GAS CROSSOVER PREDICTIVE MODELLING USING ARTIFICIAL NEURAL NETWORKS BASED ON ORIGINAL DATASET THROUGH ASPEN CUSTOM MODELER FOR PROTON EXCHANGE MEMBRANE ELECTROLYTE SYSTEM

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ABSTRACT

Proton exchange membrane electrolyzer cell (PEMEC) will play a central role in future power-to-H_2 plants. Current research focuses on the materials and operation parameters. Setting up experiments to explore operational accident scenarios about safety feasibility is not always practical. This paper focuses on building mathematical and prediction models of hydrogen and oxygen mixing scenarios of PEMEC. A mathematical model of the PEMEC device was customized in the Aspen Custom Model (ACM) software and integrated various critical Physico-chemical phenomena as the original data set for the prediction model. The results of the mathematical simulation verified the experimental results. The prediction model proposes an artificial neural network (ANN) framework to predict component distribution in the gas stream to prevent hydrogen-oxygen explosion scenarios. The presented approach by training ANN to 1000 sets of hydrogen-oxygen mixing simulation data from ACM is applicable to bypass tedious and non-smooth systems of equations for PEMEC.

1.0 INTRODUCTION

Hydrogen, as a fluctuating renewable energy source, can be installed and coupled with chemical and transportation processes as a raw material or fuel, playing a vital role in the distribution of renewable energy over different times and locations. Power-to-gas (P2G) technology is capable of converting electricity into hydrogen and natural gas, which can be used to store and utilize renewable energy during high-production periods and to supply electricity when demand exceeds supply.

The Proton Exchange Membrane Electrolyzer Cell (PEMEC) system is considered a key piece of equipment for producing "green hydrogen" due to its strong adaptability and is seen as a promising alternative to alkaline electrolysis. However, hydrogen gas is highly explosive and its gas concentration cannot be predicted under many parameters, making experiments risky and resulting in limited practical data that can be obtained.

The article presents an artificial neural network (ANN) framework that can predict hydrogen concentration in gases, an important safety parameter during the electrolysis process, with reasonable accuracy. The ANN model is based on simulation results from a comprehensive range of parameters, which form the dataset and can predict the distribution of hydrogen concentration in gases under different operating conditions. This provides a foundation for optimizing processes, controlling operations, and ensuring safety before running experimental and developmental equipment.

2.0 METHODOLOGY

2.1 Methodology and technical route

In this study, the electrolyte cell was modelled and verified using ACM software. An electrolysis system was established in Aspen Plus software, and sensitivity analysis was conducted to determine the upper and lower limits of 8 fixed variables (cathode operating pressure, cell temperature, membrane thickness, anode activation overpotential, cathode activation overpotential, bubble, area and

environment temperature). An 8-dimensional array was sampled using the Latin hypercube sampling method, and 1000 sets of data were collected as the original dataset for building an ANN prediction model. The effect of aligning the eight independent variables within the explosion limit is analysed by means of simulation, and a neural network is constructed to bypass the tedious process of solving the non-smooth equations.

