

USE OF FACTORIAL DESIGN FOR OPTIMIZATION OF THE POROUS STRUCTURE OF SINTERED NICKEL ELECTRODES*

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Investigations in the course of development work on electrodes for chemical sources of current sometimes involve solution of extremal problems, consisting of searches for the optimal parameters of a particular technological process. If the mechanism is relatively simple, optimization of the process may be based on a comprehensive study and derivation of the theory of the process. However, this approach is rarely used for solution of multifactor technical problems. The reasons are, first, that optimization of technological processes often does not require elucidation of the precise physical (theoretical quantitative) picture of the accompanying phenomena and, second, that systems requiring optimization are complex and involve numerous factors, which makes formulation of quantitative theories extremely difficult. Therefore extremal technological problems are usually solved experimentally, with incomplete knowledge of the mechanisms of the processes occurring in the given system.

In this paper we report an investigation of the influence of technological factors in production of gas-diffusion electrodes on the parameters of their porous structure, and of optimization of their electrochemical characteristics.

Mathematical methods of experimental design [1] were used for studying the dependence of the electrode parameters on technological factors, over wide ranges of variation of the latter.

The requirements with regard to the rheological properties of porous sintered-metal materials are determined to a considerable extent by their end uses. In some cases sintered products made from the same material but having porous structures of entirely different properties are required for technical purposes. For example, the gas-diffusion electrode for Bacon's hydrogen-oxygen cell [2] consists of two layers, differing in porosity and pore-size distribution. It was shown earlier [3] that when sintered nickel materials are used as barrier layers in gas-diffusion electrodes the average pore radius, apart from the total porosity, has a significant influence on electrochemical activity.

Specimens 12 cm² in area and 0.5 mm thick were used in studies of the influence of technological factors on the parameters of porous structure of sintered specimens made from carbonyl nickel having bulk density 1.0 ± 0.1 g/cm³ (State All-Union Standard GOST 9722-61, grade PNK-1). The forming pressure, which determines the mechanical strength of the specimens to a considerable extent, was 4 tons/cm² in all experiments. The pressed specimens were sintered in an MP-2U muffle furnace in a hydrogen atmosphere. The parameters of porous structure were studied by methods described in the literature [4].

We studied the influence of the sintering conditions and the percentage content and size of the filler grains on the parameters of porous structure [P, the total porosity (%); K, the absolute coefficient of filtration (cm²); r, the hydraulic-mean pore radius (cm); r_{max}, the maximum pore radius (μ)]. A full 2⁴ factorial design was adopted as the experimental design, making it possible to represent the relations studied in the form of a pure quadratic equation

$$y = b_0 + \sum_{i=1}^4 b_i x_i + \sum_{i < j}^4 b_{ij} x_i x_j, \quad (1)$$

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where b_0 is an estimate of the free term in the regression equation; b_i is an estimate of the coefficient of the linear term; b_{ij} is an estimate of the coefficient of the product $x_i x_j$; β_0, β_{21} are theoretical regression coefficients; x_i is a dimensional variable factor. The free term $b_0 - \beta_0 + \sum \beta_{21}$ in Eq. (1) is the joint estimate of the zeroth coefficient and the coefficients of the quadratic terms of the theoretical regression equation. Therefore for estimation of the contribution of the quadratic terms experiments were carried out in the center of the design, and they were also used for estimating the experimental error.

Table 1 contains the original data for the design matrix, the design in natural variables, experimental results at different points of the design, variances of the reproducibility of the experimental results, and the numbers of degrees of freedom in assessment of these variances.

