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INVESTIGATION OF THE EFFECT OF OPERATING PARAMETERS ON NERNST VOLTAGE IN HYDROGEN-OXYGEN FUEL CELLS

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Abstract: In hydrogen-oxygen fuel cells, operating parameters have an influence on the maximum expected open circuit (Nernst) voltage. Even though fuel cells have been the subject of many research, none of them have theoretically investigated the impact of various operating parameters, particularly concerning Nernst voltage and maximum thermodynamic efficiency. In this study, a computer program was developed to theoretically determine the effect of various operating parameters on the Nernst voltage in hydrogen-oxygen fuel cells. This computer program was developed in MATLAB to mathematically examine the effects of hydrogen and oxygen mole ratios, anode and cathode pressures, and operating temperatures on the maximum expected open circuit voltage. When calculating Nernst voltages and maximum thermodynamic efficiency for fuel cell reactions containing water as a by-product, the effects of higher heating value (HHV) and lower heating value (LHV) are also considered in the solutions. As a result, it was also concluded that temperature increase reduces the fuel cell Nernst voltage and maximum thermodynamic efficiency. Therefore, it was observed from the figures that the best conditions for the Nernst voltage occur when HHV is assumed, the temperature is 353 K, the mole ratios of hydrogen and oxygen are 1.0, the anode and cathode pressures are 5 atm and 6 atm, respectively. In terms of thermodynamic efficiency, it was determined that there was a maximum increase of 92.2% in the LHV assumption compared to the HHV assumption at the temperature of 1000 K, provided that other operating parameters were kept constant.
Keywords: Nernst voltage, Fuel cell, Thermodynamic efficiency, Hydrogen-oxygen.

HİDROJEN-OKSİJEN YAKIT HÜCRELERİNDE ÇALIŞMA PARAMETRELERİNİN NERNST VOLTAJINA ETKİSİNİN İNCELENMESİ

Özet: Hidrojen-oksijen yakıt hücrelerinde çalışma parametrelerinin beklenen maksimum açık devre (Nernst) voltajı üzerinde etkisi vardır. Yakıt hücreleri birçok araştırmaya konu olmasına rağmen hiçbiri, özellikle Nernst voltajı ve maksimum termodinamik verimlilikle ilgili çeşitli çalışma parametrelerinin etkisini teorik olarak incelememiştir. Bu çalışmada, hidrojen-oksijen yakıt hücrelerinde çeşitli çalışma parametrelerinin Nernst voltajına etkisini teorik olarak belirlemek için bir bilgisayar programı geliştirilmiştir. Bu bilgisayar programı, hidrojen ve oksijen mol oranlarının, anot ve katot basınçlarının ve çalışma sıcaklıklarının beklenen maksimum açık devre voltajı üzerindeki etkilerini matematiksel olarak incelemek için MATLAB'da geliştirilmiştir. Yan ürün olarak su içeren yakıt hücresi reaksiyonları için Nernst voltajları ve maksimum termodinamik verim hesaplanırken, çözümlerde üst ısıl değeri (HHV) ve alt ısıl değerinin (LHV) etkileri de dikkate alınmaktadır. Sonuç olarak sıcaklık artışının yakıt hücresi Nernst voltajını ve maksimum termodinamik verimi azalttığı sonucuna varılmıştır. Dolayısıyla Nernst voltajı için en iyi koşulların HHV kabulünde, sıcaklığın 353 K, hidrojen ve oksijenin mol oranlarının 1,0, anot ve katot basınçlarının sırasıyla 5 atm ve 6 atm olduğu durumlarda oluştuğu, grafiklerden gözlemlenmiştir. Termodinamik verim açısından diğer çalışma parametrelerinin sabit tutulması koşuluyla 1000 K sıcaklıkta LHV varsayımında HHV varsayımına göre maksimum %92,2 oranında bir artış olduğu tespit edilmiştir.
Anahtar Kelimeler: Nernst voltajı, Yakıt hücresi, Termodinamik verim, Hidrojen-oksijen.

NOMENCLATURE

F	Faraday constant	C_p	Specific heat [J/kg·K]
T	Temperature [K]	R_u	Universal gas constant [J·K/mol]
a	Thermodynamic efficiency coefficient	E^o	Reversible voltage [V]

E^{oo}	Thermal voltage [V]
η_{th}	Thermodynamic efficiency

Subscripts

H_2	Hydrogen
O_2	Oxygen
a	Anode
c	Cathode
n	Equivalent number of electrons per unit mole of the relevant species

INTRODUCTION

The energy need in the world is increasing day by day due to developing technology, increasing population and the search for continuous economic and industrial development (Cellek and Bilgili, 2021; Gonzatti and Farret, 2017; Hernández-Gómez et al., 2020). Today, the decrease in fossil energy sources such as oil and natural gas, which meet a large part of this need, and the increasing damage to the environment lead scientists to various alternative energy sources (Liu et al., 2023; Sadeghi et al., 2021; Wang et al., 2023). Due to the problems caused by fossil energy sources, there is an increasing interest in renewable energy in the world (Abouemara et al., 2024; Mitra et al., 2023; Riad et al., 2023). However, the need to store energy in the use of non-continuous alternative energy sources such as the sun and wind has brought the use of hydrogen energy to the agenda (Arıç et al., 2019). Since hydrogen is one of the most efficient, cleanest and lightest fuels, it is an alternative energy carrier (Hernández-Gómez et al., 2020). Fuel cells, which constitute the most weighty part of research on hydrogen energy, attract attention (Arıç et al., 2019).