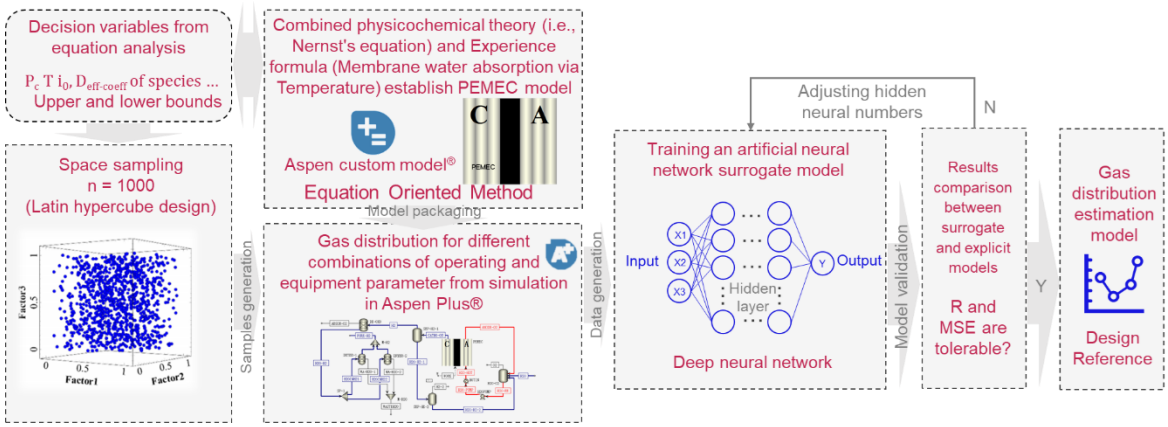

Figure 1. Technical route of ANN prediction model establish

3.0 MODELING AND VALIDATION OF CELL AND SYSTEMS

3.1 Modelling of PEMEC stack

(1) The reaction of water electrolyte

The specific assumptions are as follows:

Charge conservation inside the proton exchange membrane electrolysis cell refers to the fact that the number of substances and charges must remain constant inside the cell. In a proton exchange membrane electrolysis cell, water molecules are decomposed into hydrogen ions (H^+) and hydroxide ions (OH^-). Under the action of the proton exchange membrane, only H^+ ions can be transported through the membrane to the cathode side, while OH^- ions are restricted to the anode side. Therefore, in the electrolysis cell, H^+ ions and OH^- ions must be equal to maintain the electrical neutrality of the system.

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \qquad \text{Anode}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{Cathode}$$

(2) The electrolyte cell voltage of water-electrolyte

The polarization curve can relate voltage and current density, and the electrolysis power is positively correlated with the product of current and voltage, which constitutes the core relationship of energy conversion inside the electrolysis cell and is one of the most important pieces of evidence for evaluating the performance of the electrolysis cell[1]. In (1), the total voltage is composed of open circuit voltage, concentration polarization, activation polarization, and ohmic polarization. In (2), the open circuit voltage represents the electromotive force required to produce gas, defined by the reversible cell voltage and expressed by the Nernst equation. The change in the molar Gibbs free energy ΔG formed by the water reaction is used to define it, where T_{cell} is the cell temperature, p_{H_2O} is the water vapor pressure, and p_{H_2} and p_{O_2} are the hydrogen and oxygen partial pressures in the electrolysis cell, respectively. (3) represents the activation voltage, which is the energy required to initiate the electrochemical reaction. The overpotential of the two electrodes can be described by

current density, where a_{anode} and $a_{cathode}$ are charge transfer coefficients, and $i_{0,anode}$ and $i_{0,cathode}$ are the exchange current densities on each electrode. Concentration polarization represents mass transfer loss, mainly due to the formation of gas bubbles on the electrode surface covering active sites. The mass transfer loss effect caused by bubble coverage and water shortage is expressed by a quadratic fitting function concerning the limiting current density, using bubble coverage rate, as shown in (4). (5) is the overpotential caused by ohmic losses in the cell, which is the product of resistance and current, where the resistance mainly considers membrane resistance (7) and electrode plate resistance. Relevant studies have provided empirical equations between membrane resistance and hydration rate and membrane thickness, as shown in (8), where hydration rate is a function of temperature (9).

