times 10^{-3}}{3.075} + \frac{30 \times 10^{-3}}{50} \right) = 0.0467V \quad (15)$$

Therefore; $\eta_r = 9.6984 \times 10^{-6} + 7.8375 \times 10^{-7} + 4.671 \times 10^{-2} = 0.0467V$

At the operating condition; water in the cell remains in its vapour state and the saturated pressure of the humidified air: 0.2564 atm and 0.4706 atm were estimated at the respective temperature (65°C) and (80°C).

$$P_{\text{am}}(T) = -2846 + 411.24T - 10.554T^2 + 0.16636T^3 \quad (16)$$

The amount of oxygen in the humidified air available for the cell oxidation reactions was estimated from the concentration of the water and air using the Relative Humidity (RH) relationship. Giving that dry air contains approximately 21% Oxygen, 0.1562 fraction of Oxygen ($C_{\text{O}_2, \text{s}, 65}$) was available for the oxidative reaction at the operating condition. That is, for 0.1112 fraction of Oxygen ($C_{\text{O}_2, \text{s}, 80}$) in the humidified air at 80°C; more oxygen is available for the cell operation at 65°C.

$$RH = \frac{P_i}{P_{\text{sat}}(T)} = \frac{y_{\text{vap}} P_T}{P_{\text{sat}}(T)} \quad (17)$$

Taking a unit electron transfer ($z = 1$) and ORR order of 0.75 for negligible anodic transfer resistance at no change in exchange current density (i); 0.0073V was loss due to availability of oxygen at the electrodes, giving gas constant (R): 8.314J/mol.K for a 1 Faraday charge. That is,

$$\eta_o = \eta_{oa} + \eta_{oc} = 0 + \eta_{oc} = \eta_{o(65)} - \eta_{o(80)} = \frac{RT}{(z + \gamma)F} \ln \left(\frac{C_{\text{O}_2, \text{s}, 65}}{C_{\text{O}_2, \text{s}, 80}} \right) \quad (18)$$

And
$$\eta_o = \frac{R}{(z + \gamma)F} [T_{65} \ln C_{\text{O}_2, \text{s}, 65} - T_{80} \ln C_{\text{O}_2, \text{s}, 80}] \quad (19)$$

The **concentration** loss can be averted if EtOH transfer to the electrode surface is greater or equal the rate of consumption. Empirically, at the anode, Larminien & Dicks, (2003) have suggested polarization due to concentration as a simple model of a complex fuel cell. Taking $m = 2 \times 10^{-5}V$ and $n = 7 \text{ cm}^2/A$, at current density 1.1A/cm², the cell is inherent of 0.0442V loss due to transfer resistance.

$$\eta_m = me^{ni} = 0.0442V \quad (20)$$

Therefore, 0.0515V is lost due to concentration:

$$\eta_{\text{Conc}} = \eta_o + \eta_m = 0.0073 + 0.0442 = 0.0515V \quad (21)$$

Therefore, the simulated cell was inherent of 0.1211V Over-potential due to activation, conduction and concentration losses:

$$V_L = \eta_a + \eta_r + \eta_{conc..} = 0.0229 + 0.0467 + 0.0515 = 0.1211V \quad (22)$$

Thermodynamically, 452.47kJ energy generation is estimated per mole of EtOH consumed in the cell. As indicated in the cell reactions, 9.84kJ/g specific Energy can be generated by 1M EtOH:

$$\psi = \frac{-\Delta G^{\circ}_{cell}}{M_{EtOH}} = 9.84kJ/g \quad (23)$$

Applying the Nernst Equation for the stoichiometric cell reaction (4e⁻ transfer); the minimum possible voltage that is, thermodynamic voltage, to drive the cell reaction without irreversibility is the cell *emf* estimated as:

$$E_o = \frac{-\Delta G^{\circ}_{actual}}{nF} = 1.1724VoltsSHE \quad (24)$$

Giving the available cell potential as

$$E_{cell} = E_o - V_L = 1.0513V \quad (25)$$

Recall, the cell operates at constant temperature, however, increased thermal energy enhances the cell reaction. To maintain the operating temperature while trying to maintain and/or enhance the cell reaction, the cell voltage adjusts above the thermodynamic voltage. This adjusted voltage is the Thermoneutral Voltage (E_{th}) if its product with current generated heat to drive the process while keeping the operating temperature constant. In view that the reaction energies went into useful work and the rate of entropy change being zero, the E_{th} is the maximum voltage for the reversible adiabatic process.