Fuel cells are electrochemical devices that convert chemical energy into work in the form of electrical energy and heat, as shown in Figure 1 (Mitra et al., 2023; Wang et al., 2023; Zhao et al., 2023). Contrary to the harmful emissions resulting from the combustion of fossil fuels, only water is formed as a by-product as a result of the reactions occurring in fuel cells. For this reason, fuel cells are seen as an environmentally friendly power source (Cellek and Bilgili, 2021). In addition, these devices have advantages such as high efficiency, quiet operation, fuel flexibility and low maintenance requirements. Fuel cells are used in power plants, automobiles, laptop computers, mobile phones, etc. where power is required at different scales (Liu et al., 2023; Mitra et al., 2023).

Abbreviations

LHV	Lower heating value
HHV	Higher heating value
OCV	Open circuit voltage
PEM	Proton exchange membran
SOFC	Solid oxide fuel cell

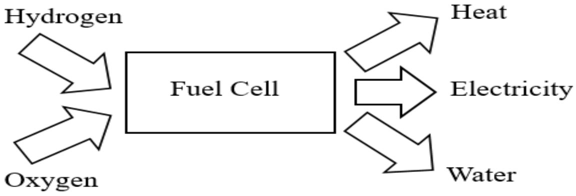

Figure 1. Simple H_2/O_2 fuel cell schematic impression

Determining the performance of a fuel cell depends on thermodynamic evaluation. Because a fuel cell is an electrochemical device that converts the chemical energy of a fuel and an oxidizing gas into electrical energy, predictions that can be made using thermodynamic equations are essential to understanding fuel cell performance. When a fuel cell is operating, some of the input is used to generate electrical energy, while some is converted into heat energy, depending on the type of fuel cell. Based on the first and second laws of thermodynamics, thermodynamic equations can be written to specify how energy can be transferred from one form to another (Khotseng, 2020).

Zhang et al. (2006) in their study on the PEM fuel cell, experimentally determined the open circuit voltage at 3 atm pressure and 6 different temperatures (between 23°C and 120°C). In their studies, it was stated that the open circuit voltage decreased with increasing temperature. Şefkat and Özel (2018) modeled a PEM fuel cell system with the help of MATLAB Simulink program. They concluded that the Nernst voltage increases with increasing hydrogen and oxygen pressures and decreases with increasing water pressure and temperature. (Sahli et al. (2017) examined the effect of various operating parameters on cell voltage and power density. As a result, they stated that the cell voltage and power density are proportional to the operating temperature and oxygen concentration, but inversely proportional to the supply pressure, fuel moisture and electrolyte thickness. In a similar study by Duncan et al. (2011) the dependence of open circuit voltage (OCV) and maximum power density on electrolyte thickness for solid oxide fuel cells (SOFCs) was investigated. As a result, it was emphasized that OCV decreases with decreasing electrolyte thickness and there is an optimum electrolyte thickness at which maximum power density occurs. Bo et al. (2009)

developed a thermodynamic model for the tubular SOFC stack and investigated the effects of various parameters on the SOFC system. They stated that the changes in current density, operating temperature, operating pressure, fuel utilization factor, air utilization factor and S/C ratio significantly affect the performance of SOFC and these parameters should be optimized for the best SOFC performance. Amadane et al. (2018) performed a PEM fuel cell model in MATLAB code and investigated the effect of temperature on PEMFC performance. As a result, they showed that the performance of the PEM fuel cell increases with temperature. In the study by Tu et al. (2020) the relationships between the reactions of methane on the nickel-based anode, fuel compositions, carbon deposition, electromotive force (EMF) and open circuit voltage (OCV) of SOFC were investigated. It was concluded that the temperature had different effects on the EMF and OCV values according to the fuel composition used. Matsui et al. (2005) emphasized that open circuit voltage in medium temperature solid oxide fuel cells (SOFCs) depends on electrode activity and electrolyte thickness, and overpotential at electrode/electrolyte interfaces affects OCV due to internal short circuit. In another study, Lyu et al. (2020) divided the voltage losses that cause the Nernst voltage drop in the hydrogen-oxygen fuel cell into three categories and said that the concentration loss does not cause the Nernst voltage loss.

The Nernst voltage is the starting point of the polarization curves that show the performance of fuel cells. Although there are many studies on fuel cells in the literature, there is no study that theoretically examines the effect of different operating parameters, especially on Nernst voltage and maximum thermodynamic efficiency. In this study, a MATLAB program was developed to theoretically examine the effect of various operating parameters on the Nernst voltage in hydrogen-oxygen fuel cells. The effects of cell temperature, hydrogen and oxygen mole ratios, anode and cathode pressures on the Nernst voltage were studied in detail theoretically. With the program developed in this context, the effect of each parameter on the Nernst voltage was calculated and the results were presented in graphics. In addition, analyzes were made considering both the lower heating value (LHV) and the higher heating value (HHV) of the fuel used. Maximum thermodynamic efficiency values for both heating value (LHV/HHV) assumptions were calculated at different operating temperatures. The results were compared by presenting them with graphics.

