Application of Response Surface Optimization Technique to the Preparation of Cathode Electrode for the Molten Carbonate Fuel Cell

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Summary: One of the fuel cells, the molten carbonate fuel cell (MCFC), comes into prominence due to its high energy potential and suitability for industrial applications. Nickel porous structures are used as anodes and cathodes for MCFC. In this study; Green sheets were obtained by means of tape casting method performing on the prepared mixtures. 23% - 37% by weight nickel oxide was used in the mixture for the purpose of synthesizing cathode green sheets. Different slurry were prepared using different ratios of polyethylene glycol (PEG) as plasticizer, polyvinyl butyral (PVB) as binder, glycerol as dispersant and butanol with hexanol as a solvent. The optimum mixture formulation for the tape casting has been determined by measuring, tensile strength on the green tape. Tensile elongation of green tape refers to resistance to dissolution, cracking and breakage for the green tape slurry. Tensile force parameters were evaluated for the green tape's slurries. Maximum tensile force and thickness of the green tape is critical factor in order to choose the optimum mixture formulation of cathode slurries. Optimum composition was determined as 23% nickel oxide, 3% binder and 3% plasticizer according to analyze two level experimental factorial design and response surface optimization technique.

Key words: Two level experimental factorial design; Molten carbonate fuel cell; Cathode; Tensile strength; Response surface

Introduction

Fossil fuels, which are one of the world's most important energy sources, are running out, meanwhile our need of energy is increasing each year. Hydrogen energy is expected to be the new energy source of our age because of its clean and high energy potential. The most important application fields of hydrogen energy are fuel cells. One of the fuel cells, the molten carbonate fuel cell (MCFC), comes into prominence due to its high energy potential and suitability for industrial applications. MCFC are called according to its electrolyte composed of a molten carbonate salt suspended in a porous ceramic matrix. MCFC has high energy conversion efficiency and operates between 600-700 ^{o}C. Usually, it comes at the beginning of the systems used in the local and regional level to high energy needs [1].

Tape casting technique is widely used in the production of plate and coating processes such as thin ceramic coating, polymeric coating, porous coating and the metal or alloy coating. In recent years, the production fuel cell electrode and electrolyte materials by tape casting technique are being used intensively [2-4]. Especially, this technique is used in the preparation of membrane, electrodes and electrolyte matrix of the polymeric membrane fuel cell (PEMFC), molten carbonate and solid oxide (SOFC) fuel cell.

Pore size distribution has a large influence on performance of the MCFC-cathode. Not only some additives like LiCoO but also the conventional lithiated NiO, efforts have recently been made to improve the pore structure. The general approach is to increase the amount of solid–liquid–gas interface where the reactions take place by decreasing the primary particle size [5].

The solubility of a NiO cathode in MCFC electrolyte is one of the major technical obstacles to the commercialization of such a fuel cell. For this; there is same work in the literature such as: ZnO/NiO materials could be alternative cathode materials for molten carbonate fuel cells [6]. LiFeO2 has been selected as a candidate cathode material for MCFC because its solubility is very small and the rate of dissolution into the melt is slower than that for NiO. However, the electrical conductivity of pure LiFeO2 is lower than that of NiO. [7].

The method of casting slurry, which is the first stage of preparation, has a direct impact on the final product. Therefore, cast slurries with different ratios of solvent, binder, dispersant, and plasticizer loading of the organic compounds were prepared to

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produce green sheets with the technique of tape casting in order to investigate the optimum tensile strength. Tensile strength is a good indicator for homogeneity of green sheet [3], which will also affect the sintering behavior Tensile strength of the green sheet is a conventional test because high temperature resistance was observed simply. MCFC operates about 750 ^{o}C. Cathode should be resistant to high temperatures such as breaking, cracking.

Additionnaly, a good tensile stress is important for handling the tapes during production. Indeed, high strain to failure in the tape is necessary for successful removal of tapes from the carrier substrate and subsequent handling. In this study, NiO cathode green sheet was manufactured for MCFC system. Mixing method (balling mill and mechanical stirrer) and mixing duration of slurry, mixing weight ratio of binder, solvent, plasticizer, dispersant, NiO powder in the slurry was examined. Buthanol and hexanol was used as a solvent in the mixture when mixing period and method was changed. Slurry had been mixed in the ball-milling before it was mixed with mechanical stirrer. To determine the optimal preparation conditions, we used a model. The experimental data used in the preparation of this model were obtained according to the use of a two-level, factorial experimental design that has been used over a wide range of industrial process [8]. According to these techniques, it was found to be about 25 % of the optimal ratio of nickel oxide. High Mechanical properties are important criteria to select this ratio. Hence, the author reports preparation of technique of the cathode materials and applications of response surface optimization technique and analyze factorial design.

