Effect of Doped Nano CeO_2 Anode and Optimum Operating Conditions for Charge Storage of 500W Polymer Electrolyte Membrane Fuel Cell using Tertius Algorithm

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Abstract:

Maintaining the Polymer Electrolyte Membrane Fuel Cell made of nano 0.5 wt% CeO_2 doped anode material under the optimum operating condition is a challenging task, which requires the careful design of efficient controllers for most significant parameters. Identification of the most relevant set of parameters for control and its validation is very critical in developing stable and improved hydrogen separation via 0.5 wt.% doped CeO_2 anode reliable PEM FC systems. This work involves the implementation of 0.5 wt.% CeO_2 doped anode and validation of optimum input parameter values obtained from a set of Neuro Fuzzy Controllers designed for a 500W PEMFC. The mathematical model is developed in Matlab/Simulink platform and simulated under various operating conditions to study the effect of various input parameters. Validation is done using the machine-learning algorithm, Tertius. The basic design for validation was developed in WEKA (Waikato Environment for Knowledge Analysis) platform and the same was implemented in a java environment. As being a single attribute oriented algorithm in machine learning suite, Tertius validates the designed model and provides accurate prediction. Performance of the model has also been analyzed using the area under the ROC curve and thus provides a validation to the model and the predicted set of input parameters which will give the desired electrical performance and efficiency.

Keywords: PEMFC; CeO_2 nano oxide; Stack voltage; Tertius algorithm, Machine learning tool.

1. Introduction:

The proton exchange membrane fuel cell equipped with doped CeO_2 (PEMFC) which uses a solid thin polymer as the electrolyte is a promising candidate as a green source of power for future. PEMFC is an electrochemical device which can convert chemical energy of reactants directly to electrical energy in a quiet, clean and efficient way and thereby reducing emission of greenhouse gases and consumption of fossil fuels. The ability of PEMFCs to operate in under low temperature conditions, low corrosion, low weight and quick start up enables them to be deployed for various applications like automobile, space units and stationery power back up [1-4]. Compared to other fuel cell types like solid oxide fuel cells(SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC) and alkaline fuel cells (AFC). PEMFC addresses challenges in all sectors of energy like transportation, commercial, residential and industry due to their application in diverse fields. But for successful commercialization of PEMFC requires extensive research focusing on developing suitable materials for each component, subsystems and appropriate control methods to optimize life, cost and performance of PEMFC systems [5]. With the increasing demand of PEMFC in various areas of application, the need for accurate on proton transfer via modified anode material, which may be doped with CeO_2 and also the system models with simulation of various operating conditions and performance evaluation becomes very critical. PEMFCs are highly nonlinear systems with multiple set of coupled parameters affecting the rate of electrochemical reactions and electrical performance. Hence simulation study helps in identifying the optimum set of input parameters and operating conditions which gives the best performance from a PEMFC system.

Two fundamental approaches in fuel cell modeling are the steady state and dynamic models. Steady state model can be analytical or empirical where the parameters are obtained from experimental results. These models do not consider the deep underlying physics or the electro chemistry of the fuel cell operation and can be used for predicting the effects of input parameters on V-I characteristics [6,7]. They can be used to study aging effects, degradation issues and for material section [8,9]. There are many previous works on dynamic mathematical models which can represent the transient dynamics efficiently and helps to understand the power performance. Study of thermal dynamics and internal resistance on cell performance is reported in [10]. These effects are very significant for low power PEMFC systems with few kilo watts than for larger systems. Simulation of dynamic models can predict the cell performance under transient conditions of reactant flow rate, cell temperature, anode and cathode pressure and load current demands [11-13]. Another nonlinear dynamic model which incorporates the electrochemical and thermodynamic effects of PEMFC operation where stack voltage is expressed in terms of load current, cell temperature, oxygen partial pressure and membrane humidity is reported in [14]. Mathematical models of PEMFCs are extensively used for predicting the stack performance under various operating conditions. [15]. Majority of these models are used for steady state analysis and also does not consider all the involved phenomena of fuel cell operation [16-19]. Also these steady state models become insufficient for practical applications like in automobiles where the load conditions and output power vary significantly over the operating period. Hence we need accurate dynamic models of PEMFC to represent the transient responses under a wide range of dynamic operating conditions. But majority of the dynamic models available in literature uses partial differential equations for representing the underlying operations of fuel cell and thus making their simulations slower. Hence there is a need for powerful mathematical models which can represent all the transient responses by considering the relevant electrochemical and thermodynamic effects.