FUEL CELL AND WORKING PRINCIPLE

A fuel cell is an electrochemical device that converts chemical energy, typically from hydrogen, directly into electrical energy (Outeiro et al., 2008). The fuel cell is generally composed of an impermeable electrolyte, an anode and a cathode electrode in a permeable structure and in contact with both sides of the electrolyte. Electron flow occurs due to the potential difference formed as a result of the electrochemical reactions that occur when the gaseous fuel is sent to the anode part and the oxidizing gas to the cathode part. After the reactions take place, electrical energy is produced and external heat and pure water are formed. By connecting the fuel cells in series, more power output can be obtained than the power output from a single fuel cell. A basic representation for a single cell is given in Figure 2 (Işık, 2019).

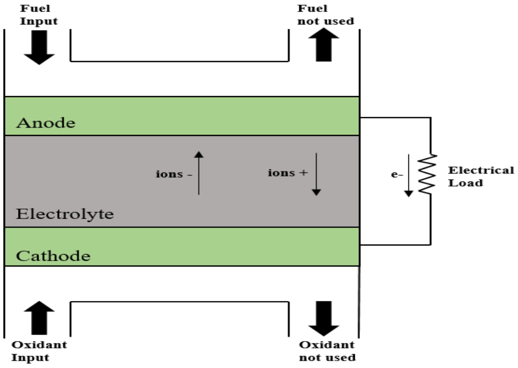

Figure 2. The basic structure of a fuel cell

Fuel cells are classified according to the choice of electrolyte, fuel and operating parameters. Hydrogen is the most used fuel for various fuel cells. It has high reactivity for anode reactions, can be produced chemically from a wide variety of fossil and renewable fuels as well as by electrolysis (Pachauri and Chauhan, 2015).

In a hydrogen fuel cell, electrochemical reactions occur simultaneously. The oxidation reaction of hydrogen occurs at the anode side, and the reduction reaction of oxygen occurs at the cathode side of fuel cell. These reactions take place at the anode, cathode and the total reaction are given in Equation (1), Equation (2), and Equation (3), respectively.

Anode reaction : $H_2 \rightarrow 2H^+ + 2e^-$ (1)

Cathode reaction : $2H^+ + 2e^- + 1/2O_2 \rightarrow H_2O$ (2)

Total reaction : $H_2 + 1/2O_2 \rightarrow H_2O$ (3)

When calculating thermodynamic voltages for reactions containing water as a product, the following defined Higher Heating Value (HHV) and Lower Heating Value (LHV) are selected:

- Higher Heating Value (HHV): It is assumed that all of the product water is in the liquid phase.
- Lower Heating Value (LHV): It is assumed that all of the product water is in the gas phase.

The difference between the two values is proportional to the latent heat of vaporization of the liquid. In practice, LHV is suitable for high temperature fuel cells, but the HHV value is also commonly used (Khotseng 2020).

NERNST VOLTAGE THEORY

The open circuit voltage for an H_2/O_2 fuel cell is the maximum operating voltage (no current) and is determined by the chemical thermodynamics of the overall cell reaction. The Nernst equation provides a relationship between the reversible voltage (E^o) and the open circuit voltage for the cell reaction (Khotseng, 2020). The cell potential at equilibrium with the Nernst voltage is calculated by the Nernst equation.

The Nernst equation is a result of the equilibrium established at the electrode surfaces. A significant gradient can exist between the concentration of a species in the channel of a fuel cell and the electrode, especially under high-current-density conditions, which cannot be considered a true thermodynamic equilibrium situation anyway (Mench, 2008).

The Nernst equation for the hydrogen-oxygen fuel cell total reaction (Equation (3)) can be written as Equation (4). In this equation, the first term represents the reversible voltage, while the second term represents a term that depends on the thermodynamic efficiency coefficients and hence the pressure. The E(T, P) value (Nernst voltage) is calculated by adding these two terms.

$$E(T, P) = E^o(T) + \frac{R_u T}{nF} \ln \left[\frac{a_{H2}(a_{O2})^{\frac{1}{2}}}{a_{H2O}}\right] \tag{4}$$

In Equation (4), $E^o(T)$ represents the reversible voltage, R_u universal gas constant, T temperature, n the equivalent number of electrons per unit mole of the relevant species, F Faraday constant, a the thermodynamic efficiency coefficient for the reacting species. We can reduce Equation (4) to Equation (5) by assuming an ideal gas and changing the thermodynamic activity coefficients. The second term in Equation (5) is seen as a pressure-dependent term.

$$E(T,P)=E^o(T)+\frac{R_u T}{2F}\ln\left[\frac{(y_{H2}P_{anode}/P^{\circ})(y_{O2}P_{cathode}/P^{\circ})^{\frac{1}{2}}}{y_{H2O}P_{cathode}/\ P_{sat}(T)}\right] \tag{5}$$

where the reversible voltage (E^o) represents the maximum theoretical voltage that can be supplied by an open-circuit cell under standard pressure and temperature conditions (1 atm and 298 K). T represents temperature in [Kelvin], R_u universal gas constant [J.K/mol], n represents the number of equivalent electrons per unit mole of the relevant species, F represents Faraday constant [C/equivalent e-]. Also, y_{H2} and y_{O2} are the mole ratios of hydrogen and oxygen, respectively, P_{anode} and $P_{cathode}$ are the anode and cathode pressures [atm], P^o standard pressure [atm], and P_{sat} saturation pressure (Nascimento et al., 2020).

The reversible voltage (E^o) can be determined as in Equation (6):

$$E^o(T) = \frac{-\Delta G^{\circ}(T)}{nF} = -\frac{\Delta H(T) - T\ \Delta S(T)}{nF} \tag{6}$$

To calculate the reversible voltage value of the fuel cell at a certain temperature, it is necessary to determine both the enthalpy and the entropy change for the reacting species.

