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Electrolyte and temperature optimization of electrochemical cells using design of expriments(DOE)

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ABSTRACT

In this paper, initially, experiments were designed and performed by using experimental design methods and response surface methodology. Then, a model was obtained for the relationship between variables and objective function using software. The linear and nonlinear effects, especially the interaction effects of variables on the objective function, were investigated according to this model and the effects were plotted. In the experiments, the voltage produced by the electrochemical cell was considered as the objective function; and the type of cathode, the kind of acid that used az the electrolyte of the cell, and the temperature of the system were the variables. Finally, an optimum electrochemical cell was introduced by considering the effect of each factor and their optimal amount. According to the performed analysis and the effect of each factor, the behaviour of similar systems with the same parameter changes in a predictable manner.

Keywords: Electrochemical cell, Respone Surface Methodology,Voltage.

INTRODUCTION

In an electrochemical cell, the oxidation and the reduction process are separated in two half-cells which are connected by an external wire. The half-cell with the oxidation process loses electrons while the half-cell with the reduction process gains electrons. Both half-cells are connected by a salt bridge for the transfer of ions between the two solutions. Thus, the electrical circuit between half cells is completed by a salt bridge and wire. The negatively charged electrons cannot pass into the solution, and the anions cannot pass into the metal [1]. An ion-exchanger membrane can be used in electrochemical cells as the salt bridge.

Electrochemical cells are used as primary and secondary batteries, and much larger rechargeable batteries have been constructed for aerospace and submarine applications [2]. Several studies have been performed on the type of electrodes and other changeable parameters [3-5]. In these researches iron, nickel and lead were used as the cathode and the effect of other parameters have been investigated. Thermodynamics is used to describe the electrochemical equilibrium within the electrolyte and at the phase boundary between the electrolyte and the electrode. Whereas, kinetics is used to outline the condition in which equilibrium is lost by permitting the flow of the electrical current through the cell. The kinetics of an electrochemical cell has been investigated and the operating potential of an anode is always more positive than its equilibrium potential, while the operating potential of a cathode is always more negative than its equilibrium potential [6]. In another study, the relationships between the geometrical properties of electrodes have been shown and Three-dimensional electrodes have been used to counteract the limitation of the low space-time yield in electro chemical processes with two dimensional electrodes [7].

The transfer of electrons through the external wire creates a current which can do work. The driving force pushing the electrons through the wire is the difference in the attraction of electrons in the two half-cells. This voltage difference is called the Cell Potential (Ecell) and is measured in volts. Here, the cell potential is considered as the objective function and in this paper, the effects of different parameters on the produced voltage has been investigated. produced voltage increases by enhancing the temperature and developing proton exchange membrane in fuel cells [2].

Different factors can affect the results of an experiment, including, the test environment, the accuracy of measurement and the changes in input variables. Experiments are based on changes in input variables in order to observe and identify output response. The first step in designing experiments is determining the primary factors which are selected from controllable variables of the system. The attributable range of these parameters must be checked in order to use these values in experiments. Changes in test parameters affect one or more output variables and are measurable. Objective functions are the output variables which are gauge-dependent variable parameters of experiments.

MATERIALS AND METHODS

In a previous study, the effects of concentration change of the electrolyte, the temperature of the cell and the surface area of each electrod were investigated [8]. In this paper, the Response Surface Methodology [RSM] for the voltage produced by the electrochemical cell is used to determine the optimal conditions. RSM is a Central Composite Design method. This method is used to determine a static model of processes, to evaluate the interaction between the effective factors and to identify the factor having the greatest effect on the objective function. In some researches, Response Surface Methodology was used to design experiments and evaluate results [9]. In this research, the variables include: the temperature of the system, the type of cathode electrode and the kind of acidthat used as the electrolyte. The type of anode is one of the system parameters which could be modified. During the experiments, graphite was used as the anode electrode. Another parameter which was fixed during the experiments is the type and the concentration of the electrolyte. Hydrochloric acid with a constant volumetric concentration of 0.05 was used as the electrolyte. Other relevant parameters to the test environment were kept constant during the experiments. The design of the experiments was achieved by Minitab software. Twenty tests were designed according to the software to evaluate the effect of the variable parameters. The detail of each test is shown in Table1.