When a fuel cell is operated with a connected load, heat and water are produced and oxygen is consumed which is represented in equation 1.

Net redox reaction (the "" reaction):

$$2H_2 + O_2 = 2H_2O + \text{heat} + \text{electricity} \quad (1)$$

This requires suitable control systems to maintain safe range of cell temperature, membrane humidity and pressure for reactants so that desired electrical performance and stack efficiency is obtained. Maintaining the optimum set of operating conditions and safe range of input parameters requires efficient controllers for regulating the most critical parameters so that the desired electrical performance is obtained from a PEMFC stack for a selected application. Thus identification of most relevant parameters of the PEMFC that affects the electrical performance is the most critical stage in developing a stable and efficient PEMFC system. Figure 1 shows the scanning electron microscope image of nano cerium oxide.

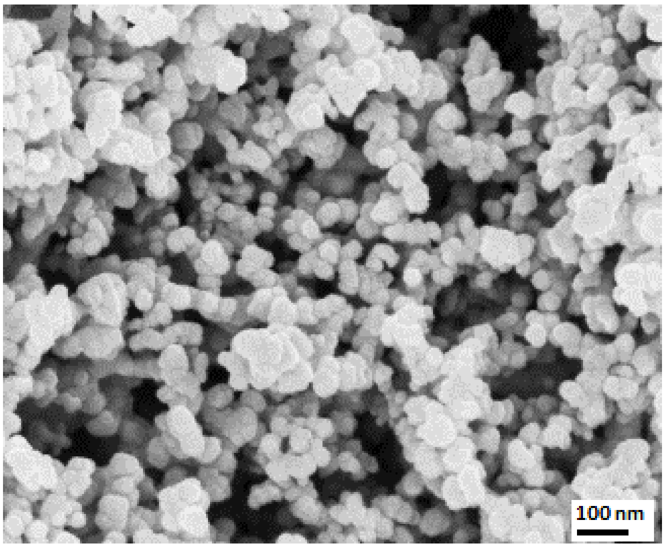

Figure 1 SEM image of CeO_2 nanoparticles

2. Modelling and validation

2.1 Modeling a PEMFC

The reversible open circuit voltage (Nernst voltage) from a hydrogen Fuel cell is given as

$$Vrevers = 1.229 - 0.85 \times 10^{-3}\left(T_{fc} - 298.15\right) + 4.3085 \times 10^{-5} T_{fc}\left[ln\, ln\left(p_{H_2}\right) + \frac{1}{2}\, ln\, ln\left(p_{O_2}\right)\right] \quad (2)$$

The fuel cell output voltage is affected by various losses and the actual cell voltage is given as in equation 3.

$$V_{stack} = Vrevers - V_{act} - V_{con} - V_{ohm} \quad (3)$$

Activation loss V_{act} is the voltage lost in driving the chemical reaction at the electrodes given by

$$Vact = \left[\frac{RT}{4F\alpha c}\right] \times ln\, ln\left(\frac{i}{ic}\right) + \left[\frac{RT}{2F\alpha a}\right] \times ln\, ln\left(\frac{i}{ia}\right) \quad (4)$$

Due to the flow of electrons through the electrodes and various interconnections, an electrical resistance is formed which includes the hindrance in the flow of ions in the membranes and results in a voltage drop proportional called Ohmic Loss given by equation (5)

$$Vohm = Ifc \times Rfc \quad (5)$$

Decrease in stack voltage due to reduction in concentration of reactants at the electrode surface is known as concentration loss given as in equation (6).

$$V_{con} = \left(i \times C_1 \times \frac{i}{i_{max}}\right)^{C2} \quad (6)$$

2.2 Dynamics of reactant pressure

The stack voltage of a PEMFC system depends on partial pressure of Oxygen (P_{O2}) and partial pressure Hydrogen (P_{H2}) as given in equation 7 and 8.

