CHAPTER 4

OPTIMIZATION OF PROCESS PARAMETERS BY RSM

4.1 Introduction

The optimization of any system or process is known as improving the performance of the system or process from which maximum benefit can be achieved. The present work focuses on the optimization of operating parameters using Box Behnken Design (BBD) in response surface methodology (RSM) to obtain maximum power density from glycerol based air breathing MFC. Till date, there are several experimental work on glycerol electrooxidation is accomplished in MFC and have been reported in published literature. As already discussed in the chapter "Literature Review and Objectives", Dector et al., (2013a) used Y-shaped MFC for glycerol electrooxidation using Pd/C and Pd/multi wall carbon nano tubes (MWCNT) anode electrocatalyst and Pt/C as cathode electrocatalyst. The maximum power density of 0.51 mW/cm^2 and 0.7 mW/cm^2 was obtained using fuel stream of 0.1 M glycerol mixed with 0.3 M KOH and O_2 saturated with 0.3 M KOH solution as oxidant stream with Pd/C and Pd/MWCNT as anode electrocatalyst, respectively. Similarly, Maya-Cornejo et al., (2016) synthesized CuPt/C and CuPd/C anode electrocatalyst for electrooxidation of crude and analytical glycerol in nanofluidic fuel cell. The maximum power density of 17.6 mW/cm^2 was obtained using CuPd/C electrocatalyst and crude glycerol (5 vol. %) as fuel, while power density of 23 mW/cm^2 was obtained using CuPt/C electrocatalyst and analytical glycerol (5 vol. %) as fuel. Martins et al., (2018a) studied on mixed media with flow through porous electrode in MFC using glycerol, ethylene glycol and methanol as fuel. Pt/C electrocatalyst was used for both anode and cathode. The KOH of 1 M was used as anode electrolyte and H_2SO_4 of 1 M as cathode electrolyte. The maximum power density of 39.5 mW/cm^2, 30.3 mW/cm^2 and 30 mW/cm^2 were obtained for the glycerol of 0.05 M, ethylene glycol of 1.5 M of and methanol of 3 M, respectively. A few more works on glycerol based MFC with flow through the porous electrodes have been reported by Martins et al., (2018b) and Martins et al., (2019). However, in all the studies optimum concentration of glycerol fuel and oxidant for highest cell performance are experimentally determined. There is no doubt that purely experimental works in such delicate MFC device is truly challenging task. Moreover, it is very much time consuming to optimize the operating parameters such as electrocatalyst loading, electrolyte concentration at anode and cathode, and glycerol concentration to achieve highest power density from the MFC. The above discussed research works on glycerol based MFC did not explain detailed study of all parameters which effect the cell performance. In addition, the experimental optimization technique does not include the interactive effects among the parameters studied. Such type of studies increases the number of experiments, time and consumptions of materials (Bezerra et al., 2008). To overcome these problems, the optimization of variables in MFC using multivariate statistic techniques i.e., response surface methodology (RSM) could be very much effective.

The RSM is a mathematical and statistical technique that co-relates with the output of the process and the independent parameters. It assists to develop the model and appraise the effects of factors and set the optimum conditions for the desired responses (Myers et al., 2016). The RSM helps to develop a polynomial equation based on experimental data to predict the response (Okur et al., 2013; San et al., 2014). The effects of parameters on the response studied using RSM shows interactive effects among variables and represent the overall effects on the process (Allaedini et al., 2016). An optimization study using RSM can be studied in three steps. The first step is to find out the independent parameters and levels of experiments. In the second step, experimental design is selected, and the model equation is predicted and verified. The output of the process as a function of the independent variables and optimum conditions are determined in the last step (Bas et al., 2007). The experimental domain that is the upper and lower limits of the experimental parameters are obtained from the preliminary experiments. The screening of parameters is necessary to get the most influencing parameters on the cell performance. The most influencing parameters are also obtained from the preliminary experiments. The major influencing parameters of the present experiment for enhancing the cell performance in MFC are glycerol/fuel concentration, anode electrolyte/KOH concentration, anode electrocatalyst loading and cathode electrolyte/KOH concentration. The oxygen from atmospheric is used as the oxidant. In the present study, among all design of MFC, the best performance in terms of power density was obtained in T-shaped air breathing MFC using Pd-Pt (16:4)/C anode electrocatalyst in the preliminary studies. Thus, T-shaped air breathing MFC was selected to optimize the process parameters in the present study. The acetylene black carbon supported laboratory synthesized electrocatalyst Pd-Pt (16:4)/C was used as anode electrocatalyst and commercial Pt/C_{HSA} as the cathode electrocatalyst for the optimization study. The quadratic model predicts the appropriate operating conditions to achieve highest power density from the laboratory designed T-shaped MFC. The main aim of present study is primarily focused on findings the optimum conditions of independent variables for the glycerol based T-shaped air breathing MFC by RSM method to achieve highest power density at the room temperature of 35 ^{o}C. The independent variables are glycerol concentration, anode electrocatalyst loading, anode electrolyte concentration and cathode electrolyte concentration. A mathematical model equation was developed to predict the variation of response with the independent process variable. The developed model was validated using analysis of variance (ANOVA) and experimental data which reasonably predicts the model.

