Journal of Power Sources, 1 (1976/77) 323 - 331

SIMPLEX OPTIMIZATION OF CARBON ELECTRODES FOR THE HYDROGEN–OXYGEN MEMBRANE FUEL CELL

JÓZEF CEYNOWA and ROMUALD WÓDZKI

Institute of Chemistry, N. Copernicus University, 87-100 Toruń (Poland)

(Received September 7, 1976; in revised form December 24, 1976)

Summary

Progress in, and the results of studies on the preparation of optimum carbon electrodes with a platinum catalyst are presented. The electrodes are of the bilayer type. Polyethylene has been used as the binding agent.

The simplex design method of Spendley, Hext and Himsworth has been applied. The temperature, pressure and time of heating and finally the content of polyethylene and carbon in both layers of the electrode have been optimized.

Introduction

Studies on hydrogen–oxygen fuel cells with an ion-exchange membrane have been carried out since 1955 - 59 [1, 2]. An increase in the quality of these cells is related mainly to the progress in the work on more and more perfect membranes [3 - 5]. On the other hand, the electrodes used determine the practical current efficiency of the cells to the same extent as the quality of membranes.

According to the published data [6], electrodes composed of platinum black bonded with polytetrafluoroethylene have been generally used in hydrogen–oxygen fuel cells. During the last years successful experiments with much cheaper carbon electrodes in cells with cation exchange membranes have been carried out [7, 8]. Similar experiments with cells with an anion exchange membrane did not give any promising results [9, 10].

In a previous paper [11], we have described the initial results of studies on the preparation, and some properties, of electrodes destined for a hydrogen–oxygen fuel cell with a cation exchange membrane. These electrodes correspond to the bilayer model and are composed of a so called "gas supplying layer" and a "catalytic layer". The layers are prepared from carbon of different particle sizes bonded with polyethylene.

The aim of this work is to determine the optimum parameters of formation, and the best composition of these electrodes. It has been realised relying on a statistical method of designing the multifactor extremum experiments. Considering the specific character of this problem, a method that permits the optimum parameters to be determined with the minimum number of experiments and does not require any unequivocal definition of quality criterion has been chosen.

For this purpose the sequential simplex method of Spendley, Hext and Himsworth [12], has been applied. With this method, experiments are carried out according to the simplex design. It determines the parameters for "initial" experiments on the basis of a so-called basic experiment as well as on the parameters of successive experiments after the analysis of the results of each step of the procedure. The parameters for the basic experiment were chosen on the grounds of the data published in the literature and some preliminary experiments.

The practical application of this method is described by Gorskij and Brodskij [13]. An example of such optimization for a catalytic layer in the model electrode is given by Szarajevskij *et al.* [14].

Experimental

Materials for the formation of the electrodes

The gas supplying layer of the electrodes has been formed from carbon obtained by sucrose carbonization and heating the coke at 1190 K for 4 h in a carbon dioxide atmosphere. Granulation, 0.20 - 0.12 mm.

The catalytic layer was made from a commercial active carbon, Carbopol N (product of ZEW Racibórz, Poland), additionally purified by extraction with azeotropic hydrochloric acid in a Soxhlet apparatus. Granulation, 0.085 - 0.075 mm.

Polyethylene was Telcothene Powder Type LD (product of Telcon Plastics Ltd, Great Britain). Granulation the same as the carbon granulation in the particular layers of an electrode.

The catalyst was platinum deposited on the carbon of the catalytic layer by the direct reduction of chloroplatinic acid with an alkaline solution of sodium formate. The prepared product has been purified by electrodialysis. Platinum content: 17% by weight.

The following components have been used in the cell: cation exchange membrane MRF-26 a product of the State Institute of Applied Chemistry U.S.S.R., saturated with 4 N H_2SO_4; oxygen and hydrogen, technical gases in steel cylinders.

Methods

In the sequential simplex method only parameters which can be changed in desirable way may be considered. The other factors ought to be estimated in another way. In the case of the present electrodes such factors were: the type of carbon and binding agent in both layers of an electrode and the type of catalyst. These factors have been chosen in a previous paper

[11]. Moreover, the literature indications [11, 15] have allowed some other parameters to be eliminated from the optimization procedure. The parameters accepted as constant and not subjected to the optimization are: the amount of catalyst per gramme of carbon in the catalytic layer and the granulation of carbon and polyethylene in particular layers of the electrode.

