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Optimization of the composition of solid-phase cathodes for lithium systems with nonaqueous electrolyte

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Abstract

By using methods of experimental design the composition of the cathode matrix for systems Li/CuO–FeS_2, Li/CuO and Li/FeS_2 has been optimized. One found a functional dependence between capacity and additions in the cathode mass. Response functions are described with regression first-order and second-order equations.

Introduction

Electrode compositions are normally optimized by successive study of chosen compositions and variants [1–4].

So in ref. 1, the authors called up seven variants of the mixture CuO + FeS_2 in pursuit of better voltage and capacity characteristics in elements FR 1130 and FR 936. In ref. 2, the optimization of carbon electrodes for electroreduction of SO_2Cl_2 consisted of a study of carbon and graphite materials with estimation of specific surface after acetone treatment. In ref. 3, one did experimental optimization of a porous cathode structure and of its packing density in lithium/thionyl cells for small and large discharge densities. These results were assumed as a basis of a computer study for producing high-energy cells in standard dimensions [4].

It appears from the above that the way to obtain high specific energy characteristics of any system depends on labour-consuming stages of optimization of compositions of electrodes, electrolytes, and the arrangement of cells, etc. Use of mathematical optimization methods will make this task lighter and simpler. In this paper the results of optimizing additions to a cathode on the basis of CuO and FeS_2 are given.

Experimental

For preparing the cathode matrix the following initial compounds were used. Iron disulphide and copper oxide delivered by NGMK, acetylene black with specific surface 80–100 m^2/g, fluoroplastic emulsion FP-4d, lithium mark LE-1. The separator is nonwoven polypropylene, nonaqueous electrolyte.

The uniformity of phase composition of FeS_2 and CuO was studied with X-ray phase method on the 'DRON-3' diffractometer with spectrum identification [5].

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Optimization of the cathode mass was carried out for two additions: acetylene black and polymer binder (FP-4d), which were assumed to be independent variable factors. So are x_1 mass% black content, x_2 mass% FP-4d content in the composition of cathode mass. The optimization was carried out in the form of a full factor experiment (FFE) in the first instance with the Box and Wilson method by steep ascension and on the KONO composition plan in the optimal region with independent factor variation on the two levels.

The prepared cathodes were tested on breadboards and elements. Breadboard discharge was done through fixed resistance at room temperature. The discharge capacity as a response function of independent factors x_1 and x_2 is described with a regression first- and second-order equation. The estimation of coefficient significance and equation adequacy was done according to Student t-test and Fisher's ratio test.

Results and discussions

In Fig. 1 is shown an X-ray pattern of the initial active components CuO and FeS_2 used for preparing cathodes on their basis.

From the data of Fig. 1 it follows that initial CuO contains a small amount (1–3%) Cu_2O+FeS_2, and about 6% Fe_3O_4.

The technological operations of preparing the mixture of cathode materials do not change the qualitative and quantitative compositions of phases in the cathode mass.

Using the ratio of active phases $CuO+FeS_2$ found in ref. 1 and accepting it as constant in all the cathode compositions studied, additions x_1 and x_2 were optimized in three cycles.

In the first stage on FFE the plan centre had the following coordinates in physical quantities: $x_1=5$ mass%, $x_2=3.5$ mass% with step ±2.0% and ±1.6%, respectively. After the finish of the first optimization stage the element discharge capacity on resistance through $R=10$ kΩ can be described with a regression first-order equation as follows:

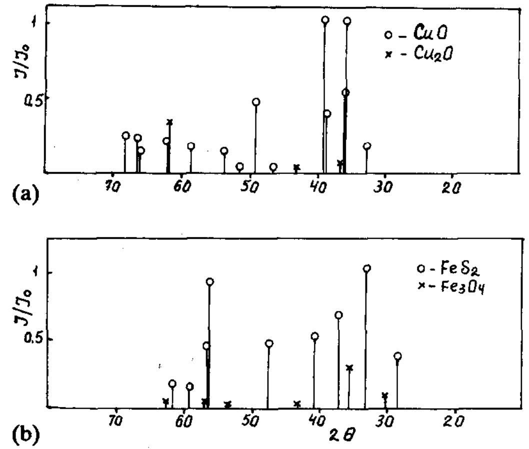

Fig. 1. X-ray patterns of initial samples: (a) CuO, and (b) FeS_2.

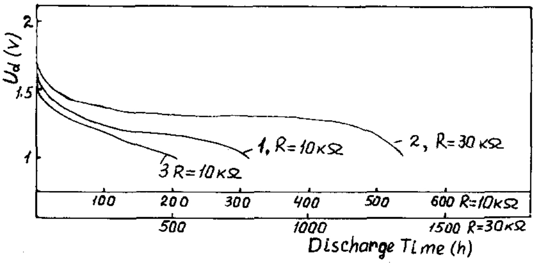

Fig. 2. Discharge curves of cells with cathode on basis of $CuO+FeS_2$: curves (1, 2): cells with optimized cathodes, and curve (3): cells with nonoptimized cathodes.

