Modeling and Optimization of Hybrid Nafion Membranes Modified With Oxides Based on Artificial Neural Networks and Genetic Algorithms

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ABSTRACT

Recent studies have demonstrated the successful application of artificial intelligence tools in modeling, optimization and design of new materials. This paper describes the application of a Backpropagation Multilayer Perceptron (MLP-BP) neural network based on Levenberg-Marquardt learning algorithm in combination with evolutionary models based on genetic algorithms (GA) to find the optimal operation conditions to provide the highest proton conductivity from a set of hybrid membranes in fuel cell applications. A total of six membranes were analyzed, each one fabricated from a polymer matrix of Nafion and then modified with several oxides (N-HfO2, N-ZrO2, N-La2O3, N-(HfO2, ZrO2), N-(HfO2-La2O3) and N-(ZrO3-La2O3)). The experimental conditions considered for optimization were: temperature of the humidifier (Th) [30-100] ° C, the cell temperature (Tc) [30-120] ° C, voltage [0.05-0.8] (V), relative humidity (RH) [50% -100%] and the membrane thickness (σ). Four-electrode method was employed in fuel cell mode and pulse voltammetry were obtained. The pressure was kept at 15 psi and the nitrogen flow at 500ml/min.

The MLP-BP -GA combination throws the following optimal condition for the Hf-La membrane 1% wt: with 100% of relative humidity and temperatures around 80 ° C in the humidifier and cell (fig. 1). This model also provides the best conditions where the highest conductivity is achieved for every membrane, this estimations were compared against experimental tests obtaining a variation of less than 10%.

Keywords: Artificial Neural Network, Genetic Algorithm, hybrid membranes.

Introduction

One of the main obstacles for mass production of proton exchange membranes fuel cell (PEMFC) is the cost and durability balance [1-2]. It is affected by the performance of proton exchange membrane (PEM) design and performance in different environments [3-4]. Investigations in the field of PEMFCs were focused on improving the efficiency of proton-conducting materials. Polymer electrolyte membrane fuel cells (PEMFCs) are electrochemical devices operating at temperatures below 130^{o}C characterized by a high energy conversion efficiency, high energy density and a good compatibility with the environment [5]. PEMFCs are promising energy devices for residential, portable, and automotive applications [6].

The properties that must be considered for polymer electrolyte membrane are: (a) chemical and electrochemical stability in the operating system; (b) mechanical strength and stability under operating condition; (c) chemical properties of compounds that are compatible with the bonding requirements of the membrane electrode assembly (MEA); (d) high proton conductivity to sustain large current densities with a minimal resistive loss and no electronic conductivity; and (e) low production cost compatible with application. Nafion®, whose primary structure consists of acid-tipped side chains dangling from a perfluorinated backbone, is currently the reference among proton-conducting materials. Nevertheless, Nafion is not exempt from drawbacks, which include: the decrease of conductivity due to dehydration at high temperature and high cost [7].

the use of specialized software in the design and simulation of electrochemical systems been increasing, this due to the high cost of materials used for this purpose, one of the most used system for this task is artificial intelligence (AI). This techniques have emerged in system simulation for more than two decades as effective tool for model, design and solve complex systems [8-9].Artificial neural network (ANN) is a class of neural network represented by a mathematical model that is inspired by the biological nervous system; The main advantages of utilizing NNs are [10]: (1)it handles stochastic variations of the scheduled operating points via the increase of data,(2)it significantly accelerates both online processing and classifications, and (3) it contains implicit nonlinear modeling and a built in function for system data filtration.

Studies about the modeling fuel cell parameter through ANN models are numerous. Lee et al.[11] have used a feed forward back propagation network in which the cell potential was modeled as a function of four input variables (i.e., current density, reactant pressures and cell temperature). It was shown that the ANN can predict well the fuel cell power system. Wu et al. [12] have applied the ANN to simulate an experimental data set with six input independent variables (i.e., operating temperature and pressure, anode and cathode humidification temperature, anode and cathode stoichiometric flow ratio) with respect to electrical power.

