CHAPTER 4

PROCESS PARAMETER OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY (RSM)

4.1 Introduction

In the context of any system or process, the term "optimization" refers to increasing the performance of the system or process to achieve the highest output at the optimized process condition. The effectiveness of direct sodium borohydride fuel cell (DSBFC) is greatly influenced by the characteristics and properties of the membrane electrolyte (Dimirci et al. 2007). The enhancement of a DSBFC performance can also be achieved by the optimization of its operating conditions. Many researchers experimentally optimized the various parameters of the DSBFC to achieve the highest power density (Kadioglu et al. 2020, Oh 2021, Haijun et al. 2010, Celik et al. 2008). Kadioglu et al. 2020 studied the direct borohydride fuel cell and experimentally optimized the different operating parameters of the direct borohydride fuel cell, such as cell temperature, electrocatalyst (Pt/C) loading for anode and cathode and fuel flow rates. The fuel was a solution of 1 M $NaBH_4$ in 3 M NaOH, the oxidant was dry oxygen, and the membrane electrolyte was Nafion® 115. Oh et al. 2021 studied the direct borohydride fuel cell that utilizes 5 wt. % $NaBH_4$ in 5 wt% NaOH solution as fuel and H_2O_2 as oxidant. The electrocatalysts used were gold (Au), silver (Ag) and Ni (Ni) supported on multiwalled carbon nanotube (MWCNT) at the cathode and Pd/MWCNTs at the anode. The membrane electrolyte used was Nafion® 212. The H_2O_2 concentration, type of cathode electrocatalyst and the cell temperature were optimized to achieve the highest power density. Similarly, Haijun et al. 2010 studied the optimization of various operating parameters of the direct borohydride fuel cell to achieve the highest power density. The Pt/C and MnO_2 were used as anode and cathode electrocatalyst, respectively. The fuel and oxidant supplied was 0.5 M $NaBH_4$ in 2 M NaOH solution and H_2O_2 in NaOH solution, respectively. The Nafion® 117 was used as a membrane electrolyte. The cell temperature, H_2O_2 concentration and catholyte NaOH concentration were optimized to achieve best performance from the direct borohydride fuel cell. The experimental determination of the optimized parameters is time taking and expensive due to the use of expensive chemicals in large quantity and equipment for the experiments. Thus, experimental optimization of various operating parameters of the fuel cell could be avoided and statistical method of optimization is adopted. There are some popular optimization techniques based on statistical analysis, which can significantly reduce time while being cost effective also.

A range of process optimization techniques like Taguchi (Chang 2011), response surface methodology (RSM) (Haijun et al. 2010), Elman neural network (ENN) (Guo et al. 2019), Salp Swarm Optimizer (SSO) (El-Fergany et al. 2018) are employed to enhance the operating condition of fuel cells. One such useful method for the optimization of process parameters is the response surface methodology (RSM). The RSM has found extensive applications in engineering design optimization studies. Originating in the 1950s through the work of Box and collaborators, RSM constitutes a robust toolkit of mathematical and statistical techniques. The core principle of RSM involves fitting polynomial equations to experimental data. The RSM serves as a valuable tool for establishing relationships between the independent variables i.e., input variables and response or output of the process, whether they act individually or in combination within processes (Panjiara et al. 2020a). Besides assessing the impact of independent variables on the response, RSM constructs a mathematical model with the aim of optimizing variable levels to achieve optimal performance concurrently. Notably, one of the primary advantages of RSM is its ability to rapidly derive variable relationships and models, demanding relatively minimal datasets for model construction in relation to input-output variables (Choudhary et al. 2021). As already mentioned, the application of RSM brings cost savings by avoiding the need for expensive analysis methods, along with their associated time and the voluminous data analysis they entail (San et al. 2014). Multiple approaches of response surface methodology (RSM) exist, including Box-Behnken design (BBD) (Panjiara et al. 2020, Choudhary et al. 2021), central composite designs (CCD) (Gautam and Mondal, 2023), and Doehlert matrix (Bezerra et al. 2008b). These methods are employed to identify the optimum values of influential parameters, with the objective of maximizing the response. In this study, a highly effective Box-Behnken design (BBD) method was employed for optimization purposes. The BBD method was chosen due to its ability to efficiently identify the optimum value by utilizing a limited number of combinations of effective operational variables (Verma et al. 2023).