$$P_{O_2} = RHC \times P_{sat_{H2o}} \times \{(\frac{1}{e^{\frac{4.192 \times \frac{I}{A}}{T^{1.334}}}}) \times (\frac{RHC \times P_{sat_{H2O}}}{P_C} - 1)\} \quad (7)$$

$$P_{H2} = 0.5 \times (RHA \times P_{sat_{H2O}} \times \frac{1}{e^{\frac{1.635 \times \frac{I}{A}}{T^{1.334}}}}) \times \frac{RHA \times P_{sat_{H2O}}}{P_a} - 1 \quad (8)$$

The saturation pressure of water depends on temperature and hence maintaining the temperature in the safe range is very important for maintaining the reactant partial pressures and also for optimum membrane humidity. For temperature above 90^0C, conductivity of Nafion membrane decreases and results in membrane cracks and damages the membrane permanently.

2.3 Thermodynamics involved in membrane humidity

The water diffusion coefficient, D_w and electro-osmotic drag coefficient, n_d, shown in equation 9 and 10 are calculated from the average membrane water content, $D_{\lambda m}$ as given in equation 11.

$$n_d = 0.0029\lambda^2_m + 0.05\lambda_m - 3.^4 \times 10^{-19}$$

$$D_w = D_{\lambda m}\, exp\, exp\left(2416\left(\frac{1}{303} - \frac{1}{T_{fc}}\right)\right) \quad (10)$$

Where $D_{\lambda m}$ is given by equation (11)

$$D_{\lambda m} = \{10^{-6},\ \lambda_m < 2\ 10^{-6}\left(1 + 2(\lambda_m - 2)\right),\ \ 2 \le \lambda_m \le 3\ 10^{-6}\left(3 - 1.67(\lambda_m - 3)\right),\ 3 < \lambda_m < 4.5\ \ 1.25 \times 10^{-6},\ \ \lambda_m \ge 4.5 \qquad (11)$$

The desired Rhc is obtained by injecting sufficient amount of vapor (W_{inj}) to the humidifier given by equation 12.

$$W_{inj} = \frac{Mv}{Ma}.\phi des.\frac{Psat}{Paco}.Waco - Wvco \qquad (12)$$

2.4 Double Layer Charging Effect

During PEM fuel cell operation, Hydrogen ions are collected in the electrolyte and electrons in the electrodes (modified anode), which actually represent a condition similar to charge accumulation in capacitor. As a result of this capacitive effect, the cell voltage cannot immediately follow the current variation in current. Models build by considering this double layer capacitive effects give more accuracy in representing the dynamics of fuel cell operation.

2.5 500W PEMFC Model in Matlab/Simulink

A mathematical model in Matlab/Simulink is developed by considering these dynamics of operation for a rated power of 500W with 25V at 20A whose layout is shown in Figure 2. Simulations are carried out to study the optimum range of input parameters for obtaining the optimum electrical response at the rated power.