Utilizes tools to find the maximum point are numerous but its use in non-linear systems is limited. Genetic algorithm is a special technique for function approximation that can be considered as a set of computational techniques more closely linked in their concepts to biological processes than traditional computational techniques. They are quite different from other more conventional optimization methods that are mainly stochastic in nature. The basic process of genetic algorithm is as follows. First, a population of chromosomes is created. Second, the chromosomes are evaluated by a defined fitness function. Third, some of the chromosomes are selected for performing genetic operations. Fourth, genetic operations of crossover and mutation are performed. The produced good offspring replace their parents in the initial population. This process repeats until a user-defined criterion is reached.

This study attempts to show how the union of different computational techniques can model and optimize hybrid Nafion membranes modified with oxides based. This work aims to demonstrate that the proposed model can find the maximum point of proton conductivity for each of the different membranes.

Experimental

To find the best operational condition must know the membrane proton conductivity obtained based on experiments previously made, this was determined by the four electrode method. A Bekktech® conductivity cell coupled to a PS-CompuCell® Test Station and an AUTOLAB PGSTAT302. Linear voltammetry was used as characterization technique; each membrane was evaluated in four different tests (fig.1).
ANN model consist of a training algorithm based on data base established. This data base contain different values of temperature of the humidifier (Th) [30-100] ° C, the cell temperature (Tc) [30-120] ° C, voltage [0.05-0.8] (V), relative humidity (RH) [50% -100%], the membrane thickness (σ) and gas pressure [15](psi). a typical ANN is show in fig 2. It is seen that an ANN consists of a network with three main elements, input vector, hidden layer(s), and output layer. As show in the fig. 3, each neuron receives an input signal P. each input is multiplied by synaptic weight W and then each input is summed an then added by a bias b. this product is used as input to the network and is taken as an argument of a transfer function f, which determines an output of a neuron. A typical transfer function is log-sigmoid f, which is also used in this study and has the following form;

$$a = f(WP + b) = \frac{1}{1 + \exp(-(WP + b))} \quad (1)$$

The database was randomly partitioned into training data, testing data and validation data, so that the training and testing data set was changed in every loop, then the data set has been normalized. The normalizing function is calculated by:

$$X_n = \frac{X}{X_{max}} \quad (2)$$

Where Xn is the normalized value of X, Xmax is the maximum value of the properties.

This transfer function takes any value and outputs a value between 0 and 1. In this work were used the multi layer perceptron (MLP) model. The MLP is the most commonly used ANN, characterized by interconnections that do not from any loop[]. The neural network are organized to form a feed-forward network. The ANN simulation consist of two main phases; training and testin, the training phase is used to minimize the difference between input and output, the training algorithm used was the levenber-Marquard algorithm (LMA) also known as the damped least-squares (DLS) that is one of the most commonly used training algorithm for MLP models.

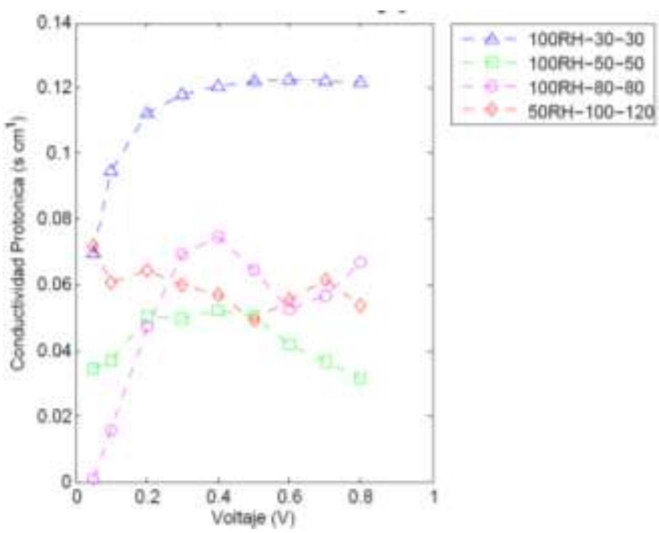

Figure 1. PC of N-La_2O_3 at different temperature and RH.