Experimental

Sample Preparation

NiO cathode electrolyte green tapes were manufactured with different ratios of a solvent, a binder, a dispersant, plasticizer. Organic compounds were prepared to produce green sheets with the technique of tape casting. After sheets were dried, physical properties (mechanical tests) were determined. Mixing method (balling mill and mechanical stirrer) and mixing duration of slurry, mixing weight ratio of binder, solvent, and plasticizer, dispersant in the slurry were examined. Initially, nickel oxide, and ethanol were mixed by ball milling and then glycerol, polyvinyl butyral and polyethylene glycol were added to the mixture and milled duration. Further. Milling period was 48 hours. Green sheets were prepared by using tape casting method. Dr.Blade was used to prepare sheet cast. 23-37 % by weight of nickel oxide powder was used in the cathode slurry. It has been chosen arbitrarily. Green sheets were prepared and analyzed in order to examine the behavior and resistance in the case of performing stress. For this purpose, the cathode green sheet specimens arranged at both ends of the device with the rate of 50 mm/min, drawn at a constant draw speed and it was until the withdrawal was broken. Meanwhile, the drawing device on the sheet by breaking strength and breaking elongation are given in Table-1.

Two Level Factorial Experimental Design and Response Surface Optimization Techniques

Two level factorial experimental design is a methodology for systematic application of statistics to experimentation and quite economical techniques. Thanks to this technique, considerably less experiments and less time are needed compared to the classical/traditional method in which all the parameters are kept constant, changing only one parameters. Two level factorial experimental designs are used both in laboratory research and optimization of manufacturing process [8]. This experimental modeling technique allows the determination of the regression equations, for this input variables (factor) such as weight of ethanol, are changed according to predetermined levels. In the two level, factorial experimental design there are K variables (factors). These factors are controlled at two different levels, namely minimum and maximum levels. For linear model, the number of required experiments can be shown as $N=S^{K}$ where S and K represent the level of one factor and number of factors respectively. Using this equation that predicts low changes in input variables interact to produce changes in output variables or responses in the process as a surface. With this method, the optimization is guided by regression equations of first Eq. (1) or second order model Eq. (2). If knowledge concerning the shape of the true response surface is insufficient or the first order model suffers from lack of fit arising from the existence of surface curvature, the second order model is used.

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_0 X_i + \varepsilon \tag{1}$$

$$Y = \beta_0 + \sum_{i=1}^{K} \beta_0 X_i + \sum_{i=1}^{K} \beta_{ii} X_i^{2} + \sum_{i=1}^{K-1} \sum_{j=1}^{K} \beta_{ij} X_i X_J + \varepsilon \tag{2}$$

where X_1, X_2 , X_K are the coded input variable which influence the response Y (tensile strength). $B_{0,}$ B_i

(i=1,2…K,), B_{ij} (i=1,2..K; j=1,2…K) are unknown parameters and ε is a random error. In these types of design, one works in a dimensionless coordinate system using following definitions. The maximum level is +1, minimum level is -1, and the central point is zero. In this work, to obtain the available tensile strength**,** Optimal values of input variables were evaluated by using two level factorial experimental design and response surface. The levels of these parameters were given in Table-1. For this reasons, 2^2 =4 experiments were done to identify the regression equations. Three replicate experiments were done to fit the model. But average values of replicate Y was given in Table-1. In this work first order model, including second interaction terms was considered as shown below.

$$Y= B_0 X_0+B_1X_1 +B_2X_2 + B_3 X_1X_2 \qquad (3)$$

Table-1: Optimal design matrix with coded values (3 replicate experiments)

% NiO uncoded	X_1 %NiO which is coded	% PVB + PEG uncoded	X_2 %PVB + PEG coded	Y tensile strength (N/m2) (N/mm2)
35	- 1	6	-1	0.65327
35	1	6	-1	0.18125
25	-1	14	1	3.60398
35	1	14	1	8.04834
25	-1	6	-1	1.19217
35	1	6	-1	0.37422
25	-1	14	1	5.12277
35	1	14	1	7.76967
25	-1	6	-1	0.56442
35	1	6	-1	0.47031
25	-1	14	1	3.66815
35	1	14	1	7.03709
30	0	10	0	2.58836
30	0	10	0	1.47675