$$V_{cell} = V_{ocv} + V_{act} + V_{con} + V_{ohm} \tag{1}$$

$$V_{ocv} = \frac{\Delta G^{\circ}(T_{std}, P_{std})}{nF} + \frac{RT_{cell}}{nF}\ln(\frac{p_{H_2}p_{O_2}^{0.5}}{\alpha_{H_2O}}) = \frac{GH_2 + \frac{1}{2}GH_2 - GH_2O}{2F} + \frac{RT_{cell}}{2F}\ln(\frac{p_{H_2}p_{O_2}^{0.5}}{\alpha_{H_2O}}) \tag{2}$$

$$V_{act} = \frac{RT_{cell}}{\alpha_{anode}F}\text{arcsinh}(\frac{i_{cell}}{2i_{0.anode}}) + \frac{RT_{cell}}{\alpha_{cathode}F}\text{arcsinh}(\frac{i_{cell}}{2i_{0.cathode}}) \tag{3}$$

$$V_{con} = \frac{RT_{cell}}{4\alpha_{ano}F}(\frac{1}{1-\theta})^2 \tag{4}$$

$$V_{ohm} = i_{cell} \times R_{ele} \tag{5}$$

$$R_{ele} = R_{ohm-membrane} + R_{ohm-electrode} \tag{6}$$

$$R_{ohm-membrane} = \frac{D_{mem}}{\sigma_{mem}} \tag{7}$$

$$\sigma_{mem} = 0.005139 * \lambda_{mem} - 0.00326) * exp(1268 * (\frac{1}{303} - \frac{1}{T_{cell}}) \tag{8}$$

$$\lambda_{mem} = 0.0533T_{cell} - 6.77632 \tag{9}$$

(3) Mass balance of PEM cell stack

The principles of electrolytic reactions dictate that water enters and is generated on the anode side, before diffusing to the cathode side. On the anode side, water is made up primarily of inlet water, water consumed in the electrolysis reaction, and water transported across the membrane from the anode to the cathode. The amount of water generated can be calculated using Faraday's law, as explained in reference (11). The transmembrane transport of water is mainly influenced by the electrical potential difference, concentration difference, and pressure difference between the anode and cathode, as described in references (13-17). At the cathode, platinum is typically used as a catalyst, and under its influence, permeable oxygen can almost immediately recombine with hydrogen to form water [2-4]. Water on the cathode side is made up of both transmembrane-transported water and water that has recombined into water.

$$n_{H_2O,Anode} = n_{H_2O,Water\ in} - n_{H_2O,Consumption} - n_{H_2O,mem} \tag{10}$$

$$n_{H_2O,Consumption} = \frac{i_{cell}}{2F} \tag{11}$$

$$n_{H_2O,mem} = n_{H_2O,Electro-osmotic\ diffusion} + n_{H_2O,Concentration\ diffusion} - n_{H_2O,Pressure\ diffusion} \tag{12}$$

$$n_{H_2O,Electro-osmotic\ diffusion} = \frac{i_{cell} \cdot \delta_{H2O} \cdot A}{F} \tag{13}$$

$$\delta_{H2O} = 0.029\ \lambda_{mem}^{2} + 0.05\ \lambda_{mem} - 3.4 \times 10^{-19} \tag{14}$$

$$n_{H_2O,Concentration\ diffusion} = \frac{\mathrm{D}_{H_2O}^{diffusion} \cdot A}{D_{mem}} (\ C_{H_2O,Anode} - \ C_{H_2O,Cathode}) \tag{15}$$

$$n_{H_2O,Pressure\ diffusion} = \frac{K_{mem}\rho_{H_2O}}{D_{mem}u_{H_2O}M_{H_2O}}\Delta p \tag{16}$$

$$K_{mem} = -5.908 \times 10^{-19} p_{cathode} + 7.831 \times 10^{-17}\ (P_{Cathode} < 700\ Bar) \tag{17}$$

$$n_{H_2O,Cathode} = \ n_{H_2O,mem} + n_{H_2O,O_2-H_2\ recombination\ reaction\ in\ cathode} \tag{18}$$

$$n_{H_2O,O_2-H_2\ recombination\ reaction\ in\ cathode} = K_{reco} \cdot X_{Anode,O_2} \cdot X_{Cathode,H_2} \cdot V \tag{19}$$