The resultant regression equations describe with confidence probability 0.95 the dependence of the parameters of the porous structure on technological factors:

$$\begin{aligned} \hat{P} &= 57.20 + 9.46x_1 - 5.41x_3 - 0.96x_4 + 0.91x_1x_3 + 0.41x_1x_4, \\ F_{\text{calc}} &= S_{\text{P}}^2/S_{\text{P}}^2 = 0.462/0.348 = 1.33 < F_{\text{tabl}}(11.4) = 5.94, \end{aligned} \quad (2)$$

$$\lg K = -9.3178 + 0.7631x_1 - 0.0684x_2 - 0.2154x_3 - 0.0680x_4 + 0.0480x_1x_2 + 0.1529x_1x_3 - 0.0519x_2x_3 - 0.0462x_3x_4, \quad (3)$$

$$F_{\text{calc}} = \frac{S_{\lg K}^2}{S_{\lg K}^2} = 0.00854/0.00365 = 2.34 < F_{\text{tabl}}(8.4) = 6.04,$$

$$\lg r = -3.8438 + 0.3471x_1 - 0.0358x_2 - 0.0962x_3 - 0.0309x_4 + 0.0242x_1x_2 + 0.0713x_1x_3 - 0.0273x_2x_3 - 0.0299x_3x_4, \quad (4)$$

$$F_{\text{calc}} = S_{\lg r}^2/S_{\lg r}^2 = 0.00231/0.00119 = 1.94 < F_{\text{tabl}}(8.4) = 6.04,$$

$$r_{\text{max}} = 4.321 + 1.960x_1 + 0.617x_2 + 0.401x_1x_2, \quad (5)$$

$$F_{\text{calc}} = \frac{S_{r_{\text{max}}}^2}{S_{r_{\text{max}}}^2} = \frac{0.0089}{0.0390} = 0.23 < 1,$$

where F is the Fisher criterion; $S_{\{y\}}^2$ is the variance of reproducibility of the experimental results; S_y^2 is the residual variance.

The regression equations (2)-(5) are written in dimensionless variables, with statistically insignificant regression coefficients disregarded.

It follows from Eq. (2) that the size of the filler grains has no influence on the total porosity (the corresponding factor is absent in the equation), while the maximum pore radius is independent of the sintering conditions and depends only on the grain size and amount of filler. The values of the coefficients b_{13} in Eqs. (2)-(4) are evidence of strong interaction between the amount of filler and the sintering temperature. Strong interaction is also found between the amount and particle size of the filler, the particle size of the filler and the sintering temperature, the amount of filler and the sintering time, and the sintering temperature and time [see the corresponding coefficients in Eqs. (2)-(5)]. The fact that increase of the grain size of the filler increases the maximum pore radius and decreases the average pore radius of the sintered produce is nontrivial. The decrease of the total porosity and of the filtration coefficient with increase of temperature and sintering time is obvious.

Equations (2)-(5) can be used for finding the values of technological factors giving a predetermined pore structure in the sintered metal. These values must satisfy the system of equations

$$Y_k = \text{const} = f(x_i) \quad k, i = 1, 2, \dots, 4, \quad (6)$$

where Y_k is the optimization parameter.

As was shown earlier [3], not only the porosity of the barrier layer but also the average pore radius should be increased in order to improve the electrical characteristics of gas-diffusion electrodes. However, the maximum value of the average pore radius is limited by the pressure drop between the gas and the electrolyte. Accordingly, it is of interest to find the region of values of factors x_i where the porous nickel plate would have maximum pore radius 2-2.5 μ , average pore radius about 1 μ , and total porosity 50-55%; i.e., would satisfy the requirements for barrier layers of fuel-cell electrodes.

TABLE 1. Design of Experiments for Study of the Influence of Technological Factors on the Parameters of Porous Structure and Experimental Results