To determine the change in enthalpy of the reaction, we can use Equation (7) between the product and reactant states:

$$\Delta H_{P\text{-}R} = \left(\sum_{i=1}^{n} n_i h_i\right)_P - \left(\sum_{j=1}^{m} n_j h_j\right)_R \tag{7}$$

where the index R represents the reactants, P products, n the number of moles of the species concerned, and h the specific enthalpy.

We can arrange Equation (7) for the reacting species as follows:

$$\Delta H_{P\text{-}R}=\left(h^o_{f,H_2O}+\int_{T_{ref}}^{T} c_{P,H_2O}(T)dT\right)H_2O-\frac{1}{2}\left(h^o_{f,O_2}+\int_{T_{ref}}^{T} c_{P,O_2}(T)dT\right)O_2-\left(h^o_{f,H_2}+\int_{T_{ref}}^{T} c_{P,H_2}(T)dT\right)H_2 \tag{8}$$

where the specific heat functions can be directly integrated or the specific heat values can be considered constant at an average temperature. Assuming constant specific heat at average temperature, Equation (8) can be written as follows:

$$\Delta H=[h^{\circ}{}_{f,H_2O}+c_{P,H_2O,ave}(T-T_{ref})]H_2O-\frac{1}{2}[h^{\circ}{}_{f,O_2}+c_{P,O_2,ave}(T-T_{ref})]O_2-[h^{\circ}{}_{f,H_2}+c_{P,H_2,ave}(T-T_{ref})]H_2 \tag{9}$$

Enthalpies of formation (h^o_f) are available in thermodynamic reference books. Specific heat values for hydrogen, oxygen, and water can be found with the help of Equation (10), Equation (11) and Equation (12), respectively:

$$\frac{c_P(T)H_2}{R_u} = 3.057 + 2.677 \times 10^{-3}T - 5.810 \times 10^{-6}T^2 + 5.521 \times 10^{-9}T^3 - 1.812 \times 10^{-12}T^4 \tag{10}$$

$$\frac{c_P(T)O_2}{R_u} = 3.626 - 1.878 \times 10^{-3}T + 7.055 \times 10^{-6}T^2 - 6.764 \times 10^{-9}T^3 + 2.156 \times 10^{-12}T^4 \tag{11}$$

$$\frac{c_P(T)H_2O}{R_u} = 4.070 - 1.108 \times 10^{-3}T + 4.152 \times 10^{-6}T^2 - 2.964 \times 10^{-9}T^3 + 0.807 \times 10^{-12}T^4 \tag{12}$$

Equation (13) can be used to determine the change in entropy:

$$\Delta S=(s^{o}_{f,H_2O}+\int_{T_{ref}}^{T}\frac{c_{P,H_2O}(T)dT}{T})H_2O-\frac{1}{2}(s^{o}_{f,O_2}+\int_{T_{ref}}^{T}\frac{c_{P,O_2}(T)dT}{T})O_2-(s^{o}_{f,H_2}+\int_{T_{ref}}^{T}\frac{c_{P,H_2}(T)dT}{T})H_2 \quad (13)$$

Again, for the specific heat terms, their values can be obtained by integrating Equation (10), Equation (11) and Equation (12), but when solved with the assumption of constant specific heat at average temperature, the error is below 1%. Therefore, solutions are realized with constant specific heat assumption. The entropy of formation ($s^{\circ}{}_{f}$) at 1 atm pressure is available in thermodynamic reference books. The entropy change is obtained by the Equation (14) (Mench, 2008):

$$\Delta S=(s^{\circ}{}_{f,H_2O}+c_{P,H_2O,ave}ln\frac{T}{T_{ref}})H_2O-\frac{1}{2}(s^{\circ}{}_{f,O_2}+c_{P,O_2,ave}ln\frac{T}{T_{ref}})\ O_2-(s^{\circ}{}_{f,H_2}+c_{P,H_2,ave}ln\frac{T}{T_{ref}})\ H_2 \quad (14)$$

The effect of pressure on the Nernst voltage in Equation (5) is shown with P and can be calculated with the help of Equation (15):

$$P=\frac{R_uT}{2F}\ ln\ [\frac{(y_{H2}P_{anode}/P^{\circ})(y_{O2}P_{cathode}/P^{\circ})^{\frac{1}{2}}}{y_{H2O}P_{cathode}/\ P_{sat}(T)}] \quad (15)$$

The energy conversion process in a fuel cell must satisfy the first law of thermodynamics and ensure energy conservation. Since the purpose of a fuel cell is to convert chemical energy into electrical energy, the thermodynamic efficiency of a fuel cell can be written as in Equation (16):

$$\eta_{th}=\frac{actual\ electrical\ work}{maximum\ available\ work} \quad (16)$$

As shown in Equation (17), the ratio of reversible voltage (E^o) to thermal voltage (E^{oo}), in other words, the ratio of maximum electrical work to total available potential electrical work, represents the maximum possible thermodynamic efficiency:

$$\eta_{t,max}=\frac{E^{O}}{E^{OO}}=\frac{-\Delta G/nF}{-\Delta H/nF}=\frac{\Delta H-T\Delta S}{\Delta H}=1-\frac{T\Delta S}{\Delta H} \quad (17)$$

While calculating the maximum thermodynamic efficiency value in the study, Equation (17) was used. Therefore, the efficiency expression was obtained after calculating the entropy and enthalpy changes.