The parameters subjected to the optimization are:

x_1, temperature of electrode formation (°C);
x_2, pressure of electrode formation (kg/cm^2);
x_3, time of electrode heating (min);
x_4, mass of the gas supplying layer components (mg);
x_5, mass of the catalytic layer components (mg);
x_6, polyethylene content in the gas supplying layer (mg);
x_7, polyethylene content in the catalytic layer (mg).

The starting plan of the experiments was therefore determined by a seven-dimensional simplex composed of eight experimental points.

The matrix of the simplex [13], in an unspecified co-ordinate system, is given in Table 1.

TABLE 1

Simplex design matrix in the unspecified coordinate system

$A =$	0.500	0.289	0.204	0.158	0.129	0.109	0.0945
	−0.500	0.289	0.204	0.158	0.129	0.109	0.0945
	0	−0.578	0.204	0.158	0.129	0.109	0.0945
	0	0	−0.612	0.158	0.129	0.109	0.0945
	0	0	0	−0.632	0.129	0.109	0.0945
	0	0	0	0	−0.645	0.109	0.0945
	0	0	0	0	0	−0.655	0.0945
	0	0	0	0	0	0	−0.6610

The values of the parameters for the experimental points of the starting and successive simplexes have been determined using the procedure of Gorskij and Brodskij [13] and Izakov [16].

The criteria of electrodes quality used in the optimization procedure were as follows:

y_1 the main criterion of electrode quality; current density in mA/cm^2 at a terminal voltage 0.70 V, after 5 h operation of the hydrogen–oxygen fuel cell with a MRF-26 membrane at room temperature,

y_2 the maximum current density of the fuel cell in mA/cm^2.

The values of these criteria have been determined from current–voltage curves for the laboratory fuel cells at room temperature, at equal oxygen and hydrogen pressures of 0.6 kg/cm^2 and at oxygen and hydrogen flow rates of 5 and 1 dm^3/h respectively.

The electrodes of 2 cm^2 surface area have been formed in a mould with programmed regulation of temperature, pressure and heating time.

TABLE 2

Parameters and results of the optimization process

No.	Experiment	Parameters							Quality criteria	
		x_1 (°C)	x_2 (kg/cm^2)	x_3 (min)	x_4 (mg)	x_5 (mg)	x_6 (mg)	x_7 (mg)	y_1 (mA/cm^2)	y_2 (mA/cm^2)
1	X_0	120.0	25	20	250.0	50.0	75.0	10.0	—	—
2	X_1	124.0	29	25	260.0	55.0	80.0	11.0	17	95
3	X_2	116.0	29	25	260.0	55.0	80.0	11.0	23	150
4	X_3	120.0	17	25	260.0	55.0	80.0	11.0	15	70
5	X_4	120.0	25	5	260.0	55.0	80.0	11.0	18	167
6	X_5	120.0	25	20	210.0	55.0	80.0	11.0	15	90
7	X_6	120.0	25	20	250.0	25.0	80.0	11.0	10	70
8	X_7	120.0	25	20	250.0	50.0	45.0	11.0	19	165
9	X_8	120.0	25	20	250.0	50.0	75.0	2.0	24	170
10	X_9	120.0	25	20	250.0	82.1	68.6	8.4	30	170
11	X_{10}	120.0	35	13	237.0	59.9	65.3	7.7	28	150
12	X_{11}	114.5	26	9	242.0	62.3	58.0	6.0	31	190
13	X_{12}	118.5	30	14	292.0	62.3	58.0	6.0	27	190
14	X_{13}	117.0	30	29	252.0	65.5	48.5	3.9	28	195
15	X_{13}^*	117.0	30	10	262.0	71.8	93.5	3.9	16	145
16	X_{14}	116.0	32	17	259.4	74.9	84.5	1.9	31	200
17	X_{15}	119.5	30	9	250.8	80.7	47.6	2.0	15	150
18	X_{16}	115.5	34	14	260.8	85.7	52.6	6.9	26	165
19	X_{15}^*	119.5	30	9	250.8	80.7	47.6	6.5	35	200
20	X_{17}	120.5	25	18	248.7	53.7	70.4	4.3	24	160
21	X_{18}	116.0	22	20	275.0	77.7	59.1	6.2	20	175
22	X_c	117.5	30	16	255.5	71.7	60.4	5.7	30	205

Note: real pressure $p = x_2 400$ kg/cm^2.