Table 1: Original plan of the designed expriments

Experiment **No.**	**Coded Parameters**			**Uncoded Parameters**		
	x_1	**x_2**	**x_3**	**Electrode**	**Acid**	**[Temperature[C**
1	1	-1	-1	Al	HCl	25
2	-1	1	-1	Cu	H2SO4	25
3	-1	1	1	Cu	H2SO4	45
4	1	-1	-1	Al	HCl	25
5	1	-1	1	Al	HCl	45
6	1	1	-1	Al	H2SO4	25
7	1	1	1	Al	H2SO4	45
8	0	0	-1	Zn	HNO3	25
9	0	0	1	Zn	HNO3	45
10	0	-1	0	Zn	HCl	35
11	0	1	0	Zn	H2SO4	35
12	-1	0	0	Cu	HNO3	35
13	1	0	0	Al	HNO3	35
14	0	0	0	Zn	HNO3	35
15	0	0	0	Zn	HNO3	35
16	0	0	0	Zn	HNO3	35
17	0	0	0	Zn	HNO3	35
18	0	0	0	Zn	HNO3	35
19	0	0	0	Zn	HNO3	35
20	-1	1	-1	Cu	H2SO4	25

In these experiments,
X_1 is variable encoded by type of cathode electrode
X_2 is variable encoded by kind of electrolyt (type of acid).
X_3 is variable encoded by temperature of system
Changing of parameters by changing X_1, X_2, X_3 is shown in Tables 2 - 4, respectively.

Table 2. Corresponding parameter related to different values of X_1

X_1	-1	0	1
Cathode	Cu	Zn	Al

Table 3. Corresponding parameter related to different values of X_2

X_2	-1	0	1
Kind of acid in electrolyte	HCl	HNO3	H2SO4

Table 4. Corresponding parameter related to different values of X_3

X_3	-1	0	1
Temperature of system	25˚C	35˚C	45˚C

According to Table 1, experiments were designed and conducted and the objective function values [produced voltage] in each experiment were recorded. Data were analysed by software and the objective function presented as a quadratic function of the encoded variables.

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_1b_2X_1X_2+b_1b_3X_1X_3+b_2b_3X_2X_3+b_1b_1X_1^2+b_2b_2X_2^2+b_3b_3X_3^2$$

In this equation, b_0 is a constant and b_1, b_2 and b_3 are linear coefficients and b_1b_1, b_2b_2 and b_3b_3 are power coefficients. With regards to the experiments, the software found the following values for the coefficients, as shown in Table 5.

Table 5. Regression Coefficients for Objective Function

Term	Coef	SE Coef	T	P
Constant	1.2944	0.03276	39.514	0.000
X_1	0.2995	0.04797	6.243	0.000
X_2	-0.0911	0.04797	-1.898	0.087
X_3	0.0052	0.03437	0.150	0.884.
X_1*X_1	-0.4610	0.05877	-7.843	0.000
X_2*X_2	-0.4110	0.05877	-6.993	0.000
X_3*X_3	0.2460	0.05877	4.186	0.002
X_1*X_2	-0.0141	0.05729	-0.247	0.810
X_1*X_3	-0.0532	0.04218	-1.260	0.236
X_2*X_3	-0.2140	0.04218	-5.074	0.000
S = 0.09313 R-Sq = 97.2% R-Sq[adj] = 94.6%				

According to Table5, the objective function is shown in the following equation:

$$Y = 1.2944+ [0.2995]X_1+ [-0.0911]X_2+ [0.0052]X_3+ [-0.0141]X_1X_2+ [-0.0532]X_1X_3+ [-0.2140]X_2X_3+ [-0.4610]X_1^2+ [-0.0141]X_2^2+ [0.2460]X_3^2$$

The relationship between the encoded variables of the system and the objective function is shown by this equation. This equation is able to predict the behaviour of the system against changes. Obviously, the values obtained from the fitted equation are similar to the experimental values once the equation is fit properly. The equation obtained was verified using RSM. The experimental values and the values obtained of the objective function are shown in Table 6.