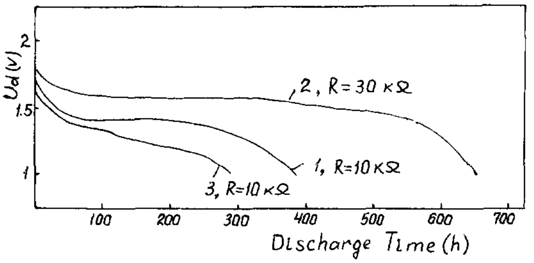

Fig. 3. Discharge curves of cells with cathodes on basis of FeS_2: curves (1, 2): cells with optimized cathodes, and curve (3): cells with nonoptimized cathodes.

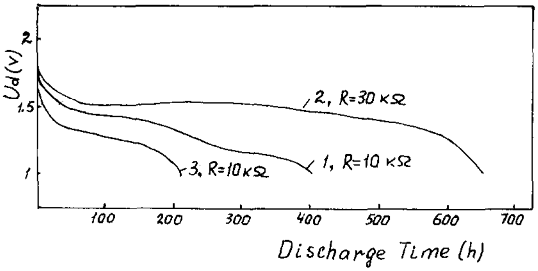

Fig. 4. Discharge curves of cells with cathodes on basis of CuO: curves (1, 2): elements with optimized cathodes, and curve (3): elements with nonoptimized cathodes.

$$y = 29.2 + 11.41\,x_1 - 5.97\,x_2 \qquad (1)$$

where x_1 and x_2 are variable factors in coded form.

According to eqn. (1) the discharge capacity is most sensitive to the changing factor x_1 and increases with its increase.

Supposing that the response function is continuous and choosing factor x_1 as basis one and fixing factor x_2 as constant one, moving on gradient with step $\lambda^* = 1\%$ allowed to go out to the optimal region.

For the description of the region close to the optimal zone experiments are carried on to composition plan KONO with a new planning centre.

After the corresponding calculations the response surface of the optimal region is described with the following regression equation of the second order:

$$y = 50.35 + 4.4\,x_1 - 3.6\,x_2 - 1.9\,x_1x_2 - 1.42\,x_1^2 - 2.72\,x_2^2 \qquad (2)$$

The estimation of significance of the eqn. (2) coefficients on Student t-test [6]:

$$[bi] > Sbi\ t \qquad (3)$$

where t-table value of Student t-test: for significance level $p = 0.05$ and degree of freedom $f = 3$, $t = 3.18$, and Sbi = mean square error. This showed that all coefficients of eqn. (2) are significant.

The adequacy of eqn. (2) on criterion $Fp = 4.4 \leqslant F = 8.68$ shows that it adequately describes the optimal surface.

Finding the point of maximum value on the response surface and reduction of eqn. (2) to the canonic form and its analysis showed that the response surface is an elliptic paraboloid. The maximum is on point S with coordinates $x_1 = 4.46$ and $x_2 = 1.77$ relative to the experiment centre in the KONO plan.

The discharge curves of elements with optimized content of additions are represented in Figs. 2–4.

The discharge curves represented show the advantage of using optimized cathodes in comparison with nonoptimized ones. The most probable causes of such effect are improving electroconductive and structural characteristics of porous cathodes which improve processes of mass transfer within an electrode and reduce ohmic losses.

Conclusions

(i) Mathematical methods of experimental design can be successfully used for optimization of the composition of cathode mass for improving characteristics of elements.

(ii) Additions are optimized for cathodes on basis of CuO and FeS_2.

(iii) The elaborated composition can be recommended for technology of the production of cathodes of elements of the systems Li/CuO, Li/FeS_2, Li/CuO–FeS_2.

References

1 K. Yokoyama, O. Okamoto and Y. Uetani, *Prog. Batteries Solar Cells, 6* (1987) 38.
2 C. M. Walker, M. Jr. Binder, W. L. Wade and Jr. Gilman, *J. Electrochem. Soc., 132* (1985) 1536.
3 N. Marincic, *J. Appl. Electrochem., 5* (1975) 313; *6* (1976) 51.
4 N. Marincic, D. B. Koffman, *J. Appl. Electrochem., 6* (1976) 263.
5 *Powder Diffraction File,* JCPDS, USA, 1987.
6 S. L. Ahmazarova, V. V. Kafarov, *Methods of Optimizing Experiment in Chemical Technology, Vysh. Shk.,* 1985, p. 327.