Hydrogen is generated by cathode catalyst, and most of it leaves the electrolyte cell through the gas diffusion layer of the cathode. Another part enters the anode through the membrane and mixes with oxygen (20). Proton exchange membrane swells upon absorbing water, and water flows from the anode to the cathode through the membrane. Based on Fick's law, the water flow on the membrane is related to the difference in water content between the two sides of the membrane (21). The concentration of hydrogen in the catalyst layer can be found in (22), and the calculation of mass transfer coefficient is described in (23). The pressure difference between the anode and cathode drives the permeation flow (24), and protons carry water molecules during the transport process to the cathode (25). The electro-osmotic drag coefficient is a function of temperature (26), and the calculation of liquid-phase water concentration is shown in (27). The cathode is where hydrogen is generated, and the generated hydrogen will diffuse towards the anode under the action of the potential difference. The generated hydrogen will react with the oxygen transported across the membrane to regenerate water under the action of Pt catalyst (28). The amount of hydrogen generated is determined by Faraday's law.

$$\begin{aligned} n_{H_2,mem} = \ & n_{H_2,Concentration\ diffusion} \\ & + n_{H_2,Pressure\ diffusion} \ - n_{H_2,Electro-osmotic\ diffusion} \end{aligned} \tag{20}$$

$$n_{H_2,Concentration\ diffusion} = \frac{\mathrm{D}_{H_2}^{diffusion} \cdot C_{H_2}^{Catalyst}}{D_{mem}} e^{\left[\frac{E_A^{diff}}{R}\left(\frac{1}{T_0} - \frac{1}{T_{cell}}\right)\right]} \tag{21}$$

$$C_{H_2}^{Catalyst} = \frac{\frac{i_{cell}}{2F} - k_L \cdot \mathrm{P}_{H_2}^{Cathode} \cdot S}{k_L + \frac{\mathrm{D}_{H_2}^{diffusion}}{D_{mem}}} \tag{22}$$

$$k_L = \mathrm{a} \cdot i_{cell}^{\ b} \tag{23}$$

$$n_{H_2,Pressure\ diffusion} = \frac{K_{mem}}{u_{H_2}} \cdot C_{H_2}^{Catalyst} \cdot \frac{\mathrm{P}_{H_2}^{Cathode} - P_{O_2}^{Anode}}{D_{mem}} e^{\left[\frac{E_A^{conv}}{R}\left(\frac{1}{T_0} - \frac{1}{T_{cell}}\right)\right]} \tag{24}$$

$$n_{H_2,Electro-osmotic\ diffusion} = \frac{i_{cell}}{F} \cdot \delta_{H_2} \cdot \frac{C_{H_2}^{Catalyst}}{C_{H_2O}} e^{\left[\frac{E_A^{conv}}{R}\left(\frac{1}{T_0} - \frac{1}{T_{cell}}\right)\right]} \tag{25}$$

$$\delta_{H_2} = 0.0134 \times T_{cell} + 0.03 \tag{26}$$

$$C_{H_2O} = X_{H_2O,Anode} \cdot C_{Liquid,Anode} \tag{27}$$

$$n_{H_2,Cathode} = n_{H_2,generation} - n_{H_2,mem} - \frac{1}{2} n_{H_2,O_2-H_2\ recombination\ reaction\ in\ cathode} \tag{28}$$

$$n_{H_2,generation} = \frac{i_{cell}}{2F} \tag{29}$$

Oxygen is generated at the cathode and a portion of it is transported across the membrane to the anode (30). The amount of oxygen generated is determined by Faraday's law (31). Due to the negative electric and pressure gradients, concentration diffusion is the main potential difference that affects the transport of oxygen across the membrane. The empirical equation for oxygen transport mainly considers the gas diffusion, pore size, thickness, and curvature of the membrane material (32). Among them, the curvature is a function of porosity (33). The oxygen concentration at the cathode mainly comes from the transport across the membrane and the hydrogen-oxygen mixed reaction (34).