Table 6. Experimental Values and Values Obtained by the Equation of Objective Function

Experiment No.	Coded Parameters x_1	x_2	x_3	[EMF[Exprimental
1	1	-1	-1	0.955
2	-1	1	-1	0.438
3	-1	1	1	0.060
4	1	-1	-1	0.955
5	1	-1	1	1.278
6	1	1	-1	1.144
7	1	1	1	0.620
8	0	0	-1	1.440
9	0	0	1	1.564
10	0	-1	0	0.840
11	0	1	0	0.850
12	-1	0	0	0.630
13	1	0	0	0.960
14	0	0	0	1.320
15	0	0	0	1.320
16	0	0	0	1.320
17	0	0	0	1.320
18	0	0	0	1.320
19	0	0	0	1.320
20	-1	1	-1	0.438

Effect of Interference:

The main value of the fitted equation is the expression of interference of the system variables and their impact on the objective function. Evidently, the impact of this effect (effect of interference) is proportional to the coefficient of the equation. Change of any single variable or set of variables could have positive or negative effects on the value of the objective function. A coefficient with a smaller value of equation in objective function indicates a smaller impact on corresponding variables. In other words, a small linear or power coefficient shows a less impact on changes of corresponding variable, similar to interference coefficient – which shows the impact of change of corresponding variables (here two variables). In order to achieve an optimum system, it is important to investigate the problem from a feasible point of view. Investigation of the effects of interference without utilization of experimental design techniques and related graphs is very difficult work. The effect of all the linear, power and interference coefficients on the objective function is shown in Figure 1.

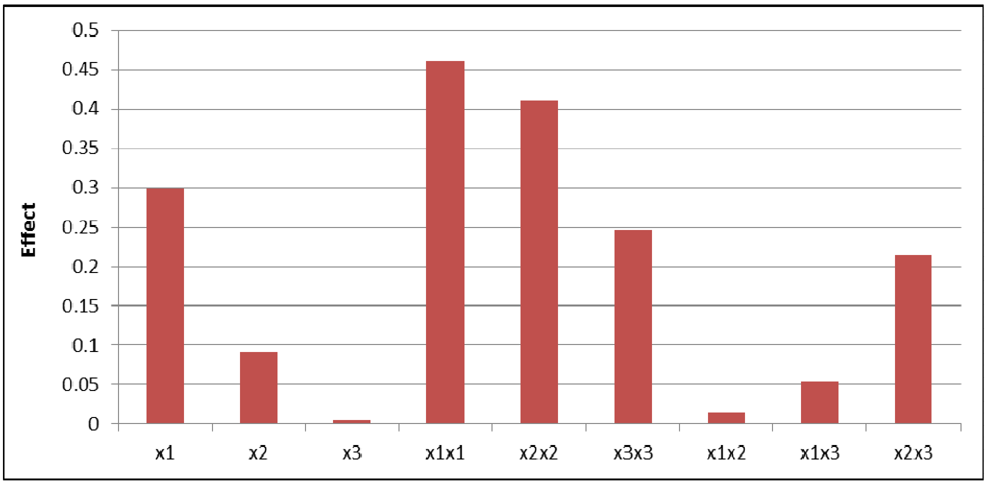

Figure 1. Effect of change of single variables and set of variables on objective function

Apparently, the changes of variable X1 has the highest effect on the objective function, while changes in variable X3 has a near insignificant effect on the produced voltage. The point is that the simultaneous change in these two variables has a considerable impact on the objective function. Other interference effects are visible in Figure 1, too. This figure should be the criterion for electrochemical cell design. Although in performed experiments, three variables could be selected to form the objective function so as to gain highest voltage productivity; it should be kept in mind that environmental factors also affect the value of the objective function. In order to reduce the effect of environmental variables on the objective function, it is better to literally make the coefficient of environmental variables insignificant. In general, in this method, systems should be constructed using items having large impacts, while the effect of other factors should be controlled.