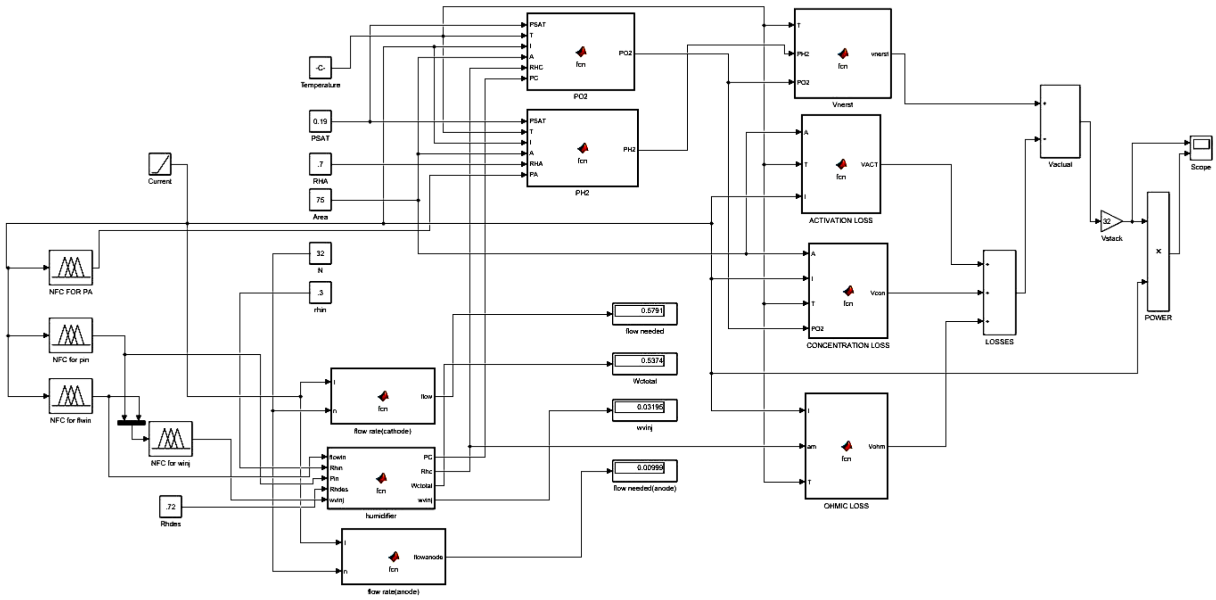

Fig 2: 500 W PEMFC Model layout in Matlab/Simulink

3. Study on the effect of input parameters on stack voltage

Simulations are performed under a large set of operating conditions with different combinations of dynamic input range to identify the most significant set of input parameters on stack performance by the introduction of CeO_2 doping which is very important in designing efficient controllers for a PEMFC system.

3.1 Study on effect of cathode input pressure on stack voltage

The variation of stack voltage for different values of cathode input pressure under a given operating condition (input relative humidity= .3 and temperature =333.17K) is given in Figure 3.

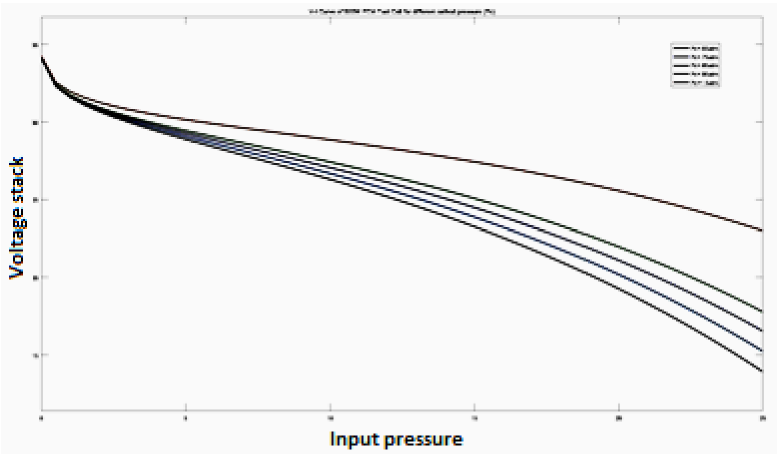

Fig 3: Effect of cathode input pressure on stack voltage

Simulation result shows that the effect of cathode pressure on stack is more for higher load currents than for low loads of less than 5A. Thus we need a control mechanism to regulate the cathode pressure according to the load. This is achieved by controlling the compressor valve at the cathode inlet.

3.2 Effect of cathode flow rate on stack voltage.

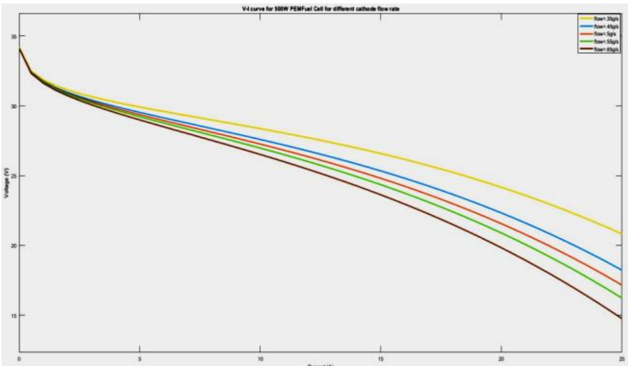

Figure.4 Effect of cathode input flow rate on stack voltage

Simulation study performed under various values of cathode flow rate and its effect on the stack performance is shown in Figure 4. From these results, we can see that under low load currents (less than5A), the effect of cathode input flow rate is less. But as the load demand increases, there is need for increased flow rate at cathode which shows a need for flow regulation at cathode. This flow regulation is possible by controlling the speed of motor which is supplying the air at cathode.