Results

Optimization procedure

The parameters of particular experiments, *i.e.* formation and composition parameters, as well as the quality criteria of electrodes are compiled in Table 2. The first line of Table 2 contains data used for the calculation of the parameters of the experiments for the starting simplex, S_1. The lines from 2 to 9 contain values of the parameters for the eight initial experiments forming the starting simplex S_1 and also the measured values of criteria y_1 and y_2. The experiments and electrodes corresponding to them which belong to the particular simplexes are listed in Table 3. Further lines of Table 2 show the parameters for successive experimental steps in the optimization procedure.

The parameters for these experiments have been determined successively after the analysis of the quality of the electrodes creating the previous simplex and after the elimination of the experiment in which the quality criteria had the lowest values.

TABLE 3

Statistical data of simplexes of the optimization process

Simplex	Electrodes	Mean values of the quality criteria		Relative standard deviations	
		$\bar{y}_1$ (mA/cm^2)	$\bar{y}_2$ (mA/cm^2)	V_{y_1}	V_{y_2}
S_1	$X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8$	17.6	122.1	25.7	36.8
S_2	$X_1, X_2, X_3, X_4, X_5, X_7, X_8, X_9$	20.1	134.6	25.8	31.3
S_3	$X_1, X_2, X_4, X_5, X_7, X_8, X_9, X_{10}$	21.8	144.6	24.8	22.9
S_4	$X_2, X_4, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}$	25.0	169.0	19.4	9.0
S_5	$X_2, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, X_{13}$	26.3	172.5	15.2	10.3
S_6	$X_2, X_8, X_9, X_{10}, X_{11}, X_{12}, X_{13}, X_{14}$	27.8	176.3	10.9	11.2
S_7^*	$X_9, X_{10}, X_{11}, X_{12}, X_{13}, X_{14}, X_{15}^*, X_{16}$	29.5	181.9	9.8	10.2
S_8	$X_9, X_{10}, X_{11}, X_{12}, X_{13}, X_{14}, X_{15}^*, X_{17}$	29.3	181.3	11.0	10.6
S_9	$X_9, X_{11}, X_{12}, X_{13}, X_{14}, X_{15}^*, X_{16}, X_{18}$	28.8	184.4	16.3	8.1

The first step in the optimization was the elimination of experiment X_6 from the S_1 simplex because the electrodes obtained in this experiment have shown the lowest value for the y_1 criterion.

After elimination of experiment X_6 the following X_9 experiment has been determined and the S_2 simplex has been formed in this way.

From this simplex, quite similarly, experiment X_3 has been eliminated and replaced with the new X_{10}. In the S_3 simplex the two experiments X_1 and X_5 have shown the worst behaviour and similar values of quality criteria. For this reason experiments X_1 and X_5 have been eliminated simultaneously according to the Izakov rule, and the parameters for the successive experiments X_{11} and X_{12} of the S_4 simplex have been thus obtained. From this simplex experiments X_4 and X_7 have been simultaneously removed and the parameters for the X_{13} and X_{13}^* experiments in the S_5 and S_5^* simplexes have been determined. For further procedure the S_5 simplex has been chosen because the quality criteria of the electrodes are more convenient in X_{13} than in the X_{13}^* experiment. In the next step experiment X_7 has been eliminated from the S_5 simplex. From the following S_6 simplex formed by removing experiment X_7, two experiments X_2 and X_8 have been eliminated simultaneously and the parameters for the X_{15} and X_{16} experiments in the S_7 simplex have been calculated.

