Pt/C Coating for Proton Exchange Membrane Fuel Cell (PEMFC) and Rule-Based Mamdani-Type Fuzzy Modeling of PEMFC Performance

Gürol ÖNAL, Kevser DİNÇER, Salih YAYLA, Yusuf YILMAZ, A.Serhat ERSOYOĞLU

Abstract **-** In this study, performance of proton exchange membrane (PEM) fuel cell was experimentally investigated. The anode side of PEM fuel cell was coated with Platinum/Carbon (Pt/C=0.4/0.5 mg.cm-2) by using spinning method. Two commercial gas diffusion layers (GDLs) were used. The active area of membrane electrode assembly (MEA) was about 5x5 cm2. In the experimental study, current density (CD), voltage density (VD), and power density (PD) performances before and after coating were recorded and then compared to each other. It was found that the performance of PEM fuel cell increases after the coating with Pt/C. After determining the overall improved performance of the PEM fuel cell membrane after coating, the membrane was subjected to seven different voltages and tested experimentally to check its current density and power density performances. Then performance of PEM fuel cell for power density was modeled with Rule-Based Mamdani-Type Fuzzy modeling (RBMTF). Input parameters (current density and time) and output parameter (power density) were described by RBMTF if-then rules. The RBMTF was trained and tested by using MATLAB fuzzy logic toolbox. R2 (%) was found to be 99.92%. With this study, it has been shown that RBMTF model can be reliably used in determination of a performance of PEM fuel cell.

Keywords-- Proton Exchange Membrane Fuel Cell (PEMFC), Coating, Modeling.

I. Introduction

PROTON exchange membrane fuel cell technology has advanced significantly in the last 20 years. Membranes based on (perfluorinated, sulfonic acid containing) PFSA ionomers are being used in systems for commercial applications such as portable and back-up power. These markets can be successful with today's technology while other markets such as stationary residential power, micro electronics applications, and automotive power systems will all require additional advances in membrane technology.

Gürol Önal, Department of Mechanical Engineering, Faculty of Engineering, Selcuk University, Konya, Turkey, gonal@selcuk.edu.tr
Kevser Dinçer, Department of Mechanical Engineering, Faculty of Engineering, Selcuk University, Konya, Turkey, kdincer@selcuk.edu.tr
Salih Yayla, Department of Mechanical Engineering Student, Faculty of Engineering, Selcuk University, Konya, Turkey,
Yusuf Yılmaz, Department of Mechanical Engineering, Faculty of Engineering, Selcuk University, Konya, Turkey, yyilmaz@selcuk.edu.tr
Ali Serhat Ersoyoğlu, Department of Mechanical Engineering, Faculty of Engineering, Selcuk University, Konya, Turkey, aersoy@selcuk.edu.tr

Significant research is underway in many laboratories around he world to address the need for membranes with improved durability, higher conductivity, and the ability to operate at higher temperatures (>100oC) without the need for external humidification of the reactant gases.

Some of the strategies being employed are based on improving existing PFSA technology by incorporating new side chain structures, stabilizing end groups, or incorporating reinforcements, while other approaches are based on the development of new membrane technology such as sulfonated hydrocarbon membranes, proton conducting additives, or polymers with acid groups other than sulfuric acids. For any of these approaches to be successful the membrane will have to meet the performance, cost, and durability targets for the desired application [1].

As a potential candidate for an environmentally benign and a highly efficient electric power generation technology, PEMFC are now attracting enormous interest for various applications such as low/zero-emission vehicles, distributed home power generators, and power sources for small portable electronics [2]. Mawdsley et al., [3] provided composite-coated aluminum bipolar plates for PEM fuel cells. The work of Mawdsley et al. shows that the targets for through-plane area specific resistance (ASR), and anodic corrosion resistance were not met due to the spraying process producing an undesirable layered microstructure and also a microstructure with connected porosity and pinholes. Dhakate et al., [4] shows that the critical weight percentage of filler content to achieve desired electrical conductivity and mechanical properties of bipolar plate as per DOE advanced series of target is found to be 50 wt %. The composite bipolar plate with 50 wt % of expanded graphite (EG) results in bulk density of 1.50 g/cm3, electrical conductivity 120 S/cm, bending strength 54 MPa, Modulus ~ 6 GPa and shore hardness 50. I–V performance ofa cell assembly with EG-based composite plate is similar witha cell assembly with commercial (Schunk) composite plates. The cell assembly with EG bipolar plates reached the power density≥600mW/cm2 at current density 1650 mA/cm2. The lower value of modulus of EG plate (6 GPa) as compared with graphite composite plate (>10 GPa) suggest that these platesare more flexible and can better withstand shock and vibration during mobile operation of PEM fuel cell. The flexible bipolar plates can also reduce contact resistance in fuel call stack. Wu et al., [5] investigated PtxNi alloy nanoparticles as cathode catalyst for PEM fuel cells with enhanced catalytic activity. Their results show thatthe prepared