3.3 Effect of Relative Humidity on stack voltage

Model was simulated under different values of relative humidity and stack performance is plotted and shown in Figure 5.

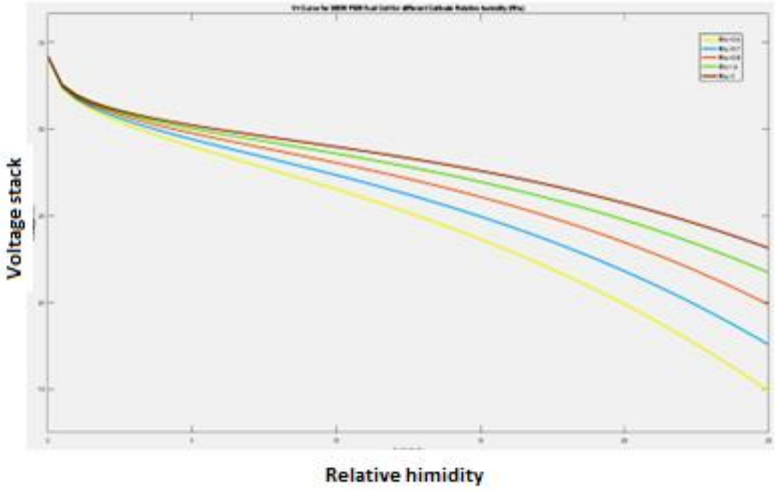

Figure 5: Effect of cathode relative humidity on stack voltage

Study on cathode humidity shows that even a slight variation in cathode relative humidity can significantly affect the stack performance and hence there is a need for highly efficient controllers on cathode side for getting an optimum value of relative humidity. Regulation of relative humidity is possible by controlling the flow of water injected from humidifier at cathode inlet.

3.4 Need for controller in PEMFC system

Results of simulation under a wide range of input conditions describe the effect of these parameters on stack performance and the suitable range of values to achieve the rated power. There is a highly nonlinear and inter related coupling between these input parameters which affects the stack voltage and hence the power at different load conditions. Table 1 shows values from simulation under different operating conditions and the need for maintaining these parameters using efficient controllers.

Table 1: Stack power under different operating conditions and loads.

Cathode Input parameters			Output parameter-Stack power ($P_{satck}W$) for different load currents at CeO2 modified anode			
$P_{a,co}$(atm) Partial pressure of dry air	W_{co}(g/s) Flow rate from compressor	W_{inj}(g/s) Flow rate of water injected to humidifier	5A	10A	15A	20A
1.2	.6	.042	154	291	417	518
1	.5	.04	155	292	412	512
.8	.46	.032	155	280	387	455
.5	.3	.028	141	255	323	333

The optimum values of cathode inlet pressure, flow and relative humidity are obtained using Neuro Fuzzy Controller to get the desired electrical performance at rated power for the 500W PEFMC model.

4. Validation.

Validation typically means to what extend the accuracy supports. In this work, a machine-learning algorithm, Tertius is used to study the performance and infer how variations in parameters affect the system.

4.1 Tertius Algorithm

Tertius algorithm builds rules out of the attribute pair values in the training data and ranks them according to how inclined they are, ie., how many times the rule holds true in the training data. A rule consists of a body and a head. The body contains the conditions (known as literals) required for the rule to hold, and consists of any number of literals. The head contains the event that occurs if the rules hold true. During rule learning, Tertius algorithm starts with an empty rule, ie., it contains a blank body and a blank head. The algorithm is shown in Algorithm 4.1

Algorithm 4.1: Tertius Algorithm

Input : Empty rule (agenda)
Output : Parameter association rules
1. Agenda ← empty rule
2. while agenda is not empty
    2.1 rule← first rule of the agenda
3. if rule can be stored in results
    3.1 Add rule to results

4. if rules can be refined
    4.1 refine rule
5. for each child
    5.1 Calculate optimistic estimate and confirmation
    5.1.1 if child can be stored in agenda
    5.1.2 Add child to agenda
6. Sort agenda according to optimistic estimate

Tertius is a single attribute oriented algorithm. The attribute that needs to be tested against is fixed and the parameters are fed-in directly from the dataset. The algorithm processes the data and provides the rules in a manner, how inclined or how much variations in input parameter causes a change in the fixed attribute.

