Indian Journal of Technology
Vol. 24, July 1986, pp. 430-434

Statistical Optimization of Iron Electrodes for Alkaline Storage Batteries*

K VIJAYAMOHANAN & A K SHUKLA
Solid State & Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India
and
S SATHYANARAYANA†
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received 24 *March* 1986

A pressed-plate iron electrode for alkaline storage batteries, designed using a statistical method (fractional factorial technique), is described. Parameters such as the configuration of the base grid, electrode compaction temperature and pressure, binder composition, mixing time, etc. have been optimized using this method. The optimized electrodes have a capacity of 300 $\pm$5 mAh/g of active material (mixture of iron and magnetite) at 7h rate to a cut-off voltage of -0.86 V vs Hg/HgO, OH^-.

Storage batteries which could be considered for large-scale energy storage applications are nickel-iron, nickel-zinc and iron-air systems[1-3]. This is because systems such as nickel-cadmium, silver-zinc and nickel-hydrogen employ materials or construction methods that are too expensive to be feasible for commercial purposes. Nickel-iron and nickel-zinc are the major competitors to lead-acid systems and at present are being developed by a number of countries throughout the world[4-9]. The major advantages of these systems are longer cycle life and longer calender life (Ni-Fe), higher energy density (Ni-Zn) and freedom from pollution (both Ni-Fe and Ni-Zn) as compared to commercial vented type lead-acid batteries. Nickel-zinc batteries suffer from serious problems of short life-time resulting from dendritic growth, shape change and densification of the zinc electrode. On the other hand, nickel-iron batteries have a long cycle-life (typically about 3000 cycles) even under adverse conditions such as overcharge, overdischarge, charge-stand, discharge-stand and inadequate maintenance. Recent developments are fast placing this battery on par with the other accumulators[6,8]. Iron-air rechargeable batteries, which can use virtually inexhaustible raw materials[10] and can also provide long cycle life under inadequate maintenance conditions, are equally promising. Iron electrode constitutes a vital component of both these storage batteries. Various types of iron electrodes which have been studied for application in these battery systems are the sintered type, the pocket type and the pressed type. Of these, the pressed-type iron electrodes are commercially most feasible owing to a significant cost-reduction in relation to the sintered iron electrodes as also due to their superior performance compared to the pocket-type electrodes[6].

The problems that adversely affect the performance of the iron electrode batteries are: spontaneous corrosion of the iron electrode in the charged state which leads to a high rate of self discharge, and low faradaic efficiency for the anodic dissolution of iron which leads to a low utilization coefficient.

In the literature, studies conducted to solve these electrochemical problems of the iron electrodes batteries are very few. It has been noticed that even minor random variations in the fabrication of the battery electrodes induce large variations in their capacity values. Determining the optimum parameters for formation of these electrodes hence seems to be critical. In this context, statistical methods have been documented to be useful[11,12]. The aim of the present work is to realise the optimum parameters for the fabrication of pressed-plate iron electrodes for alkaline storage batteries using such a statistical method, viz. the factorial optimization technique. In this technique, a series of experiments designed to test the effect of altering the factors at selected levels on any observable property of the system are conducted. Following this method it has been possible to fabricate pressed-type iron electrodes with capacity values of 300$\pm$5 mAh/g consistently.

Experimental Procedure

Preparation of iron electrodes—The active material for the electrodes was obtained by vacuum decomposition of ferrous oxalate at 773 K. X-ray diffraction pattern of the decomposed product

*Dedicated to Professor K S G Doss on his eightieth birthday.
†To whom all correspondence should be addressed.

indicated it to be a mixture of α-Fe (15 wt%) and Fe_3O_4 (85 wt%). The mean diameter of the particles of this mixture as obtained from a Cilas-Alcatel Granulometer was 16 μm; the BET surface area was 10 m²/g. Pure nickel base grids were taken and subjected to electrochemical degreasing in 20% NaOH solution containing 1% Teepol at 80°C under a current density of 20 mA/cm² for 20 min followed by chemical etching in 1% $FeCl_3$ solution for 5 min.