PtxNi alloy nanoparticles could have promising applications in PEM fuel cells as effective catalysts for oxygen reduction, with the added feature of reduced cost due to lower Pt loading. The work of Bajon et al., [6] illustrate that nafion nanofibers can be used for new design of high power density PEMFCs. Jheng et al. [7] reported the porous structure allows polybenzimidazole (PBI) to achieve a higher doping level and enhanced proton conductivity. The proton conductivity could reach around 6x10-2 S cm-1 for the asymmetric PBI membranes with high porogen feed contents. Lee et al., [8] carried out a study on electrically conductive polymer composite coating on aluminum for PEM fuel cells bipolar plate. They observed that the carbon paper attached, composite coated aluminum bipolar plates can have high corrosion resistance and low contact resistance in PEM fuel cells. Sahin and Ar [9] show that the 15% TiO2 doped membrane has the better properties such as highest proton conductivity (0.03 S.cm-1), ion exchange capacity (1.04 meq.g-1) and water uptake (45%).

In this study, the performance of PEMFC was experimentally investigated and modeled with the Rule-Based Mamdani-Type Fuzzy technique. The anode side of PEMFC was coated with Platinum/Carbon (Pt/C=0.4/0.5 mg.cm-2) by using spinning method. In the experimental study, current density, voltage density and power density performances before and after coating were recorded and then compared to each other. It was found that the performance of PEMFC increases after the coating with Pt/C. The performance of PEM fuel cell for power density was modeled with Rule-Based Mamdani-Type Fuzzy modeling. Then, RBMTF predicted results were extensively compared with actual results under different operating conditions. The actual values and RBMTF results indicated that RBMTF can be successfully used for the determination of the performance of PEM fuel cell.

II. Experimental Investigation Of Membrane Performance

Traditionally, there are five types of fuel cells: alkaline, PEMFC, phosphoric acid, molten carbonate and solid oxide. One can argue that new types have been developed recently. All cells consume hydrogen and oxygen to produce electrical current. Different fuel cell types have their strengths and weak points and, as a result, they have their application niches. It is possible to argue that the PEMFCs are the most simple ones and, as such, are very easy to understand, implement and use. The description of processes in PEMFCs and the challenges during development can be used to some extent as an example which will form a better understanding of all fuel cells. Their basic simple implementation and expected wide penetration of PEMFCs into the end user market have attracted much research and development effort of the PEMFC [10].

PEMFCs, also known as Polymer exchange membrane fuel cells typically operate on pure (99.999%) hydrogen fuel. The PEM fuel cell combines the hydrogen fuel with the oxygen from the atmosphere to produce water, heat (up to 90°C) and electricity. PEMFCs typically utilise platinum based catalysts on the anode to split the hydrogen into positive ions (protons) and negative electrons. The ions pass through the membrane to the cathode to combine with oxygen to produce water. The electrons must pass round an external circuit creating a current to rejoin the H_2 ion on the cathode. Each cell produces approximately 1.1 volts, so to reach the required voltage the cells are combined to produce stacks. Each cell is divided with bipolar plates which while separating them provide a hydrogen fuel distribution channel, as well as a method of extracting the current. PEMFCs are considered to have the highest energy density of all the fuel cells, and due to the nature of the reaction have the quickest start up time (less than 1 sec) so they have been favoured for applications such as vehicles, portable power and backup power applications. The intolerance of the catalysts to impurities such as carbon monoxide has led to developments of high temperature membranes which operate at 150°C. This enables the catalysts to tolerate greater impurities in the hydrogen supply [11].