The experiment was run over the weka.associations platform with the help of Class Tertius. The class implementing the Tertius type algorithm is given below.

public class Tertius
extends Associator
implements OptionHandler, java.lang.Runnable

Details on the java implementation is given in Reference [21]

4.2 Results and Performance Comparison

Tertius as we know is a single attribute prediction mechanism, it captures the dataset that is provided and models the system accurately from the range of values and tests it against the associated parameters. Here system accepts the dataset in. arff file format and does an initial data preprocessing using a supervised filter. The processed dataset is trained and is fed to the machine-learning algorithm, Tertius module. The predicted results will be viewed using a text viewer. The schematic knowledge flow of the process in Weka environment is shown in the Figure 6.

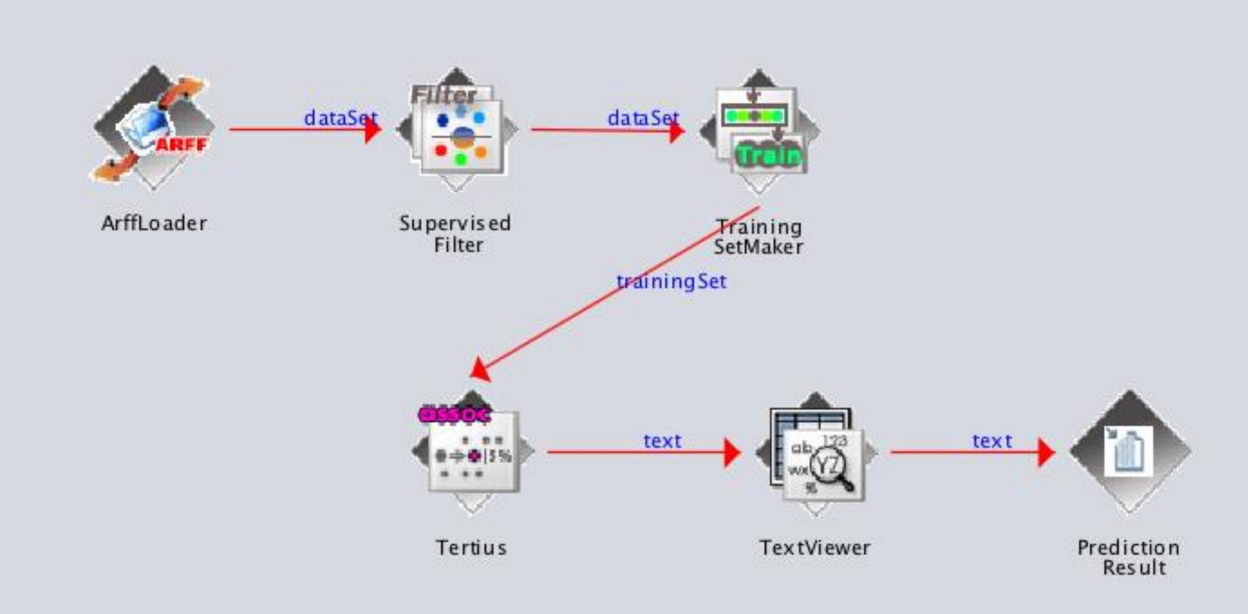

Fig 6: Schematic View of Knowledge Flow

Here the critical parameters under our observation are pressure, flow of oxygen and flow of injected water. The lower and upper limit of parameters is set and is fed for training. Tertius calculates the system performance for each instance and updates the same in the parent node of Treap [22]. As with each instance the nodes in Treap (a tree shaped data structure having the property of heap) gets larger and a traversal from bottom to top provides the best pair of parameters for optimal system performance. Stack voltage of 25V for a load of 20A is obtained when the parameter reading seized at Pa,co(atm) = 0.810,Wco(gm/s)=0.386 and Winj(g/s)=0.0369 s

For measuring the systems performance, the most common and straight away approach is the ROC curve, it shows how the system responds to a set of positive datasets and how it responds to the negative datasets. Here the random Treap nodes and the values associated with the nodes are taken into consideration and the performance is evaluated. Data sample of cumulative rate of a four level diagnostic test is shown in Table 2. The corresponding ROC is shown in the Figure 7.