4.2 Experimental procedures

The different experimental conditions obtained for the RSM experimental design were performed at 1 atmospheric pressure and room temperature of 35 ^{o}C. The cathode electrocatalyst (Pt/C_{HSA}) loading of 1 mg/cm^2 was maintained for each operating condition of experiments. While the domain of other parameters were taken from preliminary studies such as anode electrocatalyst loading which were varied from 0.5 mg/cm^2 to 1.5 mg/cm^2. Similarly, anode electrolyte/KOH concentrations were varied from 1 M to 2 M and that too for the cathode were varied from 0.25 M to 0.75 M, respectively. The flow rate of 1.2 ml/min at anode side and 1 ml/min at the cathode side were maintained using a peristaltic pump (Electrolab, India). The outlet pipes of the peristaltic pumps were connected to burette arrangements at anode and cathode side. The fluctuation free and desired flow rates of the anode and cathode stream were maintained using the stopcock of the burette at the bottom. The burettes were used to maintain constant liquid head to eliminate fluctuation of the flow which would produce from the peristaltic pump and also the steady state liquid flow is achieved within the microchannel (Rathoure and Pramanik 2016).

4.3 Statistical analysis

The use of RSM design is to obtain the maximum response of a system by analyzing the related operating conditions which have the major effect on the response. The methodology considers both the effect of individual factor and interacting terms on the response variable which is the most significant advantage of this design tool (Makela, 2017). The operating conditions to obtain the maximum power density of MFC were optimized using Box Behnken Design (BBD) in RSM. The Design Expert 7.0 (Stat-Ease, Inc., Minneapolis, MN, USA) software was used for statistical analysis. A full factorial four factor level with BBD was used which allows several numbers of experiments giving suitable data to be tested for the model to be significant (Leong et al., 2017). Prior to start of the statistical analysis, a few set of experiments were performed to select the effective factors of RSM which are required to optimize the cell parameters to achieve highest power density from the laboratory fabricated T-shaped MFC. As already mentioned, that the factor or important parameters considered in the single MFC study were glycerol concentration, anode electrolyte/KOH concentration, anode electrocatalyst loading and cathode electrolyte/KOH concentration. The various cell parameters or factors were designated by various symbols like glycerol concentration as A, anode electrolyte/KOH concentration as B, anode electrocatalyst loading as C and cathode electrolyte/KOH concentration as D. The response of the cell i.e., power density (mW/cm^2) was designated as Y. The effect of various effective factors or parameters of MFC on polarization and power density curves are shown in the Appendix B. The effect of glycerol concentration (A) on cell performance for anode electrolyte concentration (B) of 0.5 M KOH, anode electrocatalyst loading (C) 0.5 mg/cm^2 and cathode electrolyte concentration (D) at 0.5 M KOH is shown in Appendix B(Figure B1**)**. The optimum concentration of glycerol was found to be 1 M at which power density obtained was highest i.e., 1 mW/cm^2 (Figure B1). The effect of anode electrolyte concentration (B) on MFC performance is shown in Figure B2 for the optimum glycerol concentration of 1 M, anode KOH of 0.5 M, anode loading of 0.5 mg/cm^2 and cathode electrolyte concentration of 0.5 M KOH. The optimum concentration of 1.5 M KOH was recorded at anode side resulting in highest power density of 1.7 mW/cm^2 (Figure B2). Similarly, the effect of anode electrocatalyst loading is shown in Figure B3 for optimum glycerol concentration of 1 M, optimum anode KOH of 1.5 M and cathode KOH of 0.5 M, respectively. The optimum anode loading of 1 mg/cm^2 was obtained for the highest power density of 2.65 mW/cm^2 from the MFC (Figure B3). Figure B4 shows the effect of cathode electrolyte concentration for optimum glycerol concentration of 1 M, optimum anode electrolyte concentration of 1.5 M KOH and optimum anode electrocatalyst loading of 1 mg/cm^2. The optimum KOH concentration at cathode was found to be 0.5 M at the power density of 2.65 mW/cm^2 (Figure B4). The low level and high level of the factors were selected from the above mentioned preliminary experimental studies on T-shaped MFC. The experiments were performed by taking one variable at a time and keeping others variables constant as shown in the Figure B1 to Figure B4. The four variables like glycerol concentration (A), anode electrolyte/KOH concentration (B), anode electrocatalyst loading (C) and cathode electrolyte/KOH concentration (D) were included in the predicted model as depicted in Table 4.1.

Table 4.1 Full factorial four factor level for RSM study.

Factors	Low level (-1)	Middle level (0)	High level (+1)
A-glycerol concentration (M)	0.5	1.0	1.5
B-anode electrolyte concentration (M)	1	1.5	2
C-anode electrocatalyst loading (mg/cm^2)	0.5	1.0	1.5
D-cathode electrolyte concentration (M)	0.25	0.5	0.75

In BBD, the required numbers of experiments are calculated according to the Equation (4.1) (Bazerra et al., 2008).

$$N=2\,k(k-1)+cp \tag{4.1}$$

Where, k is the number of factors used in the experiments and cp is the number of the central points. The cp for four variables and three levels is 5 and other 24 are out of the central points. All 29 experiments were performed to obtain the experimental response in terms of power density. A quadratic model was selected (Myers et al., 2016) as it was found to be one of the best fitted models with a significant response ($P < 0.05$). The ANOVA analysis was performed to measure the significance of the model and independent variables. The experimental data were fitted to a second order polynomial regression model, as shown in Equation (4.2).

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i \times x_i + \sum_{i=1}^{k} \beta_{ii} \times x_i^2 + \sum_{i \text{ and } j=1, i \neq j}^{k} \beta_{ij} \times x_i \times x_j \quad (4.2)$$

Where Y is the response, x_i and x_j are the i^{th} and j^{th} independent factors. β_0, β_i, β_{ii}, and β_{ij} are the coefficients of the linear parameters, the quadratic parameters and the interaction parameters, respectively. The quality of the fit was statistically appraised by the correlation coefficient (R^2) (Caglar et al., 2018). The results obtained from the RSM analysis are discussed in the next chapter 5 (page no. 155).