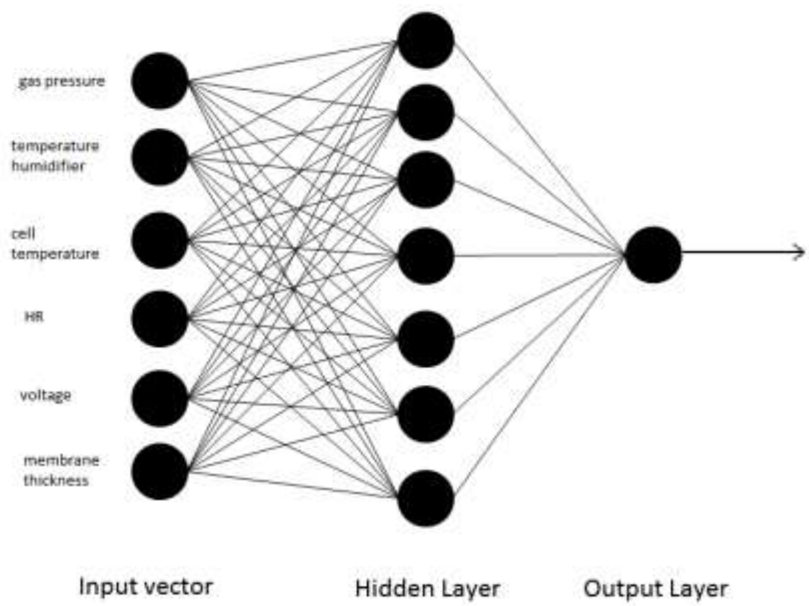

Fig. 2 Schematic diagram of a typical artificial neural network (ANN)

The obtained traininig ANN model is consequently used in GA to optimize a system and find best performance and maximum point of proton conductivity (PC) in the PEM for a given experimental parameters. GA works by generating a large set of possible solutions to a given problem. It then evaluates each of these solutions. In order to optimize the PEM a Matlab code was developed. The code stars with generating solution by randomly selecting values for the all parameter involve in the ANN model. The parameters values of genetic algorithms used are given in table1. Table 3 gives the upper and lower limits of the optimized parameters.

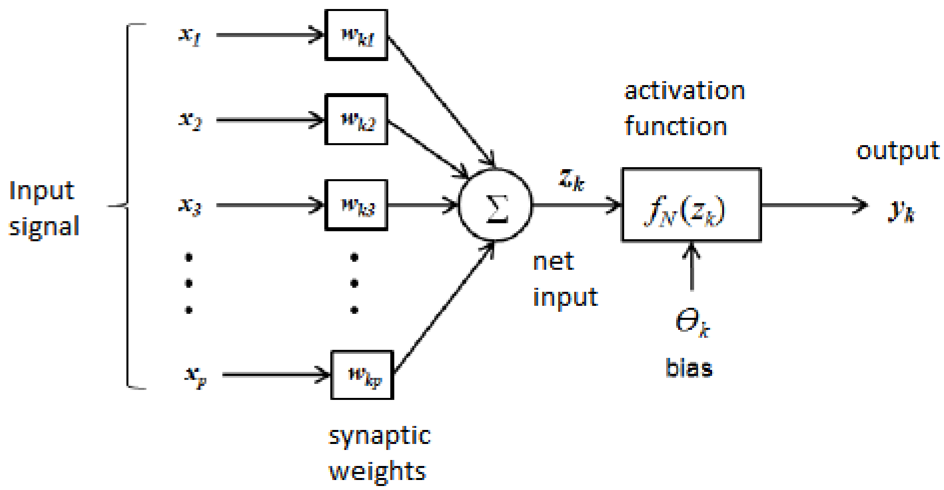

Fig. 3 Mathematical model of a neuron

Table 1. Values of genetic algorithm parameters

Parameter	Value
Number of generations	100
Population size	20
Number of parameters	5
Crossover rate	90%
Mutation rate	10%