Table 2: Data Sample

Diagnostic Level	Cumulative Rates	
	False Positive	True Positive
1	0.0108	0.5625
2	0.1935	0.7813
3	0.5806	0.9063
4	1	1

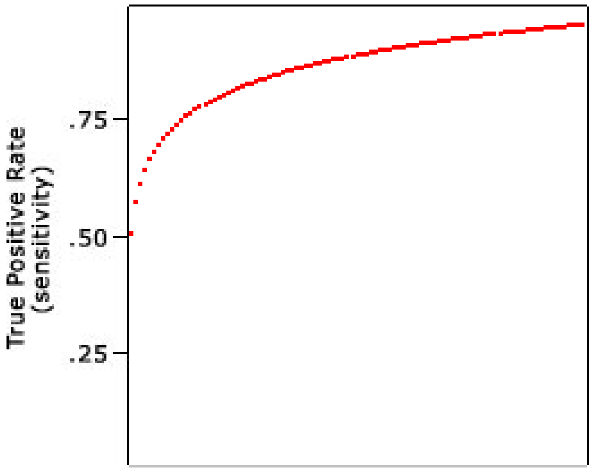

Fig 7: ROC Curve

There were a total number of 73 actual negative cases and 825 actual positive cases;
With: x = false positive rates (1-specificity)
0.0108 0.1935 0.5806
y = true positive rates (sensitivity)
0.5625 0.7813 0.9063
The Fitted curve: $y = 0.1Ln(x) + 0.97$
$R^2 = 0.9906$ and Area under curve = 0.8722
Estimated ROC curve with
Column 1 = false positive rates (1-specificity)
Column 2 = true positive rates (sensitivity)

Table3: Estimated ROC curve with true and false positive rates

Column 1	Column 2	Column 1	Column 2
0.05	0.6704	0.55	0.9102
0.1	0.7397	0.6	0.9189
0.15	0.7803	0.65	0.9269
0.2	0.8091	0.7	0.9343
0.25	0.8314	0.75	0.9412
0.3	0.8496	0.8	0.9477
0.35	0.865	0.85	0.9537
0.4	0.8784	0.9	0.9595
0.45	0.8901	0.95	0.9649
0.5	0.9007		

Area under the ROC is much convincing and is totally in align with the system that we have modeled. So with this machine learning approach we could establish the correctness of our proposed system.

5. Results

The model simulated in MATLAB / Simulink version R2016b is used to study the CeO2 doped PEMFC stack performance for the most significant parameters: Pa,co(atm), Wco(gm/s) and W_{inj}(g/s). Here in this study, the doped CeO2 anode model for effective proton exchange as well as the predicted set of input parameters from the neuro fuzzy controllers are validated using the machine learning tool with Tertius algorithm. The ROC curve in Figure 6 shows the correctness of the predicted set of optimum values of the input parameters obtained after four levels of diagnostic tests.

6. Conclusion

A novel method of machine learning based validation for the designed control strategy for a Modified anode by using nano CeO_2 oxide 500W PEMFC to achieve the following requirements.

1) To maintain required value of cathode inlet pressure (Pc) by controlling the pressure from air compressor with respect to load current(Ifc).

2) To maintain required air flow (Wco) by controlling the motor according to load current(Ifc).

3) To maintain desired value of relative humidity (Rhc) by controlling the water injected (Winj) into the humidifier for specific load conditions based on the value of dry air pressure and air flow from motor is performed successfully. Validations of the results were carried using Tertius algorithm. The results strictly adhere to the values obtained during modeling. A ranker mechanism was also used during preprocessing to prune the lower order parameters. As the machine-learning algorithm validates the model to be perfectly in align, it could be concluded as a perfect implementation strategy for getting an efficient PEMFC system.

4) Thus the nano CeO2 modified anode material inbuilt 500W PEMFC was studied and validated for optimum process parameters with Tertius algorithm.

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