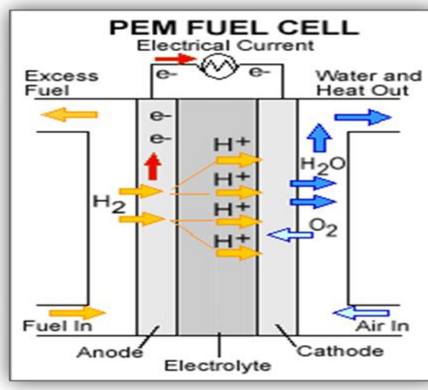


Fig.1 Proton exchange membrane fuel cell

In this study, the anode side of MEA of PEMFC was coated with Pt/C (=0.4/0.5 mg.cm^{-2}) solution by using the spinning method, then effects of the coating on the performance of the PEMFC were experimentally investigated. The experimental setup used in this study is shown in Fig. 2, [12]. The surface area of the MEA was 5x5 cm^2. After the coating, the MEA was left to dry for a period of 24 hours. In the experimental study, CD, VD and PD performances before and after coating were recorded and then compared to each other. The current density performance before and after the coating is shown on Fig.3, whereas the voltage density performance and the power density performance of the MEA before and after coating are respectively present on Figs. 4 and 5. When Figs. 3, 4 and 5 are studied, it is found that the performance with coating is better than the performance without coating.

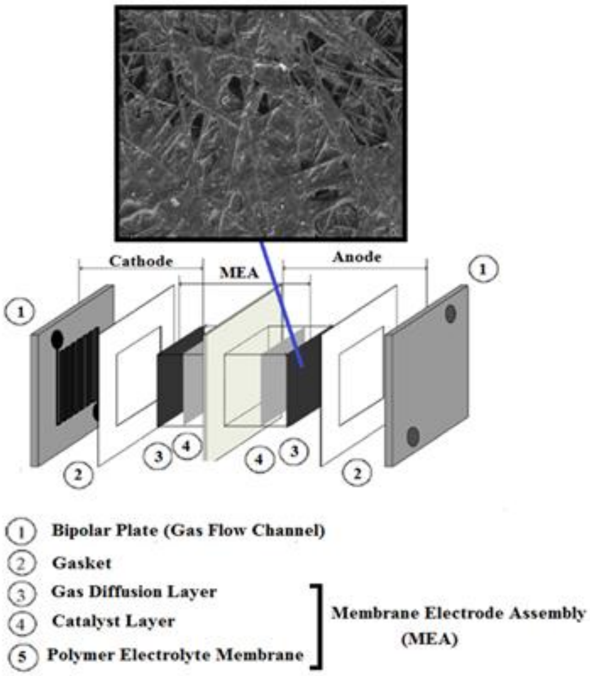


Fig. 2 The schematic of a proton exchange membrane fuel cell

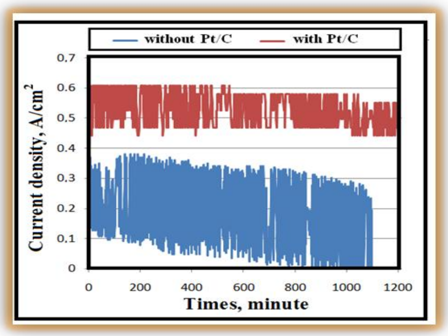


Fig.3 Variation of current density performance of the PEM fuel cell membrane with time

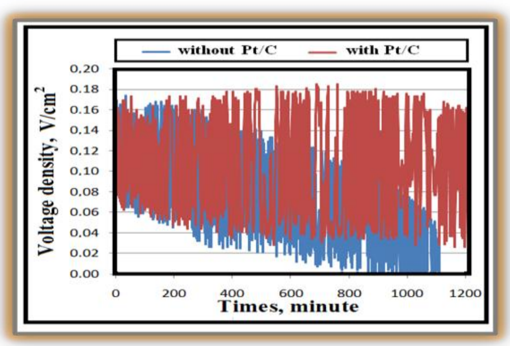


Fig.4 Variation of voltage density performance of the PEM fuel cell membrane with time