Pressed-type iron electrodes were fabricated from this mixture of iron and magnetite by hot pressing an appropriate proportion of it with polyethylene, graphite and iron sulphide (1 wt%) on a nickel base grid. These pressed-plate iron electrodes were coupled with sintered nickel-supported nickel oxide electrodes in 6*M* KOH electrolyte containing 1% LiOH to form nickel-iron secondary cells. These were subsequently charged (at C/10 rate for 16 h) and discharged (at 7 h rate to −0.86 V vs Hg/HgO, OH^-) galvanostatically until the formation of the electrodes was complete which usually required about 25 cycles. Electrode potentials were measured using a Hg/HgO, KOH (6*M*) reference electrode and charging and discharing data were recorded using a LS-6 Linsies strip-chart recorder. Electrode capacity values were calculated from the recorded discharge curves up to the end of the first step of discharge, i.e. for the reaction: $Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e^-$. All the measurements were conducted at room temperature (~30°C).

The statistical method—The pressed-plate iron electrodes employed in the present study were fabricated under specific physical and chemical conditions. These conditions influence the capacity of the electrodes which could be expressed as

$$y = f(x_1, x_2 \ldots x_n) \quad \ldots(1)$$

Here, x_i are the independent input parameters. A suitable form of Eq. (1) for factorial two-level analysis is obtained by assuming a linear relationship[13,14] between y and x_i as follows:

$$\begin{aligned} y = m_0 + m_1 x'_1 + m_2 x'_2 + \ldots + m_n x'_n + m_{12} x'_1 x'_2 + \\ + \ldots + m_{1n} x'_1 x'_n + m_{23} x'_2 x'_3 + \ldots \\ + \ldots + m_{2n} x'_2 x'_n + m_{123} x'_1 x'_2 x'_3 + \\ + \ldots + m_{12\ldots n} x'_1 x'_2 \ldots x'_n \end{aligned} \quad \ldots(2)$$

The normalized parameters, x'_1, are given by

$$x'_i = \frac{x_i - [x_i(+) - x_i(-)]/2}{[x_i(+) - x_i(-)]/2}$$

where x'_i are equal to +1 or −1, $x_i(+)$ is the upper and $x_i(-)$ is the lower limit of x_i. The effect of individual as well as interacting parameters are included in the *m*-factors present in Eq. (2). To reduce the number of experiments, higher-order interactions can be confounded* with individual parameters[13,15]. In doing so, the effect of the higher-order interactions should be negligible as compared to that of the main parameters. In the present study seven independent variables were chosen for the factorial two-level analysis. It was possible to carry out one-eighth-factorial replication, i.e. confounding of higher-order interactions resulting in the reduction of experiments to the level possible, without main effects being aliased—two indistinguishable effects both arising from the same treatment combination—with the first-order interaction[15-17]. The seven parameters could thus be analysed by means of a 2^{7-3}—factorial design. In this manner, the number of individual experiments necessary was reduced from $2^7 = 128$ to $2^4 = 16$.

The test matrix for the 2^{7-3}–factorial design is given in Table 1 along with the individual and interacting effects of various parameters. The details of the factorial design are given in Ref. 17.

Screening experiments—A number of screening experiments were conducted in order to determine the various factors – a factor is any experimental variable affecting an observable property of the system – on which the capacity of the electrodes depends. These experiments revealed that a total of seven input parameters would be desired for conducting the factorial analysis. These parameters, with their limits indicated within the brackets, are:

A, base grid geometry (perforated nickel sheet: Type I, and extended nickel wire mesh: Type II)
B, mixing time (10 min and 60 min)
C, load retention time (0 min and 5 min)
D, graphite composition (10 wt% and 30 wt%)
E, compaction temperature (100°C and 140°C)
F, compaction pressure (70 kg/cm² and 140 kg/cm²)
G, binder composition (5 wt% and 7 wt%).

A total of sixteen electrodes, labelled as F1, F2, ... F16, were fabricated according to the 2^{7-3}–scheme with these limits of the input parameters.

Results and Discussion

The formation of all the sixteen electrodes employed during the present study was found to be complete by the twentyfifth cycle. The average value of the capacities of the electrodes obtained from the succeeding five cycles have been chosen for optimization. Quantitative estimates of the contributions from the individual and interacting parameters on the capacity of the electrodes are then obtained by Yates' analysis of the capacity values as

*A set (or block) of treatment combinations is said to be confounded with another set if the difference on the effects between the sets is indistinguishably small compared to the effects within each set.