In this table, the relationship between coded (X) and real values (U) are shown below;

$$X_i = \frac{U_i - U_{iav}}{\Delta U_i} \quad i = 1,2, n \qquad (4)$$

$$U_{iav} = \frac{U_i^{max.} + U_i^{min.}}{2} \quad i = 1,2, n \qquad (5)$$

$$\Delta U_i = \frac{U_i^{max.} - U_i^{min.}}{2} \quad i = 1,2, n \qquad (6)$$

In this work, the model coefficients by using experimental data were calculated using MATLAB programs according to the analysis of variance.

Tensile Strength Measurement

Tensile Strength Measurements were made according to the EN (Europeane Norm) ISO (International Organization for standardization) 527-1:2012. Both ends of the sample is clamped between the jaws that were pulled and stretched at a particular rate. Some parameters of the sample are important fort the pulling test such as width of the narrowest part, length of the narrowest part, total width, total length, and the distance between the grippers, outer radius and thickness. Maximum tensile strength fort the specimen was found. The amount of load per unit area were measured on the sample at any time

Results and Discussions

Determination of Parameters for the Optimization Technique (fitting)

By applying the design matrix given in Table-1, the productivity values were used to evaluate the values of the constants in a linear regression model as illustrated previously. The identified model according to Table-1 is given by Eq. (7). Where X_1 and X_2 coded values of % Nickel oxide and % PVB + PEG respectively

$$\mathbf{Y= 3.224+0.756* X_1+2.651* X_2 +0.987* X_1*X_2} \quad (7)$$

R-Sq = 97, 31%

Respective influence of NiO and PVB

Pareto chart of standardized effects was shown in Fig. 1. Note that all the effects have significance greater than 95%. All the factors and interactions are statistically significant.

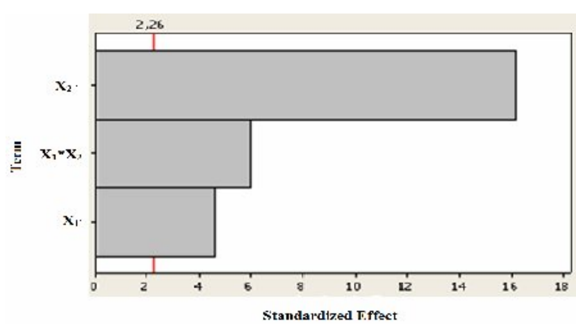

Fig. 1: Pareto chart of standardized effects of coded X_1 , X_2 and X_1*X_2 for the tensile strength.

As can be seen from the Fig. 1, X_1, X_2 and X_1*X_2 acts at a higher rate (2.26) on the tensile strength of the green sheet according to the threshold value set by the program. Main effect graph was plotted (Fig. 1) in order to understand which of the parameters ("X_1" and "X_2") has a profound effect on the tensile strength. This result shows that the amount of PVB + PEG showed coded as X_2 in the slurry has more effect than the amount of nickel oxide showed coded as X_1 on the tensile strength. The magnitude of the vertical displacement indicates the strength of the main effect for that factor. Here we see that X_2 has dramatically more effect than other factor. This plot also shows you the direction of the main effects.

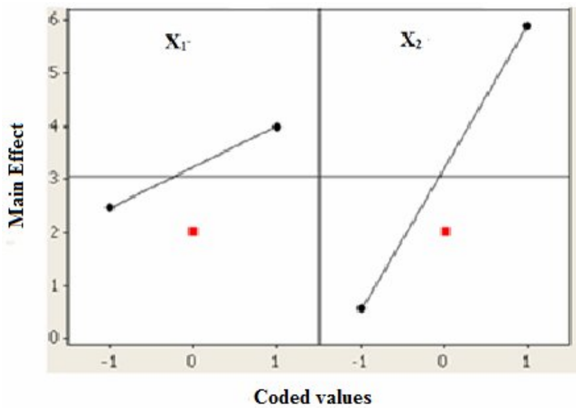

Fig. 2: Main effect graph for the tensile strength.

