CHAPTER 4

MODELING AND OPTIMIZATION

In this chapter, the response surface methodology (RSM) is applied to design the Box-Behnken design (BBD) experiments and optimize the interactive effects of major operating parameters of direct ethanol fuel cell (DEFC) for achieving the maximum power density using Program Expert Design 7.0. Operating conditions are the important parameters that influence the DEFC performance greatly. The conventional optimization practice has been performed by monitoring the effect of one parameter on the process at a time, while the other parameters are kept at a constant level and do not represent the interactive effects of all the parameters involved. Besides, these approaches are time-consuming and require several experiments to determine optimum levels, which consume not only a great deal of time but also a significant quantity of chemicals (Caglar et al., 2018). Recently, response surface methodology (RSM) is considered as the best option and is commonly used for optimizing the most effective process conditions in the presence of less experimental results.

4.1 Introduction

From the literature survey, it is evident that the DEFC electrode materials are very expensive also not easily available. In addition, the solid electrolyte material, mainly Nafion® is the most widely used proton exchange membrane (PEM) which is commercially available in the market. However, the cost of Nafion® is very high. As per information available in the online fuel cell store the cost of PEM/ Nafion™-117 (product code 591239) of 10 cm × 10 cm is $ 33.00 (www.fuelcellstore.com). The basic cost of each five-layered MEA (product code 590114) is \$ 167.00 for direct methanol fuel cell (DMFC) of an active electrode area 2.2 cm × 2.2 cm. The cost analysis shows that the PEM cost (\$ 33.00) is almost 20 % of the MEA for DMFC cost (\$ 167.00). Thus, the process parameter optimization through a purely experimental approach could be very costly and also time-consuming. Many research works have been reported to date on the performance of DEFC using experimental approach. Some of them are primarily focused on the electrocatalysts synthesis followed by characterization and performance evaluation in DEFC (Choudhary and Pramanik, 2019 and Choudhary and Pramanik, 2020a). Most of the research work deals with optimizing process parameters using industrial electrocatalysts and electrolyte membrane materials to achieve the maximum DEFC cell efficiency in terms of current density and power density via large number of experiments (Song et al., 2005, Pramanik and Basu, 2007 and Pramanik et al., 2008). Recently, a few works have also been noted on the synthesis of an alternative Nafion® membrane electrolyte based on very cheap polyvinyl alcohol (PVA) raw material doped with KOH for DEFC (Gupta and Pramanik, 2019).

There are very few papers available in the open literature on process optimization using a statistical method that could reduce the time and cost of the entire process to achieve the highest cell performance of the DEFC. Alzate et al., (2011) analyzed the performance of DEFCs by varying the value of the operating variables: ethanol concentration, cell temperature, ethanol solution flow rate, cathode backpressure, and oxygen flow rate. Experimental findings showed that cell performance is improved by increasing the cell temperature from 60 to 90 ºC, cathode backpressure up to 20 psig, and the concentration of ethanol from 0.1 M to 2 M. Heysiattalab et al., (2011) and Goel and Basu, (2012) also studied the effects of various common parameters on DEFC performance e.g., ethanol concentration, cell temperature, anode, and cathode flow rate or oxygen pressure. Both research papers reported that a rise in cell temperature, ethanol concentration, and oxygen flow rate or oxygen pressure at the cathode improved the cell performance. Pramanik and Basu, (2010) developed a mathematical model for DEFC that considers various overpotentials such as activation overpotential, ohmic overpotential, and overpotential concentration at both anode and cathode. Experiment data on current-voltage characteristics obtained from DEFC of various for ethanol concentration and temperatures are well predicted by the model with reasonable agreement.

All these experimental DEFC analyses determine the optimum process parameters for achieving the highest output of the cells. The reproducibility of data has not been reported in many studies. It may be because of the high material costs. However, the widely used statistical method surface response methodology (RSM) is currently used in the fuel cell field to optimize process parameters and uses the same process parameters in the actual fuel cell system to achieve the highest power density. It should be noted that DEFC is a complex system where cell output including cell voltage and power density depends on several operating parameters in a non-linear manner.