It should be noted that the performance of the direct sodium borohydride fuel cell (DSBFC) and all other types of fuel cells greatly dependent on the effectiveness of the membrane electrolyte (Dimirci et al. 2007). In the present work, the optimization of the process parameter of physically crosslinked PVA-TEOS membrane electrolyte was done to achieve the highest conductivity of the membrane electrolytes, which resulting the highest response i.e., power density in a single DSBFC study. The objective of this study was to optimize the preparation parameters of the membrane electrolyte, including the freeze-thaw cycle, NaOH doping concentration, and TEOS loading. The surface plots derived from mathematical models were utilized to visually depict the correlation between the performance of the direct sodium borohydride fuel cell (DSBFC) and various operational parameters. The data set generated in the experiment were analyzed using Design-

Expert 7.0 software. The objective was to determine the optimum values of the operating variables that would result in the maximum power density.

4.2 Experimental procedures

The various types of experiments were performed in direct sodium borohydride fuel cell as discussed in the **Chapter 3** (**section 3.3.6**). The freeze-thaw cycle, NaOH doping concentration and TEOS loading were taking in the range of 5 to 9 cycle, 2 M to 6 M and 5 wt. % to 15 wt. %, respectvely. The fuel supplied to the anode side was 1 M $NaBH_4$ mixed in 4 M NaOH and the oxidant supplied to the cathode side was humidified oxygen. The fuel flow rate was maintained at a constant rate of 2 ml/min, while the oxidant flow rate was kept steady at 65 ml/min. The DC electronic load bank (K-PAS, India) was used to collect the cell voltage and current data of each DSBFC experiment. The experimentally obtained data on current density and cell voltage were used to determine the power density. All the experiment of the DSBFC was operated at 1 atmospheric pressure and at a room temperature of 30 ^{o}C.

4.3 Statistical analysis

The response surface methodology is a comprehensive mathematical approach that combines statistical analysis and design optimization. The utilization of this tool enables the identification of the associations between the dependent variables and the independent variables, hence facilitating researchers in constructing models, assessing the impacts of several components, and determining the optimal conditions for achieving the intended outcome or response (San et al. 2014). The methodology takes into account the effect of both individual factors and interacting terms on the response of the system, which is a notable advantage of this instrument. In the present study, the Box Behnkem Design (BBD) was used to optimize the effective parameters of the direct sodium borohydride fuel cell (DSBFC). The design expert 7.0 (State-Ease, Inc., Minneapolis, MN, USA) software was used for statistical analysis. A full factorial Box-Behnken design with three parameters was used in the RSM investigation to analyze the effect of selected variables on the response. The Box-Behnken Design (BBD) is a composite second-order experimental design that facilitates the examination of several variables at three specific levels (-1, 0, +1). This design offers increased cost-effectiveness and efficiency compared to alternative factorial designs, as it requires reduced time, resources, and experimental runs while maintaining an equivalent number of components. Furthermore, all data points are confined within the boundaries of feasible procedures, hence preventing the manipulation of variables under impractical circumstances.

It is observed from the thorough literature review that the cell performance i.e., power density primarily dependent on the cell operating condition such as electrocatalyst loading, cell temperature fuel concentration. These parameters are generally optimized through various optimization techniques (Panjiara and Paramanik 2020a, Choudhary and Pramanik 2021, Sanet et al. 2014). However, the performance of Fuel cell is also dependent on the other design/synthesis parameters of various components of the fuel cell, such as the preparation of electrocatalysts, manufacturing of electrodes and manufacturing of membrane electrolytes, etc. The membrane electrolyte is one of the crucial components of the DSBFC and optimization of the process parameter of the preparation method of the membrane electrolyte is necessary to achieve the highest power density. The primary function of membrane electrolyte is to transport ion through it. The high ionic conductivity of membrane electrolyte helps to achieve high power density. The ionic conductivity of membrane electrolyte depends on various factor such as internal structure, degree of crosslinking, presence of water in the electrolyte matrix, presence of dopant in the electrolyte, etc and these characteristics are affected by the number of freeze-thaw cycles, NaOH doping concentrations and TEOS loading.

Thus, a preliminary study was done to investigate the effect of freeze-thaw cycle, TEOS loading and NaOH doping concentration on the performance of DSBFC. Accordingly, in the present optimization analysis by RSM method, A- freeze-thaw cycle, B- TEOS loading (wt. %) and C- NaOH doping concentration were taken as effective variables. The range of A, B and C were taken as 5 to 9, 5 wt. % to 15 wt. % and 2 M to 6 M, respectively. The other parameters like anode electrocatalyst loading (1 mg/cm^2) cathode electrocatalyst loading (2 mg/cm^2), cell temperature (30 ^oC), $NaBH_4$ concentration (1 M), supporting electrolyte (NaOH) concentration of fuel (4 M), fuel flow rate (2 ml/min) and oxidant flow rate (65 ml/min) were kept constant. The maximum power density was chosen as the response or output of the developed model equation.