Evaluation and selection of the best mode for each variable in order to produce the highest voltage (maximum value of objective function): After assessing the impact of each variable, the amount of variable where in the maximum value of objective function (voltage) is reached should be determined. Moreover, the investigation of variables showing considerable interference effect on fitted equation is more important. The impact of interference of two variables on the objective function (produced voltage) is shown in figures 2 and 3.

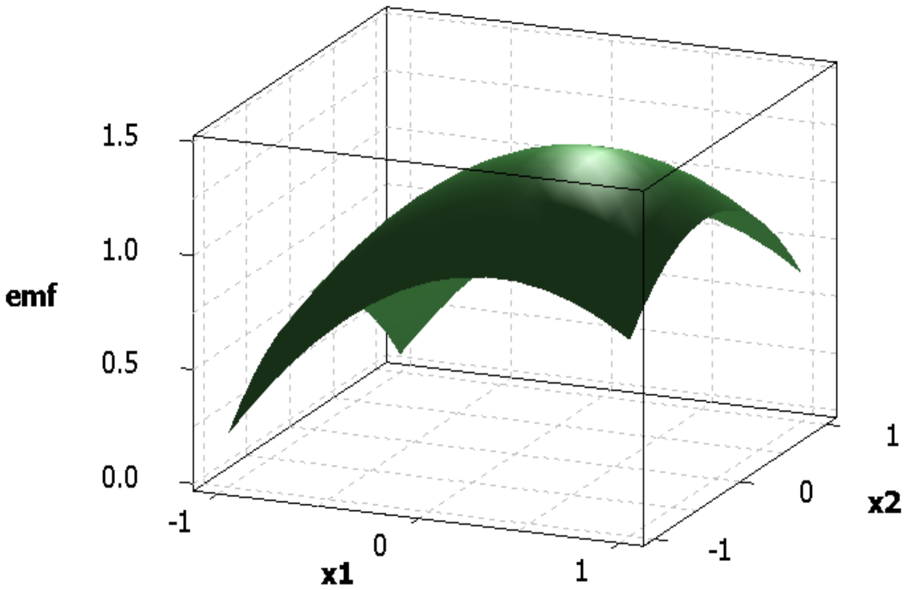

Figure 2. Effect of simultaneous change in X_1[type of cathode] and X_2 [kind of acid] seen in 3-Dimensional graph