$$n_{O_2,Anode} = n_{O_2,Recycle} + n_{O_2,generation} - n_{O_2,mem} \tag{30}$$

$$n_{O_2,generation} = \frac{i_{cell}}{4F} \tag{31}$$

$$n_{O_2,Concentration\ diffusion} = \frac{A_{cell} \cdot Porosity^{1.5} \cdot Diffusivity \cdot \left(c_{O_2,Anode} - c_{O_2,Cathode}\right)}{Tortuosity \cdot D_{mem}} \tag{32}$$

$$Tortuosity = 1.353 - 0.03343 Porosity + 0.1145 Porosity^2 \tag{33}$$

$$n_{O_2,Cathode} = n_{O_2,mem} - \frac{1}{2} n_{O_2,O_2-H_2\ recombination\ reaction\ in\ cathode} \tag{34}$$

(4) Heat balance of PEM cell stack

The energy balance inside the electrolytic cell can be found in (35). In this electrolytic cell, the common anode-inlet water structure is used, where energy is inputted by the inlet water and the applied current (36-37). Energy is carried away by the cooling water circulation, anode-cathode effluent flow, and heat loss (38-40).

$$Q_{in} + Q_w = Q_{cooling} + Q_{out} + Q_{loss} \tag{35}$$

$$Q_{in} = n_{Total-in,Anode} H_{in,Liquid} \tag{36}$$

$$Q_w = i_{cell} V_{cell} A_{cell} \tag{37}$$

$$Q_{cooling} = n_{cooling\ water} C_{pc} (T_{cooling,in} - T_{cooling,out}) \tag{39}$$

$$\begin{aligned} Q_{out} = {} & n_{Total-out,Anode} V_{Anode} H_{out,Vapor,Anode} \\ & + n_{Total-out,Anode} (1 - V_{Anode}) H_{out,Liquid,Anode} \\ & + n_{Total-out,Cathode} V_{Cathode} H_{out,Vapor,Cathode} \\ & + n_{Total-out,Cathode} (1 - V_{Cathode}) H_{out,Liquid,Cathode} \end{aligned} \tag{38}$$

$$Q_{loss} = (n_{Hold,Anode} + n_{Hold,Cathode}) C_{pt} (T - T_{amb}) \tag{40}$$

4.0 VALIDATION OF PEMEC STACK

4.1 Modelling of PEMEC stack

Tsinghua University has built an experimental apparatus to study the diffusion behavior of hydrogen[1]. This modelling work mainly refers to the parameters and empirical equations involved in the experiment, taking into account the diffusion of oxygen and the reaction of hydrogen and oxygen recombining at the cathode. Polarization curves and hydrogen concentration distributions inside the gas are verified under multiple operating temperatures and pressures. Based on an accurately modeled electrolytic cell, an electrolysis system was built to simulate gas distribution under a wide range of operating conditions, greatly enriching the dataset beyond the limitations of actual experiments.