$$\Delta H_{298} = -1370kJ/molEtOH$$

$$E_{th} = \frac{-\Delta H}{nF} = 3.549V \quad (26)$$

Based on the conservation of current ($i_{cell} = i_a = i_c$), and for the current flow area of 50cm² and a current density of 0.6A/cm² from the Ohmic region of the polarization curve (Fig 2); the cell is capable of a 30A. Evoking the Watt's law: 106.50W power was generated from the maximum voltage and

the irreversible power (P_L) of the cell (3.633W) was estimated from the 0.1211V lost Voltages:

$$P = IV = I\eta_{i=a,r,C} \quad (27)$$

$$P_L = I(\eta_{act} + \eta_r + \eta_{conc}) = 0.6871 + 1.4011 + 1.5451 = 3.633W \quad (28)$$

In view of fuel dilution and low fraction of oxygen in the humidified air in operation, the emf of the cell cannot be considered as the ideal voltage of the cell hence cannot assess the ideal power of the cell (Gaggioli & Dunbar, 1993). The Specific Electrical power generated for a 90 second operation (kW/g) .

$$P_{cell} = \frac{-\Delta G^{\circ}_{cell}}{90MW} = 0.1092kW / g \quad (29)$$

Therefore, at 0.31g EtOH feed, 90 seconds operation, 3.05kJ of Energy is produced resulting in 33.89W of ideal power generation and 1.1267V ideal voltage.

$$P_G = 0.31 * p_{cell} = 0.03389kW \quad (30)$$

Efficiency

Under reversible conditions, the possible thermodynamic efficiency gives the ratio of the actual electrical work to the potential electrical work. Thus the ratios: minimum expected voltage: E_o (1.1724V) to thermoneutral voltage: E_{th} (3.549V) gave a 33% reversible efficiency (ϵ_r) and actual cell voltage E_{cell} (1.0513V) to the thermoneutral voltage give a 30% actual efficiency (ϵ_i)

$$\epsilon_r = \frac{E_o}{E_{th}} = \frac{\Delta G^{\circ}}{\Delta H} = \frac{1.1724}{3.549} = \frac{452.45}{1370} = 0.33 \quad (31)$$

$$\epsilon_i = \frac{E_{cell}}{E_{th}} = \frac{1.0513}{3.55} = 0.30 \quad (32)$$

The proportion of the actual power output (P_{act}) with respect to the ideal power (P_i) indicates the FC Efficiency (ϵ_{cell}). Therefore, 89% efficiency is expected for a 1.0513V cell of 1.1724V emf.

$$\epsilon_{cell} = \frac{P_{act}}{P_i} = \frac{30.16}{33.89} = 0.89 \quad (33)$$

Considering 0.5V working ideal voltage and 0.1A/cm², a conforming electrochemical efficiency of 43% was calculated.

$$\epsilon_{\text{elect}} = \frac{V_i}{E_o} = \frac{0.5}{1.1724} = 0.4265 \quad (34)$$

Ideally, the FC is expected to have 39% and 14% Potential efficiencies under reversible and ideal electrochemically operating conditions respectively:

$$\epsilon_{P,rev} = \epsilon_{\text{cell}} * \epsilon_{\text{elect}} = 0.90 \times 0.43 = 0.387 \quad (34)$$

$$\epsilon_{P,ideal} = \epsilon_{\text{th}} * \epsilon_{\text{elect}} = 0.33 * 0.43 = 0.14 \quad (35)$$

The DEFC Operation

The 30W simulated DEFC operated with a 3.4M aqueous ethanol solution prepared from 95% ethanol and distilled water, and fed to the anode via the cell flow channels. Through the DL, the EtOH solution diffused to the catalyst where the oxidation of EtOH and reduction of water took place. At 2cm³/s EtOH dosed, considering PtSn/C electrocatalyst at 65°C, the redox reactions released charges (H⁺ and e⁻) and produce CH₃CHO which oxidized further to CH₃COOH and CO₂. The protons (H⁺) were transferred by potential difference via the PEM (Nafion®127) to the cathode and the electrons drawn from the anode, passing through the external circuit (Load) as direct electric current, to the cathode. At the cathode, oxygen from the humidified air promoted the cathodic charge transfer reactions thus producing water. Note; at the membrane, the electrodes, layers and the electron transfer materials; as well as operating conditions, potentials were lost thus power generated was not the power available.