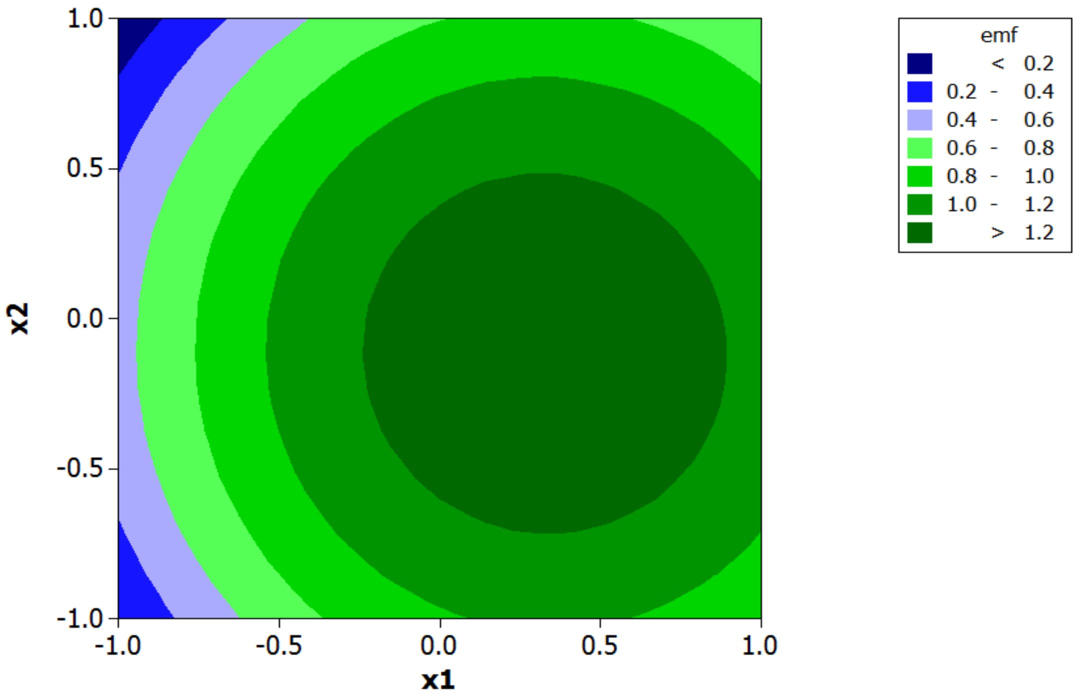

Figure 3. Effect of simultaneous change in X_1 [type of cathode] and X_2 [kind of acid] seen in 2-Dimensional graph

So,the objective function (produced voltage) is a regular function of both variables which are changed simultaneously. in order to produce more voltage, it is better to use Zn (X_1=0) as the cathode material. It is evident that the type of the electrolyte should be HNO_3 (X_2=0) so as to increase the level of produced voltage.

The amount of effect of simultaneous change of X_2 (kind of acid used as electrolyte) and X_3 (temperature of system) are shown in figures 4 and 5.

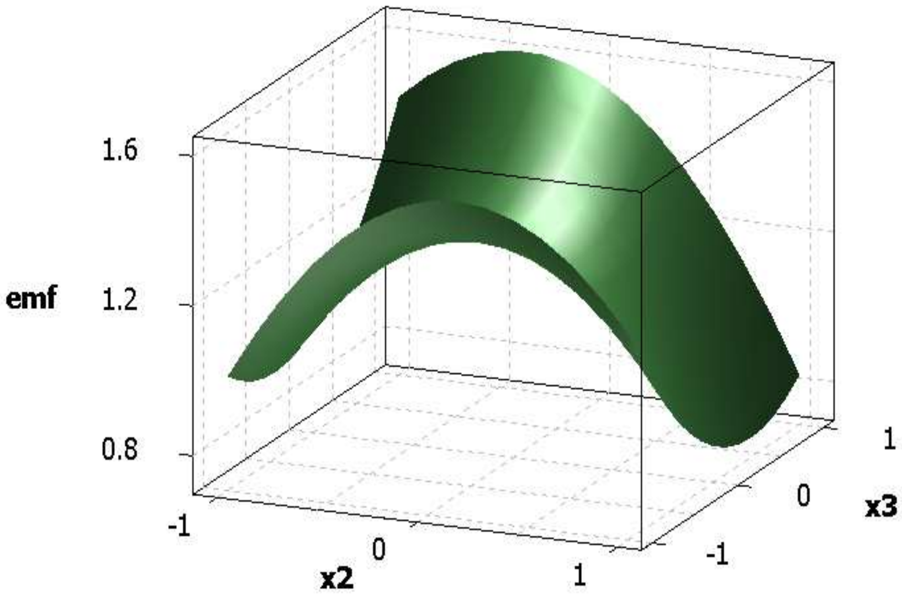

Figure 4. Simultaneous effect of changes in electrolyte type [X_2] and temperature of system [X_3] in 3-D graph