Variable factor, x_i					Base level, x_i		Variation interval, h_i			
x_1 , NH_4HCO_3 content (wt. %)					15		10			
x_2 , size of filter grains (μ)					76		15			
x_3 , sintering temperature ($^{\circ}\text{C}$)					650		20			
x_4 , sintering time (min)					30		20			
(continued)										
Experiment No.	Factor level				Values of parameters					
	x_1	x_2	x_3	x_4	P	$\lg K$	$\lg \bar{r}$	$r_{\max}$		
1	5	61	500	10	54.7	-9.659	-4.005	2.10		
2	25	61	500	10	71.7	-8.375	-3.425	5.34		
3	5	91	500	10	55.6	-9.765	-4.064	2.57		
4	25	91	500	10	72.0	-8.492	-3.485	7.25		
5	5	61	800	10	42.5	-10.080	-4.161	2.23		
5	25	61	800	10	61.8	-8.529	-3.470	5.38		
7	5	91	800	10	43.9	-10.539	-4.403	2.68		
8	25	91	800	10	63.4	-8.535	-3.476	7.42		
9	5	61	500	50	52.9	-9.703	-4.025	2.08		
10	25	61	500	50	50.5	-8.592	-3.532	5.12		
11	5	91	500	50	53.3	-9.729	-4.030	2.50		
12	25	91	500	50	70.5	-8.475	-3.476	7.25		
13	5	61	800	50	39.9	-10.424	-4.325	2.14		
14	25	61	800	50	61.1	-8.609	-3.507	5.18		
15	5	91	800	50	39.5	-10.764	-4.500	2.53		
16	25	91	800	50	62.4	-8.766	-3.589	7.25		
17	15	76	650	30	56.8	-9.366	-3.871	4.44		

$$S_{\{P\}}^2 = 0.348, \quad f = 4; \quad S_{\{\lg K\}}^2 = 0.00365; \quad f = 4;$$

$$S_P^2 = 0.462, \quad f = 11; \quad S_{\lg K}^2 = 0.00854, \quad f = 8;$$

$$S_{\{\lg \bar{r}\}}^2 = 0.00119, \quad f = 4; \quad S_{\{r_{\max}\}}^2 = 0.0390, \quad f = 4;$$

$$S_{\lg \bar{r}}^2 = 0.00231; \quad f = 8; \quad S_{r_{\max}}^2 = 0.0089, \quad f = 13.$$

Note. f is the number of degrees of freedom in assessment of variance.

As increase of the filler grain size increases the maximum pore radius and diminishes the average pore radius, this factor should be fixed at the lower level. The sintering time should be increased in order to raise the strength of the barrier layer; i.e., the value of +1 should be assigned to the factor x_4 . The system of equations (6) then becomes

$$\left. \begin{aligned} \text{const} = P &= 56.26 + 9.87x_1 - 5.41x_3 + 0.91x_1x_3, \\ \text{const} = \lg \bar{r} &= -3.839 + 0.3229x_1 - 0.0968x_3 + 0.0713x_1x_3, \\ \text{const} = r_{\max} &= 3.704 + 1.560x_1. \end{aligned} \right\} \quad (7)$$

Problems of this kind for the case of two factors are usually solved graphically, by plotting traces of surfaces representing equal values of the parameters on the factor plane. Figure 1 shows traces of surfaces of equal porosity and of equal average and maximum pore radii on the x_1x_3 plane ($x_2 = 56-63 \mu$, $x_4 = 50$ min), and the region in which porous plates suitable for use as barrier layers in gas-diffusion electrodes can be made.

These mathematical models of the dependence of porosity parameters on the conditions of production of sintered-metal materials can also be used for predicting the properties of the products both within the region studied and outside it (but not too far from the boundaries $x_i^0 \pm h_i$); this is valuable in development of porous materials.

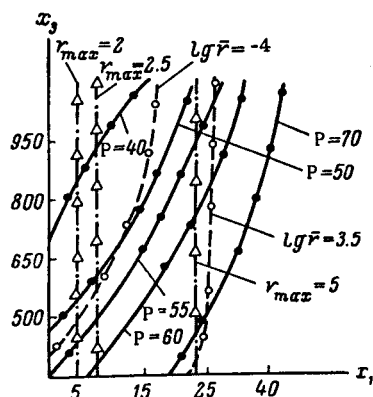


Fig. 1. Traces of surfaces representing equal values of the parameters of porous structure on the x_1x_3 plane ($x_2 = 56-63 \mu$, $x_4 = 50$ min), and the region corresponding to conditions for production of barrier layers.

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