The calculations have shown that parameter x_7 (polyethylene content in the catalytic layer) for the X_{15} electrode would have a negative value. In this situation X_{15} electrodes have been prepared with as little polyethylene as possible in the catalytic layer, equal to 4% by weight. It appeared, however, that the mechanical stability of the catalytic layer prepared by this method was too low. For this reason, in the next steps the value of the x_7 parameter was accepted as 8% by weight polyethylene content, which secures good mechanical properties. Thus, further procedure has been continued including

TABLE 4

Properties of the optimized electrodes

	Thickness (cm)	Resistivity (ohm-cm)	Nitrogen permeability (cm^3/cm^2 s)	Volume of pores of radii $R > 1500$ Å (%)	Pore volume (cm^3/g)	Current density after 500 h operation at 0.70 V (mA/cm^2)
Electrode	0.15	6.70	0.17	67	2.09	45 ± 8
Gas supplying layer	0.12	4.50	0.46	78	2.09	
Catalytic layer	0.03	16.0	—	67	4.98	

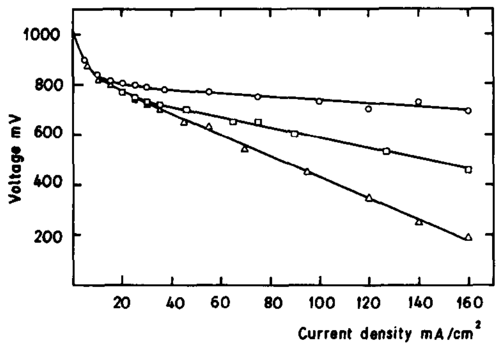

Fig. 1. Current–voltage curves of the hydrogen–oxygen fuel cell with MRF-26 membrane (hydrogen and oxygen pressure 0.6 kg/cm^2, room temperature). ○, "resistance free" current–voltage curve; □, after 500 h operation; △, after 5 h operation.

only six variable parameters. Accordingly electrode X_{15}^* was prepared from the S_7^* simplex. This electrode had a very stable performance and satisfactory mechanical stability.

In the S_7^* simplex electrode X_{16} had the lowest values of the quality criteria. The electrode X_{17} prepared in the successive experiment calculated after the elimination of X_{16}, did not, however, show better properties (simplex S_8).

Therefore experiment X_{10} with slightly higher values of the quality criteria than X_{16} has been eliminated from the S_7^* simplex. The X_{18} electrodes obtained in this way had still lower values of the quality criteria compared with X_{17}. At this stage the optimization procedure was considered to be finished accepting electrode X_{15}^* as the optimum one.

Properties of optimized electrodes

Several pairs of the electrodes denoted X_c were made with the parameters corresponding to the middle of the optimum S_7^* simplex. The data for these electrodes are presented in line 22 of Table 2.

The optimum electrodes were subjected to quality control. Porosity, electrical resistivity of individual layers and the rate of nitrogen flow through the electrode were measured. The results are given in Table 4.

The performance of the cell with the optimum electrodes used on both the hydrogen and oxygen sides is illustrated by the current–voltage curves in Fig. 1.

Discussion

Evaluation of the optimization procedure

The results presented show that the simplex method enables the parameters for the optimum electrode to be determined as early as in the 18th experiment.

The correctness and the course of the optimization process can be evaluated by means of statistical tests. For this purpose the mean values for the quality criteria y_1 and y_2 in the particular simplexes, relative standard deviations V_{y_1} and V_{y_2} and finally factors E_1 and E_2 were calculated.

The relative standard deviations were calculated from:

$$V_y = \frac{\left[\frac{1}{n-1} \Sigma (y - \bar{y})^2 \right]^{1/2}}{\bar{y}} \times 100 \tag{1}$$

The values $\bar{y}_1$ and $\bar{y}_2$ as well as V_{y_1} and V_{y_2} for successive simplexes are listed in Table 3. The data corresponding to the S_5^* and S_7 simplexes are omitted because they have been eliminated from the procedure as false steps. It must be noted here that only the first criterion y_1 determines unequivocally the optimization progress. The changes of both values $\bar{y}_1$ and V_{y_1} determine S_7^* simplex as the optimum one.

The low value of E_1 (1.69) calculated from formula (2) for the y_1 criterion,

$$E_1 = \frac{y_c - \bar{y}_{S_7^*}}{\bar{y}_{S_7^*}} \times 100 \tag{2}$$

shows also that the optimum simplex is well situated in the multifactor space and the particular electrodes corresponding to the vertices and to the middle of the simplex show no major differences.