A computer program was written, which was developed in the light of the above-mentioned theory and primarily calculates the Nernst Voltage. In addition, maximum thermodynamic efficiency values were calculated at different temperatures. The flow chart of the working of the developed program is given in Figure 3. In the program, first of all, temperature, pressure, hydrogen/oxygen mole ratios, and determined heating value (lower/higher) of the fuel are used. Specific heat values are calculated for hydrogen, oxygen, and water for the species in the fuel cell's overall reaction. Then, the reaction enthalpy and entropy changes are calculated for 41 different operating conditions. Nernst voltage and maximum thermodynamic efficiency values are obtained with the help of the developed program.

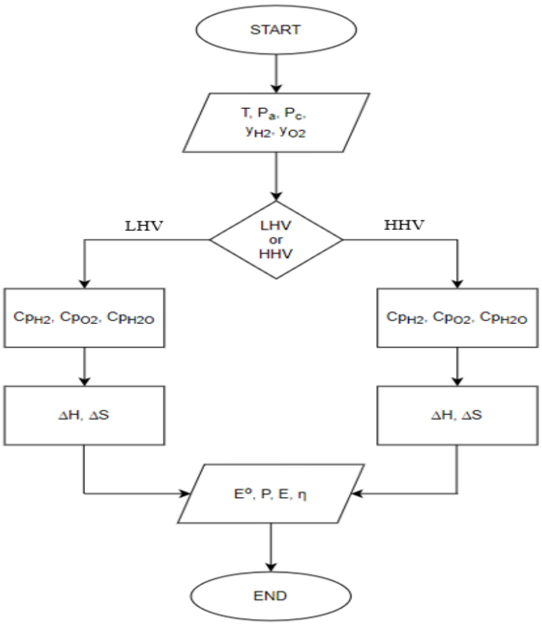

Figure 3. Flow chart of the developed program

MATHEMATICAL ANALYSIS

It is necessary to examine the Nernst voltage, which represents the voltage produced in the fuel cell, by taking into account the most important parameters affecting it. In this study, the effects of hydrogen mole ratio, oxygen mole ratio, operating temperature, anode and cathode pressures on the Nernst voltage were analyzed analytically. The thermodynamic equations written for the fuel cell were analyzed sequentially for the determined cases. In the numerical study, at a cell temperature of 353 K, the mole ratio of hydrogen (y_{H_2}) on the anode side is 0.8, the mole ratio of water vapor (y_{H_2O}) is 0.2, and the anode pressure (P_a) is 2 atm. On the cathode side, the mole ratio of oxygen (y_{O_2}) is 0.15, the mole ratio of water vapor (y_{H_2O}) is 0.1, the mole ratio of nitrogen (y_{N_2}) is 0.75 and the cathode pressure (Pc) is taken as 3 atm. These counted operating parameters were accepted as the reference case (Case-7) for future validation purposes and the Nernst voltage was calculated over this case. Then, the effect of each operating parameter such as temperature, anode and cathode pressure, hydrogen and oxygen mole ratios on the Nernst voltage was examined and compared with this reference case. The data for each case examined are given in Table 1.

Table 1. Different cases examined in the study

Case	y_{H_2}	y_{O_2}	T [K]	P_a [atm]	P_c [atm]
1	0.5	0.15	353	2	3
2	0.55	0.15	353	2	3
3	0.60	0.15	353	2	3
4	0.65	0.15	353	2	3
5	0.70	0.15	353	2	3
6	0.75	0.15	353	2	3
7	0.80	0.15	353	2	3
8	0.85	0.15	353	2	3
9	0.90	0.15	353	2	3
10	0.95	0.15	353	2	3
11	1.00	0.15	353	2	3
12	0.80	0.21	353	2	3
13	0.80	0.25	353	2	3
14	0.80	0.35	353	2	3
15	0.80	0.45	353	2	3
16	0.80	0.55	353	2	3
17	0.80	0.65	353	2	3
18	0.80	0.75	353	2	3
19	0.80	0.85	353	2	3
20	0.80	0.95	353	2	3
21	0.80	1.00	353	2	3
22	0.80	0.15	400	2	3
23	0.80	0.15	500	2	3
24	0.80	0.15	600	2	3
25	0.80	0.15	700	2	3
26	0.80	0.15	800	2	3
27	0.80	0.15	900	2	3
28	0.80	0.15	1000	2	3
29	0.80	0.15	353	1	3
30	0.80	0.15	353	1.5	3
31	0.80	0.15	353	2.5	3
32	0.80	0.15	353	3	3
33	0.80	0.15	353	3.5	3
34	0.80	0.15	353	4	3
35	0.80	0.15	353	4.5	3
36	0.80	0.15	353	5	3
37	0.80	0.15	353	2	1
38	0.80	0.15	353	2	2
39	0.80	0.15	353	2	4
40	0.80	0.15	353	2	5
41	0.80	0.15	353	2	6

Effect of Mole Ratios

It is known that the reactions in the fuel cell occur simultaneously at both the anode and the cathode. Therefore, the effect of both the hydrogen mole ratio at the anode and the oxygen mole ratio at the cathode on the voltage can be examined separately.