In addition, interaction graph was plotted in order to understand the interaction between the X_1 and X_2 parameters which are given by Fig. 2

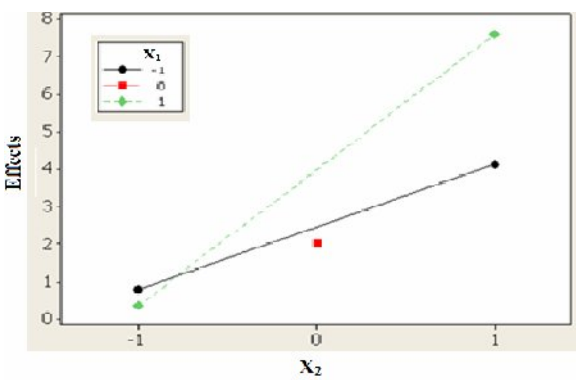

Fig. 3: Interaction graph of parameters.

Verifies the parameters, as shown in Fig. 3 are not parallel and intersect at a point. This indicates that the amount of nickel oxide and PVP + PEG not act independently on the material. We know from our earlier analysis that these interactions were statistically significant for this experiment.

Resulting Optimized Composition

Surface forms of the tensile strength are shown in Fig. 4 by using this model. X_1 and X_2 ratio which maximizes the tensile strength in this way been achieved according to the highest level for each term.

Global Solution: X_1= 1, X_2 = 1; Predicted Responses: Y = 7.61837

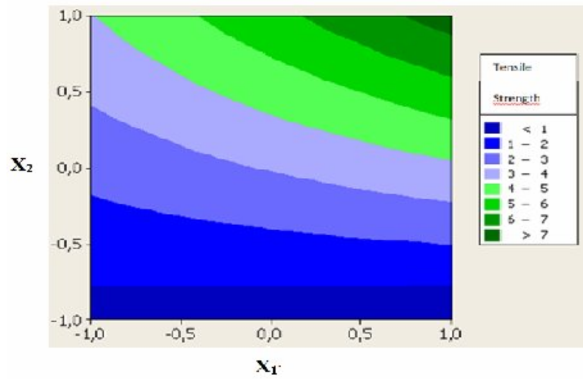

Fig. 4: Contour Graph X_1 (coded values of amount of nickel oxide) and X_2 (coded values of amount of PVP + PEG).

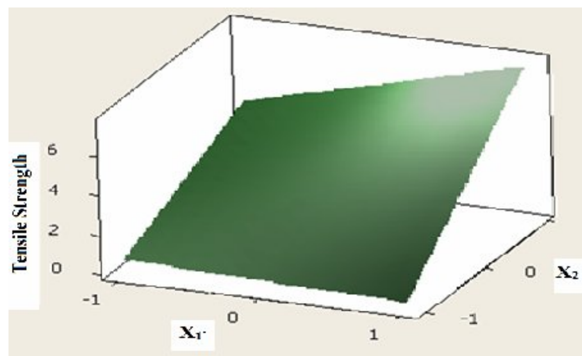

Fig. 5: Surface plot using Eq . (7).

Consequently, contour graph and surface plots (Fig. 5 and 6) were drawn in order to determine optimal values of X_1 and X_2 to give maximum tensile strength value. Based on the results obtained in Fig. 3 and 4, the optimum tensile strength is calculated as 7.61837. Optimum tensile strength of the X_1 and X_2 parameters are proved to be derived from the encoded first value. As a result, 35% of nickel oxide and 14% of PVB + PEG ratio should be accepted as an optimum ratio.

Conclusion

In the tensile test strips applied to the cathode number 2 and 5 mixture (Table-1) showed the worst performance. This is because in the mixture of nickel oxide powder ratio is too high, is correspondingly less than the plasticizer and binder. In this case, despite the high ratio of nickel, nickel is not sufficient to bind chemicals. Number 3, 4 and 7 no green sheets which has high binder and plasticizer content showed better performance to other green sheets in the tensile test. No.4 green sheet showed the highest tensile strength of the green sheets. Therefore, it has an average nickel ratio and high plasticizer with high binder ratio. Nickel powder is an inorganic material and it leads to increase Z rate.

Z= 100* (inorganic material in the mixture)/ (inorganic +organic material)

This will cause the rupture and with a smaller force to be crisp, reducing the elasticity of the green sheet. For this reason, a high ratio of nickel containing only a small amount of plasticizer and binder of No. 2 green sheet which cause to a very low elongation resistance, was broken in a much shorter time than other green sheets. The green sheet showed the highest elongation at Number 3. The very low rate of nickel oxide in said strip, it is rather high rate of response plasticizer and binding, elastic green sheet makes it possible.

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