The effect of various effective process parameters of the physically crosslinked PVA-TEOS membrane electrolyte of the DSBFC on polarization and power density curve are shown in Appendix A. **Figure A1 – A3** depicts the effect of several effective independent variables on single cell DSBFC performance. **Figure A1** shows the effect of the freeze-thaw cycle (A) on DSBFC performance. The TEOS loading and NaOH doping concentration of 5 wt. % and 2 M were kept constant in the membrane electrolyte. It was observed that the cell performance in terms of power density increases as the freeze-thaw cycle increases from 5 to 7 Cycle and the power density of the DSBFC decreases beyond 7 Cycle. The highest power density of 33.01 mW/cm^2 at current density of 70.4 mA/cm^2 was obtained for 7 freeze-thaw cycle. The maximum power density of 31.10 mW/cm^2 and 28.68 mW/cm^2 at the current density of 64 mA/cm^2 57.56 mA/cm^2 were obtained for the 5 and 9 freeze-thaw cycles, respectively. **Figure A2** shows the effect of

NaOH doping concentration on DSBFC performance. The freeze-thaw cycle of 7 and TEOS loading of 5 wt.% were kept constant. The optimum concentration was found to be 4 M NaOH which exhibited the highest power density of 60.96 mW/cm^2 at current density of 140.8 mA/cm^2. Whereas, **Figure A3** shows the effect of TEOS loading on the DSBFC performance and the optimum TEOS loading was found to be 10 wt.%. The highest power density of 66.57 mW/cm^2 at current density of 152 mA/cm^2 was obtained. The low and high amounts of variables were determined based on the preliminary experimental research on single cell DSBFC tests discussed above. **Table 4.1** shows the levels and coding limitations of the three independent variables.

Table 4.1 Process parameters and levels in the BBD design.

Process Parameter	**Experimental level (Coded)**		
	Low level (-1)	**Middle level (0)**	**High level (1)**
A-Freeze-thaw cycle	5	7	9
B- NaOH doping concentration (M)	2	4	6
C- TEOS loading (wt. %)	5	10	15

The total number of experiments for three variables was calculated using Equation 4.1 according to the BBD model (Choudhary et al. 2021).

$$\mathrm{N} = 2\mathrm{K}(\mathrm{K} - 1) + \mathrm{C_p} = 2 \times 3(3 - 1) + 5 = 17 \qquad (4.1)$$

Where N, k and Cp indicate the total number of experiments, number of independent variable and number of reptations at the central points. All 17 tests were carried out in order to visualize the impact of various selected variables on the DSBFC power density. At the central point of the variables, a series of five experiments were conducted in order to forecast the experimental error and ascertain the repeatability of the data. Additionally, a total of twelve experiments were carried out in locations outside of the central point. The experimental data was analyzed and incorporated into a second-order polynomial equation, as recommended by the BBD approach (Equation 4.2).

$$\mathrm{Y} = \alpha_{\mathrm{o}} + \sum_{\mathrm{i}=1}^{\mathrm{k}} \alpha_{\mathrm{i}} \times \mathrm{X}_{\mathrm{i}} + \sum_{\mathrm{i}=1}^{\mathrm{k}} \alpha_{\mathrm{ii}} \times \mathrm{X}_{\mathrm{i}}^{2} + \sum_{\mathrm{i}=1}^{\mathrm{k}} \sum_{\mathrm{j}=\mathrm{i}+1}^{\mathrm{k}} \alpha_{\mathrm{ij}} \times \mathrm{X}_{\mathrm{i}} \times \mathrm{X}_{\mathrm{j}} \qquad (4.2)$$

In the given equation (Equation 4.2), Y represents the predicted response value, specifically the power density. Xi and Xj, where i and j range from 1 to 3, denote the coded values of the independent variables under investigation. α_o represents the model intercept coefficient, while α_i, α_{ii}, and α_{ij} represent the coefficients for the linear effect, quadratic effect, and interaction effect, respectively. The performance evaluation of the constructed model, as represented by Equation 4.2, was conducted by considering several criteria, including P-values, F-values, regression coefficients, analysis of variance (ANOVA), and degree of freedom (DF). These statistical measures were employed to assess the fitness of the Box-Behnken design (BBD) mode. The statistical representation of the adequacy of fit for the quadratic model equation was determined by the coefficient of determination, R^2. The study utilized three-dimensional graphical and contour plots to examine the impact of independent variables on the power density of direct sodium borohydride fuel cell (DSBFC). These plots were employed to analyze both the individual effects of the variables as well as their interactions. The resulting values of F and p obtained from ANOVA are utilized to assess the statistical significance of the elements within the equation. The model exhibits a P-value <0.05, indicating a statistically significant fit to the experimental data. Additionally, the P-value >0.05 for the lack of fit tests suggests that the model adequately represents the observed data.