Membrane simulation result

To complete the simulation of any system using artificial neural networks, we first need to identify its experimental behavior of any system. The simulation model based on the MATLAB/SIMULINK software of the PEM to obtain the best proton conductivity of each membrane, the total number of experimental data set was 36. After the training the optimized ANN model the network performance parameter described was very similar in all tests. The mean square error (MSE) and sum of square errors (SSE) of training and testing data sets for the membranes simulate are shown in table 3.

Table 2. Upper and lower values of the parameters to be optimized (search space)

Parameter	Lower limit	Upper limit
Gas pressure	15	30
Temperature humidifier	30	100
Cell temperature	30	120
HR	50%	100%
Voltage	.05	.8

Table 3. Upper and lower values of the parameters to be optimized (search space).

Membrane	MSE	SSE
N-HfO_2	7.6044	0.00027376
N-ZrO_2	4.3648	0.000157
N-La_2O_3	5.1832	0.00018659
N-(HfO_2, ZrO_2)	4.6256	0.0017
N-(HfO_2-La_2O_3)	2.251	0.00081035
N-(ZrO_3-La_2O_3)	1.5849	0.00057055

Proton conductivity of N-La2O3 and its simulation are shown in the following diagram (fig 4). The highest proton conductivity reached experimentally of N-La2O3 occurs at 100°C and 50%RH with values of 0.1225 S cm-1, the conductivity reached in ANN model is 0.1242 S cm-1.
All model reached values close to the experimental proton conductivity. GA technique was used to find the optimum configuration of inputs to reach the maximal PC, in the table 4 the maximum proton conductivities were achieved using genetic algorithm.

Table 4. best point reached for genetic algorithm.

Membrane	PC
N-HfO_2	0.135
N-ZrO_2	0.072
N-La_2O_3	.127
N-(HfO_2, ZrO_2)	0.22
N-(HfO_2-La_2O_3)	0.05
N-(ZrO_3-La_2O_3)	0.065

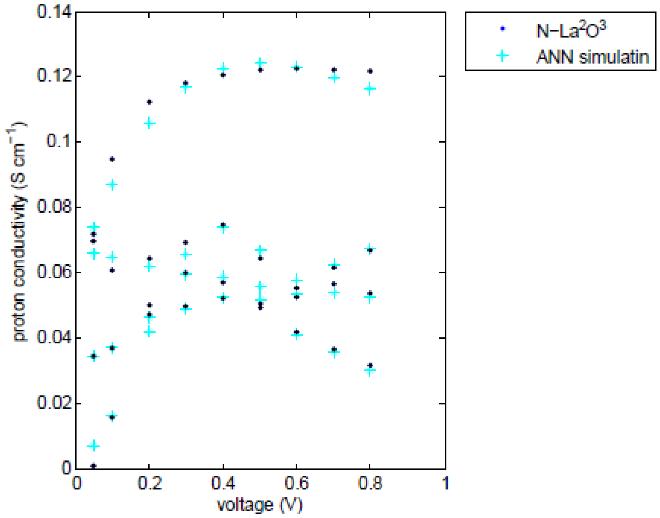

Fig 4. PC of N-La_2O_3 Vs ANN simulated

Summary and perspectives

In this research work, a feed-forward back propagation neural network model and genetic algorithm was used for simulate Six membranes, each one fabricate from polymer matrix of nafion. The aim of the model was to specify the optimal conditions with wich is reached the best proton conductivity that could be acquired by linear voltammetry and know the conditions in which is reached.

The next work will simulate fuel cells with different membranes, and knowing the conditions under which each operates better, this in order to improve the PEMFC performance to various working conditions.

Acknowledgements

CONACYT for the scholarship, UAdeC and CIDETEQ the opportunity afforded by the use of facilities and equipment

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