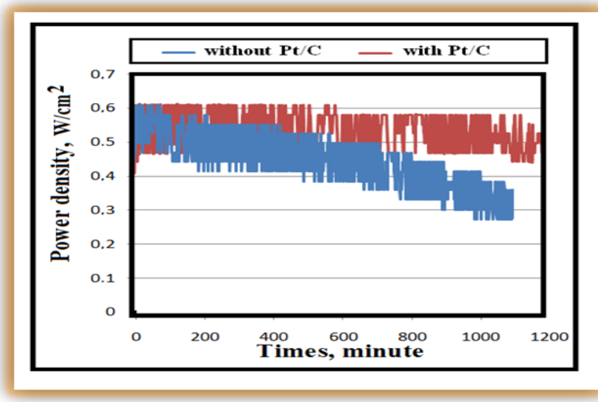


Fig.5. Variation of power density performance of the PEM fuel cell membrane with time

After determining the overall improved performance of the PEM fuel cell membrane after coating, the membrane was subjected to seven different voltages and tested experimentally to check its current density and power density performances. Variation of current density performance with time is shown on Fig. 6; variation of voltage density performance with time is given on Fig. 7

whereas the variation of power density performance with time is presented on 8.

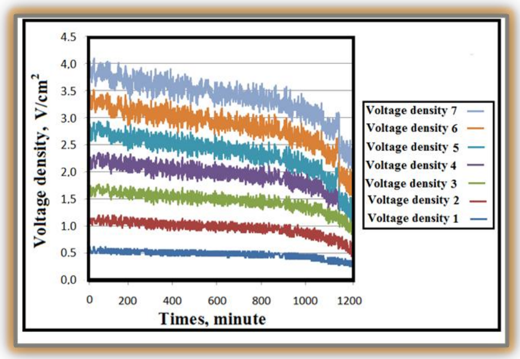


Fig.6 Performance of PEM fuel cell membrane after being coated with Pt/C (at different current density values)

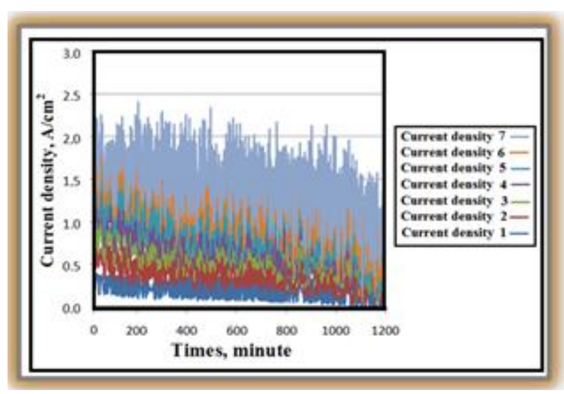


Fig.7 Performance of PEM fuel cell membrane after coated with Pt/C (at different voltage density values)

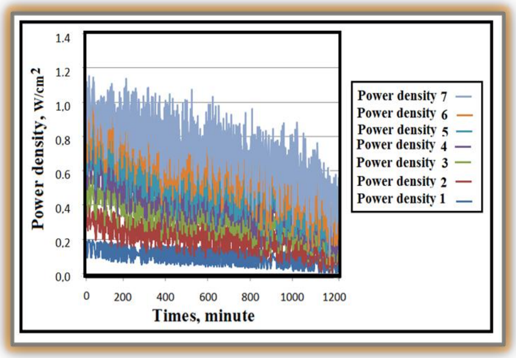


Fig.8 Performance of PEM fuel cell membrane after coated with Pt/C (at different power density values)

The highest current density occurred at the 185 th minutes on current density 7, while the lowest current density occurred at the 1200 th minutes on current density 1 and the highest voltage density was recorded at the 23 rd minutes on voltage density 7, the lowest voltage density occurred at the 1200 th minutes on voltage density 1, whereas the highest power density took place at the 15 th minutes on power density 7, the lowest power density appeared at the 1200 th minutes on power density 1.

III. Rule-Based Mamdani-Type Fuzzy Modelling Of PEMFC Performance Pt/C Coating

The fuzzy subsets theory was introduced by Zadeh in 1965 as an extension of the set theory by the replacement of the characteristic function of a set by a membership function, whose values range from 0 to 1. RBMTF is basically a multi-valued logic that allows intermediate values to be defined between conventional evaluations like yes/no, true/false, black/white, large/small, etc. [13].