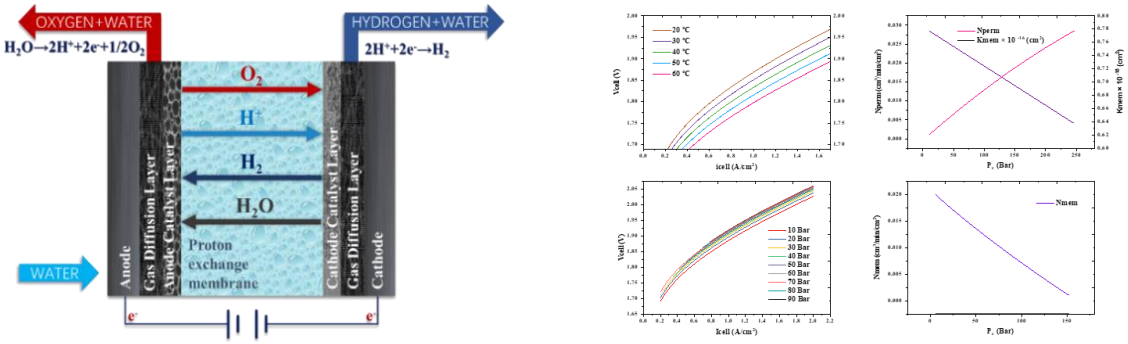

Figure 2. Validation cure of PEMEC stack

4.2 Modelling of PEMEC system

The PEM electrolysis system comprises an electrolyzer, an oxygen separator, two hydrogen separators, a heat exchanger, and a circulation pump. During operation, water is pumped from the heat exchanger into the PEMEC, where it undergoes a chemical reaction to produce oxygen and hydrogen. These gases are then separated by oxygen and hydrogen separators, respectively. The circulating water is mixed with makeup water before entering the heat exchanger. The conservation of protons within the proton exchange membrane electrolyzer is a critical condition for maintaining stable system operation. This study considers the conservation of charge, mass, and heat. The process of proton exchange membrane electrolysis hydrogen production system is shown in Figure 3. The red line represents logistics where the main component is oxygen, and the blue line represents logistics where the main component is hydrogen.