Especially important conclusions result from the relatively high value of the E_2 factor (18.64) calculated from the formula (3) for the y_1 criterion:

$$E_2 = \frac{y_{opt} - \bar{y}_{S_7^*}}{\bar{y}_{S_7^*}} \times 100 \tag{3}$$

This shows that the optimum electrode quality differs considerably according to the y_1 criterion from the mean value $\bar{y}_1$ for the electrodes of the optimum simplex. The best electrodes can be thus prepared in very narrow ranges of the parameter values. This range includes the nearest environment of the point in the simplex corresponding to the optimum electrode. A closer determination is, however, difficult and requires many additional investigations [17] in which changes of the particular parameters would be close to the experimental error.

Characteristics of the optimized electrodes

The electrochemical properties of the electrodes depend to a great extent on the catalytic layer because its character determines the dimensions and the state of the electrochemically active three phase boundary: catalyst, gas, electrolyte. The present results indicate that the catalytic layer thickness should be about 0.030 cm (see Table 4). This result is in agreement with literature data [18, 19] pointing to the 0.05 - 0.02 cm range as the optimum thickness for the catalytic layer.

The best properties would be exhibited by a porous catalytic layer with an as-low-as possible electrical resistivity and dominant hydrophilic character. That is why the optimization progress has tended towards the elimination of polyethylene which makes carbon less hydrophilic and increases its resistivity [15, 20]. In these circumstances the polyethylene content has been stabilized at 8% and eliminated as a parameter from the optimization procedure.

The content of polyethylene in the gas supplying layer, which is the main factor determining the life time of the electrodes, was fixed at 20% by weight.

The electrodes presented in this paper are designed for cells with a cation exchange membrane and they have been tested at room temperature. In a cell with MRF-26 membrane a current density of 45 ± 8 mA/cm^2 was obtained at a voltage of 0.70 V after 500 h operation. The quality of the electrodes is also characterized by the current density at the voltage determined with an interrupter equipment. The current density reaches 150 mA/cm^2 at a "resistance free" voltage of 0.70 V (see Fig. 1).

Acknowledgement

The authors are indebted to Doc. dr. hab. Anna Narebska for her interest and valuable discussion and for critical comments.

References

1 W. T. Grubb and L. W. Niedrach, J. Electrochem. Soc., 106 (1959) 275.
2 W. T. Grubb and L. W. Niedrach, J. Electrochem. Soc., 107 (1960) 131.
3 A. P. Fickett, Proc. Symp. Battery Separators, Columbus, Ohio, 1970, p. 354.
4 W. Grot, Chem. Ing. Tech., 44 (1972) 167.
5 W. B. Alston, NASA Tech. Note, NASA TN D-7482 (1973).
6 M. W. Breiter, Electrochemical Processes in Fuel Cells, Springer-Verlag, Berlin (1969).

7 L. Kreja and J. Ceynowa, Pr. Nauk. Inst. Technol. Org. Tworzyw Sztucznych Politech. Wroclaw., 2 (1973) 261.
8 A. Narebska, J. Ceynowa and L. Kreja, Chem. Stosow., 18 (1974) 245.
9 D. M. Drazic, R. R. Adzic and A. R. Despic, J. Electrochem. Soc., 116 (1968) 885.
10 T. Suzuki and S. Matsumoto, Denki Kagaku, 40 (1972) 239.
11 J. Ceynowa and R. Wódzki, Chem. Stosow., to be published.
12 W. Spendley, G. R. Hext and F. R. Himsworth, Technometrics, 4 (1962) 441.
13 W. G. Gorskij and W. Z. Brodskij, Zavod. Lab., 31 (1965) 831.
14 A. P. Szarajevskij, L. I. Stoliarenko and W. A. Kasatkina, Zavod. Lab., 38 (1972) 331.
15 J. Jindra and J. Mrha, Collect. Czech. Chem. Commun., 33 (1971) 583.
16 F. J. Izakow, Zavod. Lab., 37 (1971) 330.
17 W. W. Nalimow and N. A. Czernowa, Statystyczne metody planowania doświadczeń extremalnych, WNT, Warszawa (1967).
18 K. R. Williams, An Introduction to Fuel Cells, Elsevier, Amsterdam (1966) p. 100.
19 A. B. Hart, G. I. Womack, Fuel Cells, Chapmann and Hall, London (1967) p. 152.
20 M. Brezina, M. Franz, J. Jindra and J. Mrha, Abh. Sachs. Akad. Wiss., Leipzig Mat. Naturwiss., Kl., 49 (1968) 137.