In this study, performance of PEM fuel cell was experimentally investigated. The anode side of PEM fuel cell was coated with Platinum/Carbon by using spinning method. After determining the overall improved performance of the PEM fuel cell membrane after coating, the membrane was subjected to seven different voltages and tested experimentally to check its current density and power density performances. Then performance of PEM fuel cell for power density was modeled with RBMTF. This stimulus model is constructed into RBMTF using current density (CD), time (m) as input and power density (PD) as output parameter described by RBMTF if-then rules. RBMTF was designed using the MATLAB fuzzy logic toolbox. General structure of the RBMTF is shown in Fig. 9.

The shape of the membership function distributions is assumed to be triangular. The membership functions were developed for the performance of PEMFC. Input variables CD and m are as shown in Fig. 10. Output variable is the difference between the temperatures of the output stream (PD, Fig.11).

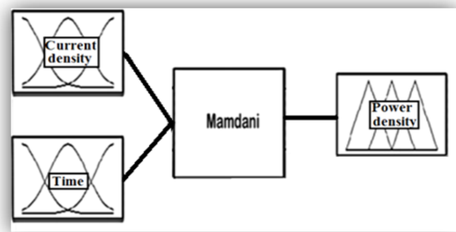
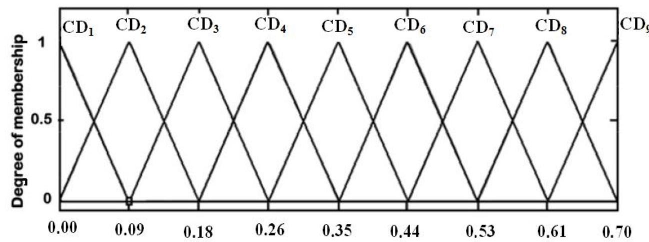
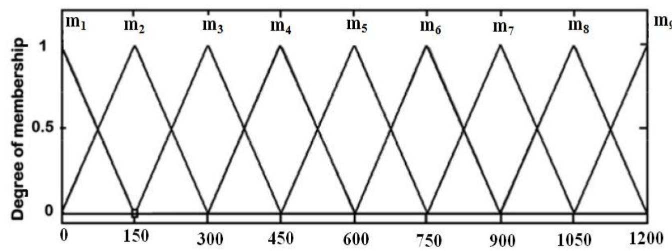


Fig. 9 Designed RBMTF structure



(a)



(b)

Fig. 10 Fuzzy membership functions for two input variables: (a) CD fuzzy set graphic; (b) m fuzzy set graphic

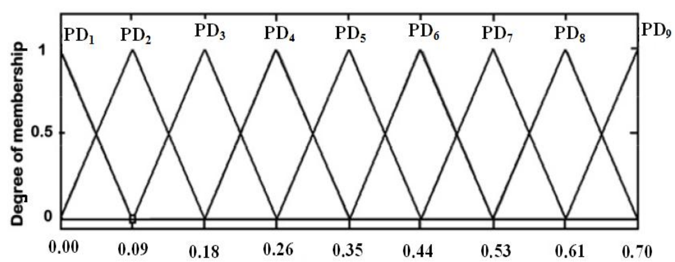


Fig. 11 Fuzzy membership function for output variable: PD fuzzy set graphic

Numerical parameters of input and output variables are fuzzificated as linguistic variables: very very low (L_1), very low (L_2), low (L_3), negative medium (L_4), medium (L_5), positive medium (L_6), high (L_7), very high (L_8) and very very high (L_9) (Table 1).

TABLE I
FUZZY SETS OF İNPUT AND OUTPUT VARİABLES

Membership Name	Very very low	Very low	Low	Negative Medium	Medium	Positive medium	High	Very high	Very very high
	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8	L_9
Current density (A/cm^2)	**CD_1**	**CD_2**	**CD_3**	**CD_4**	**CD_5**	**CD_6**	**CD_7**	**CD_8**	**CD_9**
	-0.08-0.09	0.00-0.018	0.09-0.26	0.18-0.35	0.26-0.44	0.35-0.53	0.44-0.61	0.53-0.70	0.61-0.78
Time (minute)	**m_1**	**m_2**	**m_3**	**m_4**	**m_5**	**m_6**	**m_7**	**m_8**	**m_9**
	-150-0	0-300	150-450	300-600	450-750	600-900	750-1050	900-1200	1050-1350
Power density (W/cm^2)	**PD_1**	**PD_2**	**PD_3**	**PD_4**	**PD_5**	**PD_6**	**PD_7**	**PD_8**	**PD_9**
	-0.08-0.09	0.00-0.018	0.09-0.26	0.18-0.35	0.26-0.44	0.35-0.53	0.44-0.61	0.53-0.70	0.61-0.78