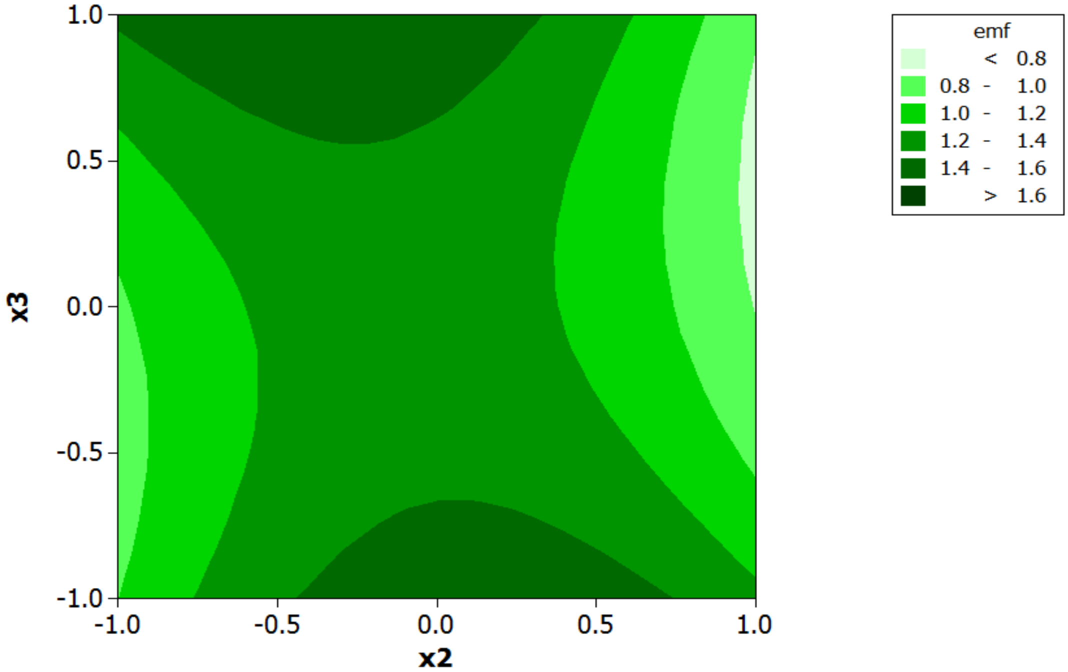

Figure 5. Simultaneous effect of changes in electrolyte type [X_2] and temperature of system [X_3], seen in 2-D graph

Considering the effect of X_2X_3 coefficient on the objective function, as shown in Figure 1, it can be seen that the voltage changes are more than the current changes in the previous mode.

The best mode of coded system obtined from figure 4-5 is shown in below table (Table 7).all af the below modes have the same value.

Table7.modes that have same value[obtined from figure 4-5]

Mode No.	Coded Parameters		Uncoded Parameters	
	acid	temperature	acid	temperature
1	0	1	HNO3	45
2	0	-1	HNO3	25
3	-1	1	HCl	45

Figure 6 and 7 show the effect of interference changes by altering the type of cathode and system temperature, simultaneously.

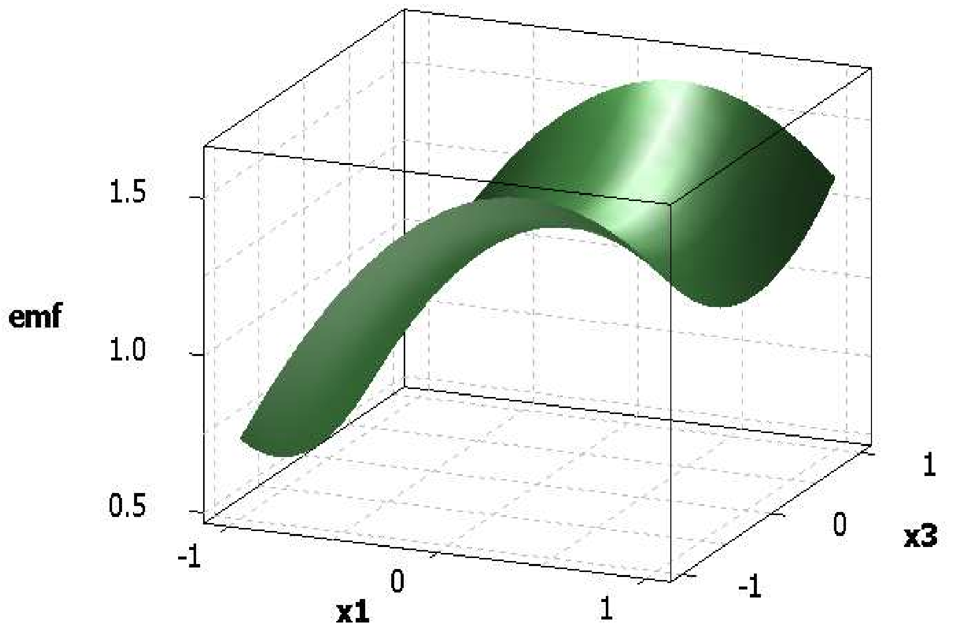

Figure 6. The effect of simultaneous changes of type of electrode [X_1] and system temperature [X_3] on the objective function – 3-Dimensional graph

Considering the effect of X_1X_3 coefficient on the objective function, as shown in Figure 1, it can be seen that the voltage changes are lower than the current changes in the previous mode.