Effect of oxygen mole ratio at the cathode on the Nernst voltage

Analyzes were made for different mole ratios of the oxygen gas at the cathode. Other parameters (pressure, temperature, hydrogen mole ratio) kept constant in the analyzes were taken from the reference case.
Numerical analyzes were performed at a cell temperature of 353 K. Numerical analyzes were performed for 11 different determined cathode oxygen mole ratios (0.15, 0.21, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95 and 1.0). The effect of the oxygen mole ratio at the cathode on the Nernst voltage was numerically investigated and the change is given in Figure. 4.

When Figure 4 is examined, it is seen that the Nernst voltage increases with the increase in the mole ratio of O_2 in the cathode in both HHV and LHV cases, but this increase gradually decreases. For the LHV case, when the O_2 mole ratio is taken as 0.15, the Nernst voltage value is calculated as approximately 1.173 V. When the mole ratio of O_2 is taken as 1, that is, when the cathode is completely fed with pure oxygen, the Nernst voltage value is calculated as 1.187V. When these two values are compared, it is seen that there is an increase of 1.19% in the Nernst voltage. When the Nernst equation (Equation 5) is examined, it is seen that the mole ratio of oxygen is directly proportional to the Nernst voltage. Therefore, it is expected that the Nernst voltage will increase as the mole ratio of oxygen at the cathode increases. In some studies in the literature, it has been stated that Nernst voltage is directly proportional to the oxygen-mole ratio (Sahli et al., 2017).

For the HHV case, when the O_2 mole ratio is taken as 0.15, the Nernst voltage value is calculated as approximately 1.184 V, while the Nernst voltage value is calculated as 1.199 V when the O_2 mole ratio is taken as 1. When these two values are compared, it is seen that there is a 1.27% increase in Nernst voltage.

Ambient air is more preferred at the cathode because of the cost and storage problems caused by the use of pure oxygen in fuel cells. Therefore, the use of air is also analyzed. For this case (O_2 mole ratio 21%), the Nernst voltage was obtained as 1.175 V in the case of LHV and 1.186 V in the case of HHV.

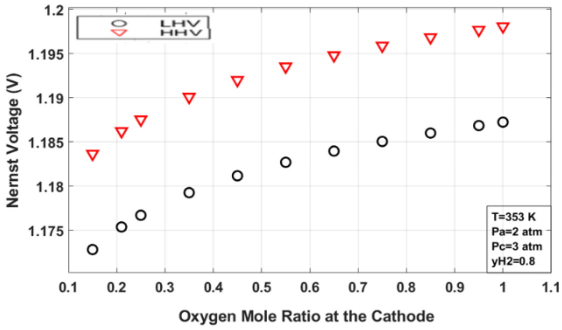

Figure 4. The Effect of Oxygen Mole Ratio at the Cathode to the Nernst Voltage

Effect of mole ratio of hydrogen at the anode on Nernst voltage

Analyzes were made for different mole ratios of hydrogen gas at the anode. Other parameters (pressure, temperature, oxygen mole ratio) kept constant in the analyzes were taken from the reference situation. The mole ratio of H_2 was repeated with increasing values such as 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95 and 1.00. The effect of the hydrogen mole ratio at the anode on the Nernst voltage is given in Figure 5.

It is seen that the Nernst voltage increases almost linearly for increasing hydrogen mole ratio in both HHV and LHV cases in Figure 5. For LHV assumption when the mole ratio of H_2 is taken as 0.50, the Nernst voltage value is calculated as approximately 1.166 V. When the mole ratio of H_2 is taken as 1, the Nernst voltage value is calculated as 1.176 V. As the mole ratio of H_2 in the anode side is increased from 50% to 100%, it has been observed that there is an increase of 0.86% in the Nernst voltage value. As explained in the previous section, considering the Nernst equation, it is seen that the hydrogen mole ratio at the anode affects the Nernst voltage directly. Since the hydrogen concentration in the fuel flow is high, a higher Nernst voltage is obtained (Mench, 2008; Pachauri and Chauhan, 2015).

For HHV assumption, when the mole ratio of H_2 is taken as 0.50, the Nernst voltage value is calculated as approximately 1.177 V. When the mole ratio of H_2 is taken as 1, the Nernst voltage value is calculated as 1.187 V. When these two values are compared, it is seen that there is an increase of 0.85% in the Nernst voltage.

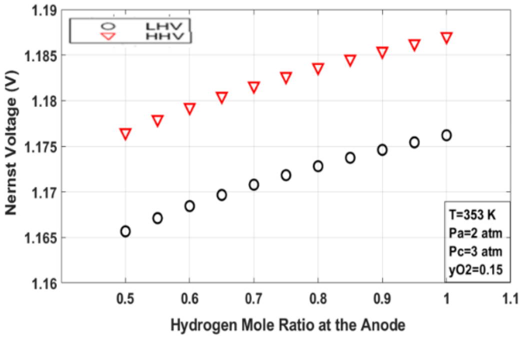

Figure 5. The effect of hydrogen mole ratio at the anode on the Nernst voltage

Pressure Effect

Different anode and cathode pressure values were determined in the computer program. The partial pressure of hydrogen can be calculated by multiplying the determined anode pressure with the mole ratio of hydrogen. The partial pressure of oxygen can be calculated by multiplying the determined cathode pressure with the mole ratio of oxygen.
It can be seen in Equation 5 that the partial pressures of hydrogen ($P_{H_2} = y_{H_2} \times P_{anode}$) and oxygen ($P_{O_2} = y_{O_2} \times P_{cathode}$) gases, and therefore the anode and cathode pressures, affect the Nernst voltage. In the numerical analysis, nine different anode pressures and six different cathode pressures are selected and solved. Effects of these pressures on the Nernst voltage are given separately following sections.