As mentioned earlier, when evaluating the importance of independent factors and their interactions, the RSM has been suggested to be particularly useful in optimizing the most effective process conditions in the presence of less experimental data and minimized error. It is one of the most efficient and promising techniques for designing experiments, building models, and optimizing the most effective process conditions and their interaction with less experimental data on the process (Sharifi et al., 2019). The RSM is a regression method with a set of advanced mathematical and statistical techniques that use quantitative data from relevant experiments to develop empirical models that co-relate the independent variables and output of the process (Charoen et al., 2014 and Zainoodin et al., 2015). It was developed by Box and Wilson in 1951 (Bezerra et al., 2008). The main RSM comprises the full factorial design at three-levels (3-FFD) using the Box-Behnken design (BBD), the Central Composite design (CCD), the Doehlert Matrix design (DMD) and the Plackett-Burman design (PBD) which can approximate the limit surface by fitting the response surface via a set of experimental data (Bezerra et al., 2008 and Candioti et al., 2014). Among these, the BBD requires less time, less resources and fewer experiments with the same number of variables. This methodology is based on the use of regression analysis to suit a linear or quadratic polynomial equation to describe the system under investigation. Additionally, optimizing the parameters over traditional single parametric optimization approaches is considered the better option, as this requires fewer experiments and experimental data offers optimized parameters as well as less time, space, labor, and material consumption. In addition, this approach tests the interaction effects of various variables by three-dimensional figures in different ranges. For RSM, the independent variables that influence the system-dependent variable (response value) are selected based on the researcher's intent and experience using the literature survey.

Thus, the RSM with BBD model was used in the present study to determine the possible optimum values of the primary operating variables in order to achieve the highest power density from a laboratory fabricated single cell DEFC. Three main parameters like concentration of ethanol, anode electrocatalyst loading, and cell temperature were chosen as process parameters (independent), while DEFC power density was chosen as the response. The surface plots obtained from mathematical models were used to illustrate the interaction of the DEFC performance between each operating parameter. Optimum values of operating variables for maximum power density were achieved using RSM and validated with experimental data collected through the set of experiments as discussed in chapter 3 (Section 3.3.6, Page no. 98). The electrocatalyst considered in the experiment was tri-metallic Pt-Ru-Re (1:1:0.5)/f-MWCNT as it produces the highest power density among all the synthesized electrocatalysts.

4.2 Experimental design methodology

As mentioned earlier, a full factorial Box-Behnken Design (BBD) was deployed with the three variables/parameters to evaluate the effect of selected variables on the response. The experimental design and statistical data analysis were carried out using Design Expert Version 7.0 software (Stat-Ease, Inc., Minneapolis, MN, USA). The BBD is a rotating composite second-order design that allows multiple testing of each variable at just three levels (–1, 0, +1). It needs less time and resources and fewer experimental runs with the same number of factors that make this design more economical and efficient compared to other factorial designs. In addition, all points fall within the limits of manageable operations and prevent variables from being manipulated under unrealistic conditions (Bezerra et al., 2008). In this study, the ethanol concentration (A) of the range 1 M to 3 M, the electrocatalyst loading (B) of the range 0.5 to 1.5 mg/cm^2, and the operating cell temperature (C) of the range 40 ºC to 80 ºC were selected as independent variables for RSM investigation. The maximum power density (mW/cm^2) of the DEFC was chosen as the dependent variable i.e. response.