The best mode of coded system obtined from figure 6-7 is shown in below table (Table 8).all af the below modes have the same value.

Table8. modes that have same value[obtined from figure 6-7]

Mode No.	Coded Parameters		Uncoded Parameters	
	Cathode	Temperature	Cathode	Temperature
1	0	-1	Zn	25
2	0	1	Zn	45
3	1	-1	Al	25

Table 9. The optimum condition of electrochemical cell

Parameters			**EMF(volt)**
Cathode	**Kind of acid used as electrolyte**	**Temperature**	
Zn	HNO3	45	1.564

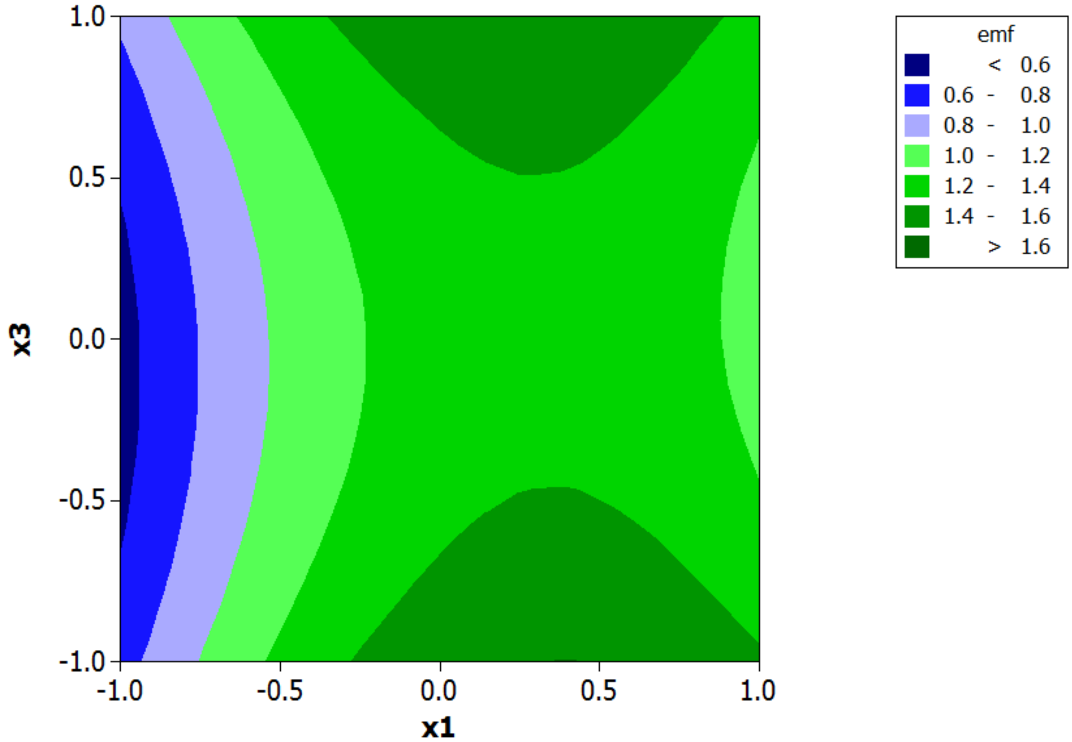

Figure 7. The effect of simultaneous changes of type of electrode [X_1] and system temperature [X_3] on the objective function – 2-Dimensional graph

CONCLUSION

The analysis of this research shows that the type of positive electrode (cathode) plays a major role in gaining an optimum amount of produced voltage. The effect of the type of positive electrode (cathode) is so high that in comparison with other paremeters in this research. If the type of electrode is not considered, the system temperature and the kind of acid in electrolyte solution have clear interference effect. In conclusion, the best design of an electrochemical cell is presented in Table 9.

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