Effect of anode pressure

The effect of anode pressure on Nernst voltage is shown in Figure 6. The anode pressure was taken at different values such as 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 atm, and its effect on the Nernst voltage was examined. As seen in Figure 6, the Nernst voltage increases with the increase of anode pressure for both the HHV case and the LHV case, but this increase gradually decreases. There are other studies in the literature stating that increasing pressure positively affects fuel cell Nernst voltage (Arıç et al., 2019; Lyu et al., 2020; Nascimento et al., 2020).

In the case of LHV, the Nernst voltage value obtained as 1.162 V at 1 atm pressure increased to 1.187 V at 5 atm pressure. Accordingly, it is seen that there is an increase of approximately 2.15% in the Nernst voltage value as the anode pressure rises from 1 to 5 atm.

In the case of HHV, the Nernst voltage value obtained as 1.173 V at 1 atm pressure increased to 1.198 V at 5 atm pressure. Therefore, as the anode pressure increased from 1 to 5 atm, there was an increase of approximately 2.13% in the Nernst voltage value.

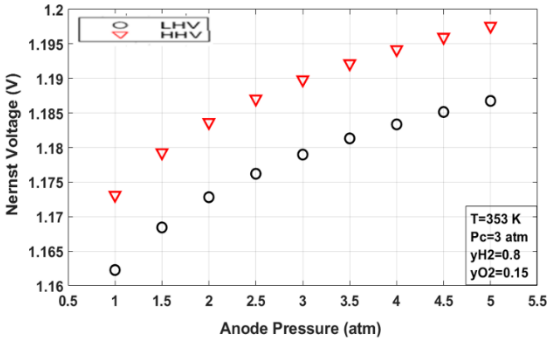

Figure 6. Effect of anode pressure on Nernst voltage

Effect of cathode pressure

The effect of cathode pressure on Nernst voltage is shown in Figure 7. The cathode pressure was taken at different values such as 1, 2, 3, 4, 5 and 6 atm, and its effect on the Nernst voltage was investigated. It is seen that the increase in cathode pressure positively affects the Nernst voltage for both the HHV and the LHV assumptions (Figure 7). The increase in pressure has some beneficial effects on fuel cell performance due to higher reactant partial pressure, gas solubility, and mass transfer values. In addition, electrolyte losses due to evaporation are reduced at high operating pressures. System efficiency tends to increase with increasing pressure (Çavuşoğlu, 2006).

In the case of LHV, increasing the cathode pressure from 1 to 6 atm increased the Nernst voltage value from 1.164 V to 1.178 V. When these two values are compared, it is seen that there is an increase of approximately 1.2% in the Nernst voltage. In the case of HHV, increasing the cathode pressure from 1 to 6 atm increased the Nernst voltage value from 1.175 V to 1.189 V. Considering these two values, it is understood that there is an increase of approximately 1.19% in the Nernst voltage.

In summary, when the cathode pressure increased from 1 to 6 atm, the Nernst voltage increased by about 1.2% for both LHV and HHV cases.

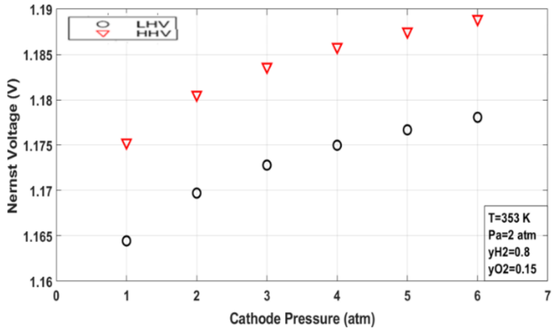

Figure 7. Effect of cathode pressure on Nernst voltage

Temperature Effect

Thermodynamic analyzes were carried out at different operating temperatures to see the effect of temperature, which is another important parameter for Nernst voltage. The findings obtained for the Nernst voltage and the maximum thermodynamic efficiency of the fuel cell in both the LHV case and the HHV case are explained in detail below.

Effect of LHV and HHV values on Nernst voltage

The Nernst voltage was calculated one by one using the LHV and HHV assumptions for different temperature values. The variation of the calculated Nernst voltage values with different temperature values is shown in Figure 8. The solutions were first started at 353 K and continued at increasing temperature values such as 400, 500, 600, 700, 800, 900, and 1000 K. As a result of the analysis, it was seen that the temperature increase caused a decrease on the fuel cell Nernst voltage. Since the entropy change of the H_2/O_2 reaction is negative, the Nernst voltage of H_2/O_2 fuel cells decreases with an increase in temperature of 0.84 mV/ºC (Çavuşoğlu 2006). There are other studies in the literature where it is observed that the fuel cell Nernst voltage decreases with increasing temperature (Arıç et al., 2019; Lyu et al., 2020; Outeiro et al., 2008; Riad et al., 2023; Sahli et al., 2017; Şefkat and Özel, 2018).

The Nernst voltage values decreased more rapidly when the analyzes with HHV assumption were compared with those with LHV. For the LHV case, the Nernst voltage value was obtained as 1.173 V at 353 K and 1.003 V at 1000 K. Nernst voltage decreased by approximately 14.49% as the temperature increased from 353 K to 1000 K. For the HHV case, the Nernst voltage value at 353 K was obtained as 1.184 V. In the case where the temperature was 1000 K, the Nernst voltage value was 0.616 V. The temperature increase from 353 K to 1000 K resulted in a 47.97% decrease in the Nernst voltage. Therefore, the decrease in Nernst voltage was much greater in the HHV case compared to the LHV case.