The effects of different effective independent test variables were observed by performing some preliminary in single DEFC experiments. The experiments in preliminary studies on single cell DEFC were conducted by varying one variable at a time and holding the other variables at fixed values as depicted in Appendix B (Fig (B.1) to Fig (B.3) (Page no. 276-278). Fig (B.1) demonstrates the effect of ethanol concentration (A) on cell performance for anode electrocatalyst loading of 0.5 mg/cm^2 and operating cell temperature at 40 °C. The optimum ethanol concentration was observed to be 2 M, resulting in the highest power density of 7.50 mW/cm^2. The effect of anode electrocatalyst loading (B) on DEFC performance is presented in Fig (B.2) for the optimum ethanol concentration of 2 M and operating cell temperature of 40 °C. The optimum anode electrocatalyst loading of 1 mg/cm^2 was recorded, for which the maximum power density of 10.66 mW/cm^2 was achieved. Similarly, the effect of operating cell temperature (C) on DEFC performance is depicted in Fig (B.3), for the optimum ethanol concentration of 2 M and anode electrocatalyst loading of 1 mg/cm^2. The optimum operating cell temperature was detected at a temperature of 80 °C with a maximum power density of 23.2 mW/cm^2. From the preliminary experimental studies on single cell DEFC tests as mentioned above, the low level and high level of factors/variables were chosen as presented in Table 4.1. It is worth noting that the operating temperature of the cell was varied from 40 ºC to 80 ºC only from the point of view of the ethanol boiling point at around 78.4 °C (Choudhary and Pramanik 2019 and Choudhary and Pramanik 2020a). Moreover, the properties of Nafion® membrane such as high conductivity of the proton, high mechanical strength, chemical stability, flexibility are true only in a highly hydrous state and temperatures below 80 °C (Barati et al., 2019). The coding limits, levels, and ranges of the three independent test variables are indicated in Table 4.1.

Table 4.1 Experimental ranges and levels of independent test variables studied in the BBD model.

Independent variables	Range and levels (coded)		
	Low level (-1)	Middle level (0)	High level (+1)
A-Ethanol concentration (M)	1	2	3
B-Anode electrocatalyst loading (mg/cm^2)	0.5	1	1.5
C- Cell temperature (°C)	40	60	80

According to the BBD model, the number of experiments for three variables was derived to be 17 using the following Equation (4.1) (Bezerra et al., 2008 and Barati et al., 2019):

$$N = 2k\,(k - 1) + c_p = 2 \times 3\,(3 - 1) + 5 = 17 \quad (4.1)$$

where N, k and c_p stands for the total number of experiments, number of independent variables and number of repetitions at the central points, respectively. All seventeen experiments were performed to visualize the effects of selected variables on the DEFC power density. At the center point of variables, five experiments were repeated to predict the experimental error and data reproducibility, and twelve experiments were performed out of the centre. The results of the experimental data were fitted into the following second order polynomial equation as suggested by the Box-Behnken design technique (Equation 4.2):

$$Y = \alpha_o + \sum_{i=1}^{k} \alpha_i \times X_i + \sum_{i=1}^{k} \alpha_{ii} \times X_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \alpha_{ij} \times X_i \times X_j \quad (4.2)$$

where Y represents the predicted response value (power density); X_i and X_j (i and j = 1–3) are the coded values of independent variables being studied; α_o is the model intercept coefficient and α_i, α_{ii}, α_{ij} are linear effect, quadratic effect and the interaction effect coefficients, respectively.

The performance of the developed model (Equation 4.2) was analyzed in accordance with several factors such as p-values, F-values, values of regression coefficients, analysis of variance (ANOVA), degree of freedom (DF) to check the statistical fitness of the BBD model. The goodness of fit of the quadratic model equation was represented statistically by the determination coefficient, R^2. Three dimensional graphical and contour plots were incorporated to analyze the individual and their interaction effects of independent variables on the power density of DEFC. The values of F and p derived from ANOVA are used to check the statistical significance of the terms of the equation. The p-value < 0.05 for the model and p-value > 0.05 for lack of fit testing suggest a well-adapted model for the experiments. The optimization and validation of process parameters using RSM are presented in chapter 5 (Results and Discussion, Page no. 224).