IV. RESULT AND DISCUSSION

A fuzzy model expresses a complex system in the form of fuzzy implications. Mamdani model can be built by using these implications (linguistic relationships) and observed data. The Mamdani-based fuzzy models use excessive number of rules for system modelling. Let X be input (regression) matrix and g an output vector defined as follows:

$$X = [x_1, \ldots\ldots\ldots, x_2]^T = \begin{bmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \\ & \\ x_{n1} & x_{n2} \end{bmatrix} \quad (1)$$

where upper script T denotes the transpose. In the Mamdani fuzzy model, both the antecedent and consequent are fuzzy propositions. A general form of linguistic fuzzy if-then rule is given as follows:

$$R_i : \text{if x is } A_i \text{ then y is } B_i,\ i = 1, 2, \ldots\ldots\ldots, K \quad (2)$$

where R_i is the rule number, A_i and B_i are the fuzzy sets, x is the antecedent variable representing the input in the fuzzy system, and y is the consequent variable related to the output of the fuzzy system. The triangular membership function for Fig. 12 can be shown as (Eq. 3). The membership function, $\mu_a(x)$ is defined as the fuzzy subset a in the universe of discourse, x. The triangular fuzzy membership functions is defined by (a, b, and c), where a and c represent the minimum and maximum values, respectively, and b represents the most likely value [14].

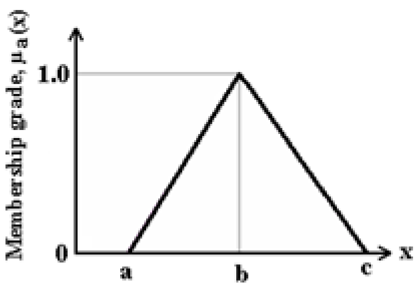


Fig. 12 Construction of membership function

$$\mu_a(x) = \begin{cases} (x-a)/(b-a), & a \le x \le b \\ (x-c)/(b-c), & b \le x \le c \\ 0 & , \textit{otherwise} \end{cases} \quad (3)$$

Fuzzy membership functions in analytical form are expressed in Eqs. 4,5,6 for m, CD and PD for this study

$$m_5(x) = \begin{cases} 0 & x \le 450 \\ \dfrac{x-450}{150} & \text{if} \quad 450 \langle x \le 650 \\ \dfrac{750-x}{150} & \text{if} \quad 600 \langle x \le 750 \\ 0 & x \le 750 \end{cases} \quad (4)$$

$$CD_5(x) = \begin{cases} 0 & x \le 0{,}26 \\ \dfrac{x-0{,}26}{0{,}09} & \text{if} \quad 0{,}26 \langle x \le 0{,}35 \\ \dfrac{0{,}44-x}{0{,}09} & \text{if} \quad 0{,}35 \langle x \le 0{,}44 \\ 0 & x \le 0{,}44 \end{cases} \quad (5)$$

$$PD_5(x) = \begin{cases} 0 & x \le 0{,}26 \\ \dfrac{x-0{,}26}{0{,}09} & \text{if} \quad 0{,}26 \langle x \le 0{,}35 \\ \dfrac{0{,}44-x}{0{,}09} & \text{if} \quad 0{,}35 \langle x \le 0{,}44 \\ 0 & x \le 0{,}44 \end{cases} \quad (6)$$

In this study, performance of PEMFC was experimentally investigated and modeled with a Rule-Based Mamdani-Type Fuzzy modeling technique. Input parameters (current density and time) and output parameter power density were described by RBMTF if-then rules. The RBMTF was trained and tested by means of the MATLAB software on a personal computer. The comparison of actual data with RBMTF is given on Fig. 13 for the variation of CD with m. The comparison of actual data with RBMTF is given on Fig. 14 for the variation of PD with m. From a comparison of the experimental results with the results of the fuzzy logic study, one can see that the results are quite compatible (Figs. 13-14).