Table 1: Summary of exergy analysis of the direct 95% ethanol fuel cell (DEFC)

| Parameter | Value |
|---|---------|
| Thermodynamic Voltage (E _o) | 1.1724V |
| Cell Voltage (E _{cell}) | 1.0513V |
| Cell Overpotential | 0.1211V |
| Ideal Voltage of Cell | 1.1267V |
| Electrical Energy | 3.050kJ |
| Ideal Power | 33.79W |
| Actual Power | 30.16W |

| | | |
|--|--|---------------|
| Irreversible Power | | 3.633W |
| Reversible efficiency | | 33% |
| Irreversible efficiency | | 30% |
| Cell efficiency | | 89% |
| Gibbs Free Energy (ΔG°) | | -452.47kJ/mol |
| Enthalpy (ΔH°) | | -1370kJ/mol |

Discussions

The low feed concentration of 20% EtOH and the 2cm³/s dosing rate that generated the 3.042kJ energy was a pointer ascertaining the viability of ethanol in substantive power generation even at very low amount.

Though high cell operating temperature will ensure quick and easy start of the cell reactions, the energy expended in the cell ignition enhances the losses due to activation. The nonspontaneous 65°C operating temperature resulted in the 0.0216V considerable loss. At low operation temperature typical of low to negligible loss; a feasible and readily functional cell is very likely unattainable. From the model, increase in operating temperature brings about an increase in activation over potential; for every 10° rise in operation temperature; the over potential increases by 0.0006V.

Following the advent of very suitable membrane and layer materials inherent of adequate ion, and electron mobility and transfer; 59µm thick wet Nafion® 112, 0.025cm thick woven-carbon-cloth DL of 20% polytetrafluoroethylene (PTFE) was considered thus ensuing the 8.91x10⁻⁶V loss due to ionic and electronic conductivity. This loss is a very negligible proportion of the 0.0467V Ohmic loss and it is typical of the loss due to componental contact. This points the need to ensure proper contact area, and conscious component fittings and tightening. The highest loss of 0.0515V recorded was due to concentration: largely due to EtOH transfer resistance; signifying the fuel availability at site is very key. Componental contact enhanced charge transport, concentration and permeability improves fuel transport thus the losses and generation were chiefly due to transport. Therefore, the major losses in the simulated cell as indicated: 0.0467V and 0.0515V were due to charge and reactant transport. Transport dependent on material features and properties: permeability of membranes and layers, available contact surface area and material specifications. These losses due to transport amounted to circa 80% of the 0.1211V loss inherent of the simulated cell. The specification of thin material of high conductivity and permeability was inherent in ensuring portability and optimal operation of the cell in its application for power generation.

At a loss of 0.1211V from the 1.1724V OCV, the simulated cell was inherent of 1.0513V potential hence probable of generating 31.539W of power. Considering the OCV was estimated from stoichiometry, the 31.539W generation was due to $4e^-$ stoichiometric release. The cell operating at 2cm^3 20% EtOH feed per second released $0.0272e^-$ from the 0.0068 moles fed.

Thermodynamically, EtOH has 452.47kJ/mol energy available for reversible power generation; therefore, the 9.84kJ/g energy density for 20% EtOH solution was an assenting certification to the propensity of EtOH as a viable power generation biofuel. At this energy density; for a 0.31g EtOH feed at 0.0068mol/s molar rate and 1.5min operation time, the cell was able to generate 0.109kW/g power density, thus producing 3.050kJ energy and 33.79W useful reversible power. Therefore at 0.1211V overpotential, the simulated cell lost 3.633W power and to produce 30.16W of useful irreversible power.

Higher temperature has been indicated to enhance fuel cell reaction, thus making it an endothermic process. As the cell reaction proceeded the electrodes get cold due to endothermicity hence the excess energy due to E_{th} sustained the reaction and kept the operating temperature constant.

Since the cell capacity was based on the available power, the ratio of the thermodynamic voltage to the the Thermoneutral voltage indicated that 33% of the power generated in the cell was actually available for external use for negligible operational losses giving the reversible efficiency. However, considering the inherent significant losses, the DEFC operated at a 30% irreversible efficiency. The DEFC was capable of approx. 89% available power as the useful power output.

Taking proper and cognizant material specification, adjusting operating temperature and considering suiting materials' parameters; DEFCs capable of generating any amount of power can be simulated from existing models.

Conclusions

Application of ethanol in DEFCs will foster the economy of producing nation in forestalling, leveraging and the control of the global menace hounding human existence: the greenhouse effect.

The promise of materials and parameters manipulations in the application of ethanol in fuel cell would encourage speedy diversifications in power generation seeing the current leap the world is aiming towards remediation of environmental threat due to fossil fuel.

Generating significant energy: 3.042kJ and 30.16W power from a low feed concentration: 20% EtOH at 2cm³/s dosing rate was a pointer ascertaining the viability of ethanol in fuel cells.

Taking proper and cognizant materials' parameters and specification, and adjusting operational parameters including temperature; DEFCs capable of generating any given amount of power can be simulated from extant fuel cell models.

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