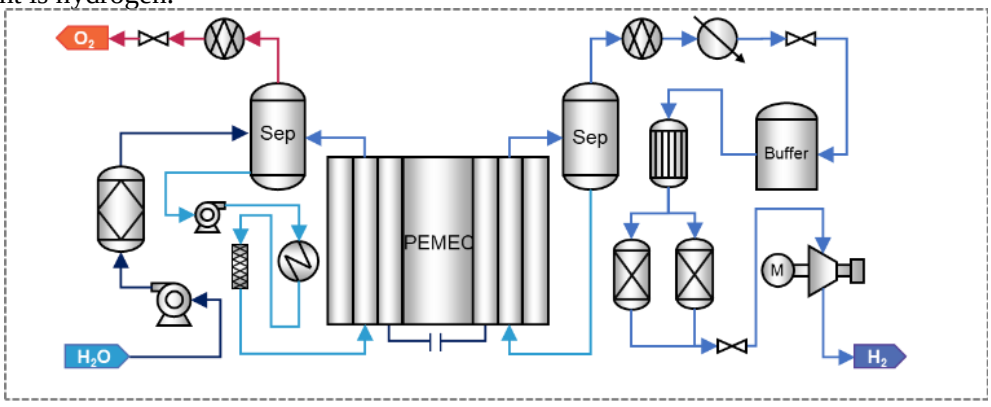

Figure 3. Structure diagram of PEMEC system

5.0 DATA COLLECTION

5.1 ANN-BASED GAS DISTRIBUTION MODELING

5.2 ANN DETAILS

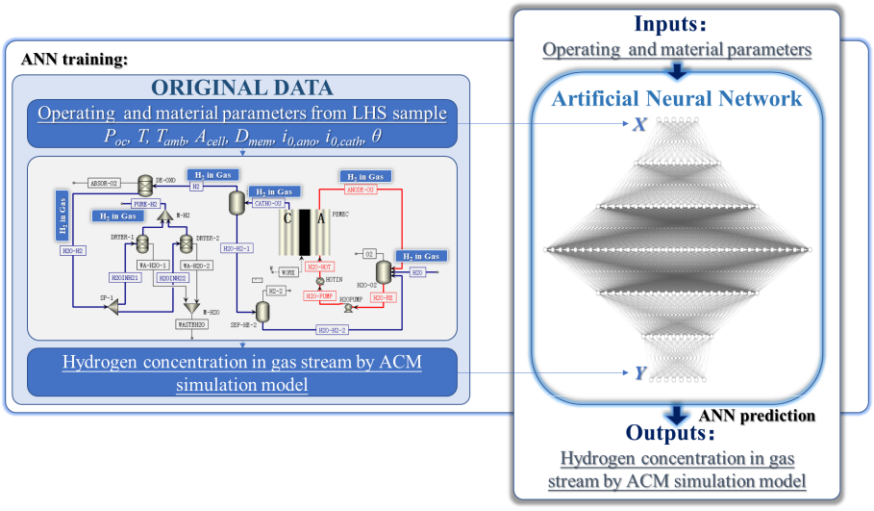

Figure 4. ANN-based gas distribution prediction modelling

Although there are various architectures of ANN, we will be using a deep neural network, illustrated in Figure 4, for our result modelling. This neural network consists of an input layer, an output layer, and multiple hidden layers, with multiple nodes in each hidden layer. The number of hidden layers will depend on the expected accuracy of the output. To calculate the weights in the neural network, it needs to be trained on a large dataset. In the case of an electrolytic cell, a set of simulated data consisting of eight input variables related to materials and operations will be used, and the output will be the concentration of hydrogen gas in the electrolysis system gas stream. By using real-time safety measures based on the ANN, we can measure the gas distribution in the system under different conditions of the 8-dimensional data combination. This can enable us to predict a variety of experimental and production conditions on a large scale. Due to the wide range of characteristics of the original dataset, the neural network can continuously forecast the gas distribution in the system, which is crucial for ensuring safety[5].

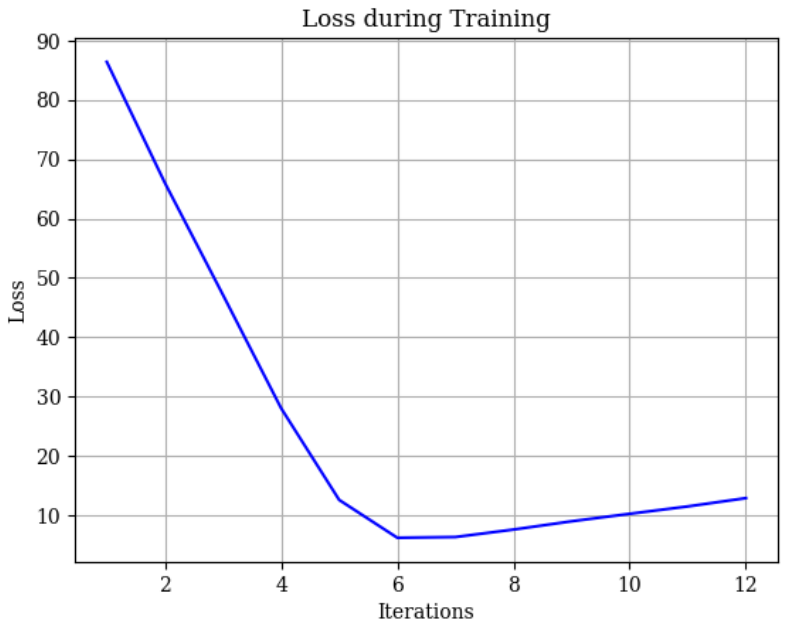

Figure 5. Loss of ANN model

The artificial neural network models with different parameters have shown good performance in terms of R2 and loss function, indicating their ability to predict gas distribution in the system under varying operational and device parameters. Among them, the model with a batch size of 50, 800 epochs, and learning rate of 0.01 has shown the best trend in the loss function curve.

5.0 CONCLUSION

This study utilized system modelling to abstract the core electrolysis reaction and the associated electrolysis system, which converts electricity into gas, into mathematical models. This approach facilitated a better understanding and analysis of the system's behavior, as well as predicting its future development. The focus of the study is on hazardous scenarios involving hydrogen. The main objective is to analyze the distribution patterns and interactions of hydrogen in the various parts of the system, which was crucial for the safe design and optimization of the proton exchange membrane electrolysis system.

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