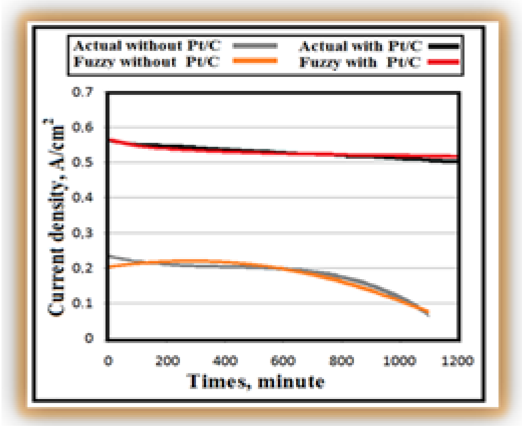


Fig. 13 Comparison of actual data with RBMTF for the variation of CD with m

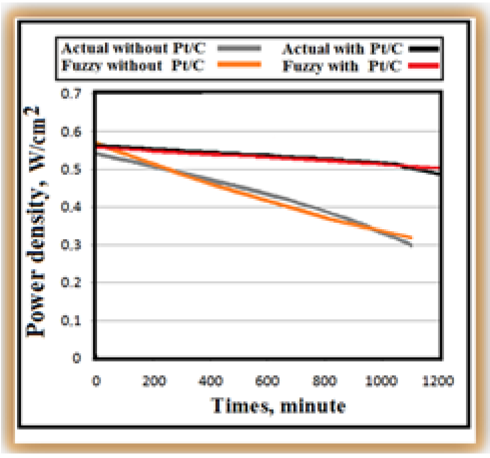


Fig. 14 Comparison of actual data with RBMTF for the variation of PD with m

Some statistical methods, such as the coefficient of multiple determination (R^2) are defined as follows:

$$R^2 = 1 - \frac{\sum_{m=1}^{n} \left(t_{m,m} - y_{p,m}\right)^2}{\sum_{m=1}^{n} \left(t_{m,m} - t_{m,m}\right)^2} \quad (7)$$

where n is the number of data patterns, $y_{p,m}$ indicates the predicted, $t_{m,m}$ is the actual value of one data point m, and $t_{m,m}$ is the mean value of all actual data points [15]. R^2 (%) was found to be 99.92%.

V. Conclusion

The aim of the study is to demonstrate that RBMTF can be successfully used for the determination of PEMFC performance. Firstly, the performance of PEMFC was experimentally investigated. The anode side of MEA of PEMFC was coated with Pt/C solution by using the spinning method, then effects of the coating on the performance of the PEMFC were experimentally investigated. In the experimental study, current density, voltage density and power density performances before and after coating were recorded and then compared to each other. It was found that the performance of PEMFC increases after the coating with Platinum/Carbon. Then performance of PEMFC for power density was modeled with RBMTF. Input parameters (CD and m) and output parameter (PD) were described by RBMTF if-then rules. The RBMTF was trained and tested by using MATLAB fuzzy logic toolbox. The data set was obtained from 250 selections of data. 175 of them were chosen for training, whereas 75 of them were chosen for the test data. R^2 was found to be 99.92 %. The actual values and RBMTF results indicated that RBMTF can be successfully used for the determination of the performance of PEMFC. Many other engineering problems can be formulized using the RBMTF methodology suggested in this study.

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Assist.Prof.Dr. Gürol ÖNAL was born in NİĞDE /Turkey on June, 1967. He received the B.Sc. degree in Mechanicals Enginering Department from Graduate School of Natural and Applied Sciences at Selçuk University in 1989, He received M.Sc. degree in Mechanics Engineering Department from Graduate School of Natural and Applied Sciences at Erciyes University in April 1993. He received Ph. D. degree in Mechanics Engineering Department from Graduate School of Natural and Applied Sciences at Selçuk University in April 2002. He is worked as a Assist. Prof. Dr. of Mechanics Engineering Department of Selçuk University. His research interest are in the area of Mechanics, fracture mechanics, composite materials and elevators.