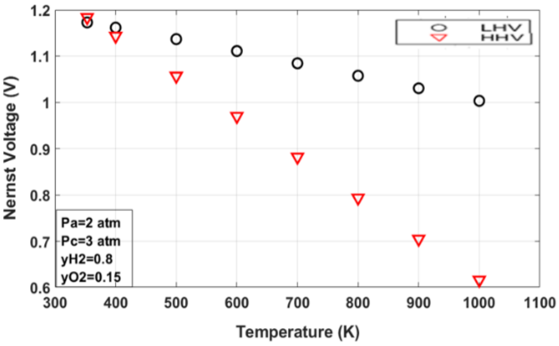

Figure 8. Variation of Nernst voltage with temperature for LHV and HHV status

Effect of LHV and HHV values on maximum thermodynamic efficiency

Maximum thermodynamic efficiencies were calculated one by one using LHV and HHV cases for different temperature values. The variation of the calculated efficiency values with different temperatures is shown in Figure 9. It is seen that the maximum thermodynamic efficiency of the fuel cell decreases with increasing temperature. This decrease is considered as a correct change in terms of fuel cell thermodynamics. When the electrochemical reaction occurring in the hydrogen fuel cell is examined in terms of the equilibrium equation, the total number of moles of the reactants is greater than the products. This means that the reaction entropy change (ΔS) value is less than zero. This result shows that the maximum thermodynamics efficiency decreases with increasing temperature for hydrogen fuel cells (Tu et al., 2020).

It is understood that the thermodynamic efficiency values decrease more rapidly in the HHV assumption compared to the LHV assumption, and the efficiency is higher in the LHV assumption under the same conditions. The maximum thermodynamic efficiency value for the LHV case was obtained as 0.933 at 353 K and 0.778 at 1000 K. As the temperature increased from 353 K to 1000 K, there was a decrease of approximately 16.61% in efficiency.

For the HHV case, the maximum thermodynamic efficiency value at 353 K was obtained as 0.797. In the case where the temperature was 1000 K, the efficiency value was 0.405. An increase in temperature from 353 K to 1000 K resulted in a decrease of approximately 49.18% in efficiency. Therefore, when the temperature increased from 353 K to 1000 K, there was a 16.61% decrease in the maximum thermodynamic efficiency in the LHV case, while the decrease in the maximum thermodynamic efficiency was 49.18% in the HHV case.

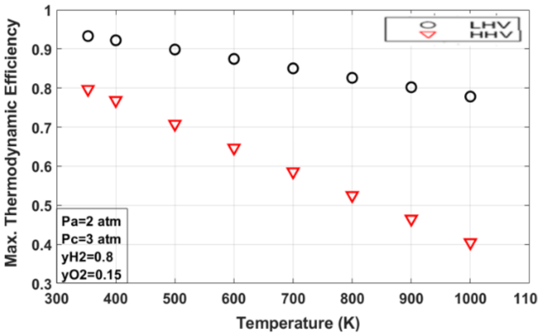

Figure 9. Effect of temperature on maximum thermodynamic efficiency for LHV and HHV assumption

CONCLUSIONS

In this study, the effects of different operating parameters on Nernst voltage and maximum thermodynamic efficiency were numerically investigated using the developed computer program. The findings obtained as a result of the analyzes are given below.

1) It was observed that the Nernst voltage increased with the increase in the mole ratio of O_2 in the cathode, but the amount of increase gradually decreased. When the mole ratio of O_2 in the cathode was increased from 15% to 100%, the Nernst voltage value increased by 1.19%.

2) It was found that the Nernst voltage also increased linearly for increasing hydrogen mole ratio on the anode side. As the mole ratio of H_2 in the anode was increased from 50% to 100%, the Nernst voltage value increased by 0.86%.

3) Nernst voltage values also increased with the increase of anode pressure. As the anode pressure rises from 1 to 5 atm the Nernst voltage value increased approximately 2.15% and 2.13% for LHV and HHV assumption, respectively.

4) It has been observed that the increase in the cathode pressure has a positive effect on the Nernst voltage. In both the LHV and HHV assumption, the Nernst voltage increased by about 1.2% as the cathode pressure increased from 1 to 6 atm.

5) Increasing the operating temperature caused a decrease in both the fuel cell Nernst voltage and the maximum thermodynamic efficiency.

6) In the case of LHV, the decrease rate of Nernst voltage with the increase in temperature from 353K to 1000K was obtained as 14.5%, while in the case of HHV, this decrease rate was obtained as approximately 48%. The decrease in Nernst voltage was much greater in the HHV case compared to the LHV case.

7) When the temperature increased from 353 K to 1000 K, there was a 16.6% decrease in the maximum thermodynamic efficiency in the LHV case, while the decrease in the maximum thermodynamic efficiency was 49.2% in the HHV case.

The Nernst voltage, which is seen as the starting point of fuel cell polarization curves, has been numerically calculated according to different operating parameters. By calculating this voltage value, the effects of different operating parameters were examined. The results obtained from this study may be informative for researchers considering various applications of fuel cells in the future. Additionally, different operating parameters and fuel cell types can be considered for future research.

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