Table 1—Test Matrix for the 2^{7-3} Design of the Iron Electrodes

Electrode No.	Treatment combinations*	Level of factors A	B	C	D	E	F	G	Effects ascribed to individual/interactive components
F1	(1)	−	−	−	−	−	−	−	Total
F2	abcd	+	+	+	+	−	−	−	*D*
F3	bce	−	+	+	−	+	−	−	*E*
F4	ade	+	−	−	+	+	−	−	*DE*
F5	acf	+	−	+	−	−	+	−	*F*
F6	bdf	−	+	−	+	−	+	−	*DF = AG*
F7	abef	+	+	−	−	+	+	−	*EF = AB*
F8	cdef	−	−	+	+	+	+	−	*C*
F9	abg	+	+	−	−	−	−	+	*G*
F10	cdg	−	−	+	+	−	−	+	*DG*
F11	aceg	+	−	+	−	+	−	+	*EG*
F12	bdeg	−	+	−	+	+	−	+	*B*
F13	bcfg	−	+	+	−	−	+	+	*AD*
F14	adfg	+	−	−	+	−	+	+	*A*
F15	efg	−	−	−	−	+	+	+	*EFG = ABG*
F16	abcdefg	+	+	+	+	+	+	+	*AE = CG*

* The selected combinations of levels of factors to be tested

Table 2—Yates' Analysis of the Data

Electrode No.	Average capacity values (mAh/g)	Yates' Analysis* I	II	III	IV	Mean effect	Factor interaction responsible
F1	225	419	863	1650	3391	423	Mean total (T)
F2	194	444	787	1741	3	0.375	*D*
F3	216	479	911	80	−191	−23.8	*E*
F4	228	308	830	−77	193	24.1	*DE*
F5	246	459	−19	−146	−157	−19.6	*F*
F6	233	452	99	−45	163	20.3	*DF = AG*
F7	98	434	−61	168	−227	28.3	*EF = AB*
F8	210	396	−16	25	113	14.12	*C = DEF*
F9	244	−31	25	−75	91	11.37	*G*
F10	215	12	−171	−81	−157	−19.65	*DG*
F11	242	−13	−7	118	101	12.6	*EG*
F12	210	112	−38	45	−143	−17.8	*B = DEG*
F13	228	−29	43	−196	−5	−0.625	*FG = AD*
F14	206	−32	125	−31	−73	−9.125	*DEF = A*
F15	195	−22	−3	82	165	20.6	*EBG = ABG*
F16	201	6	28	31	−51	−6.37	*AE = CG*

* Pair-wise addition to get first 8 values in column I followed by pair-wise substraction to obtain another 8 values to be repeated till IV column.

illustrated in Table 2. The magnitudes of the mean effect values show the relative significance of each of these input parameters and their interactions with the others[13]. The sign of the values denote whether the particular component should be increased or decreased from its mean value in order to obtain the optimum capacity values of the electrodes.

To examine the effect the base grid configuration (parameter – *A*) has on the capacity of electrodes, two types of nickel base grids were taken. The parameter – *A* has got a negative mean effect value (F14 of Table 2) and is also aliased with a second order interaction term *DFG* which is considered to have negligible effect on the capacities of the electrodes. The analysis suggests that perforated nickel sheet is better than the extended nickel wire mesh for the purpose.

In the analysis, the mixing time parameter, *B*, has been taken to be a dummy parameter and is found to have a negative mean effect value (F12 of Table 2) and is aliased with the higher-order interaction term *DEG*. In such a situation, the interaction term *DEG* would affect the capacity of the electrodes significantly and one cannot neglect it. The time for retaining the pressure during electrode compaction (parameter-*C*) is

Table 3—Parameters for the Final Design of Electrodes

Electrode No.	Parameters					Capacity* mAh/g
	B min	*C* min	*E* °C	*F* kg/cm²	*G* wt %	
F17	35	2.5	120	105	6.5	—
F18	28	3	112	93.5	6.8	305
F19	20	3.5	104	82	7	235
F20	13	4	96	70	7.3	155
F21	8	4.5	88	58.5	7.6	200

*Average capacity values obtained from the capacity values of five discharge cycles succeeding the 25th formation cycle

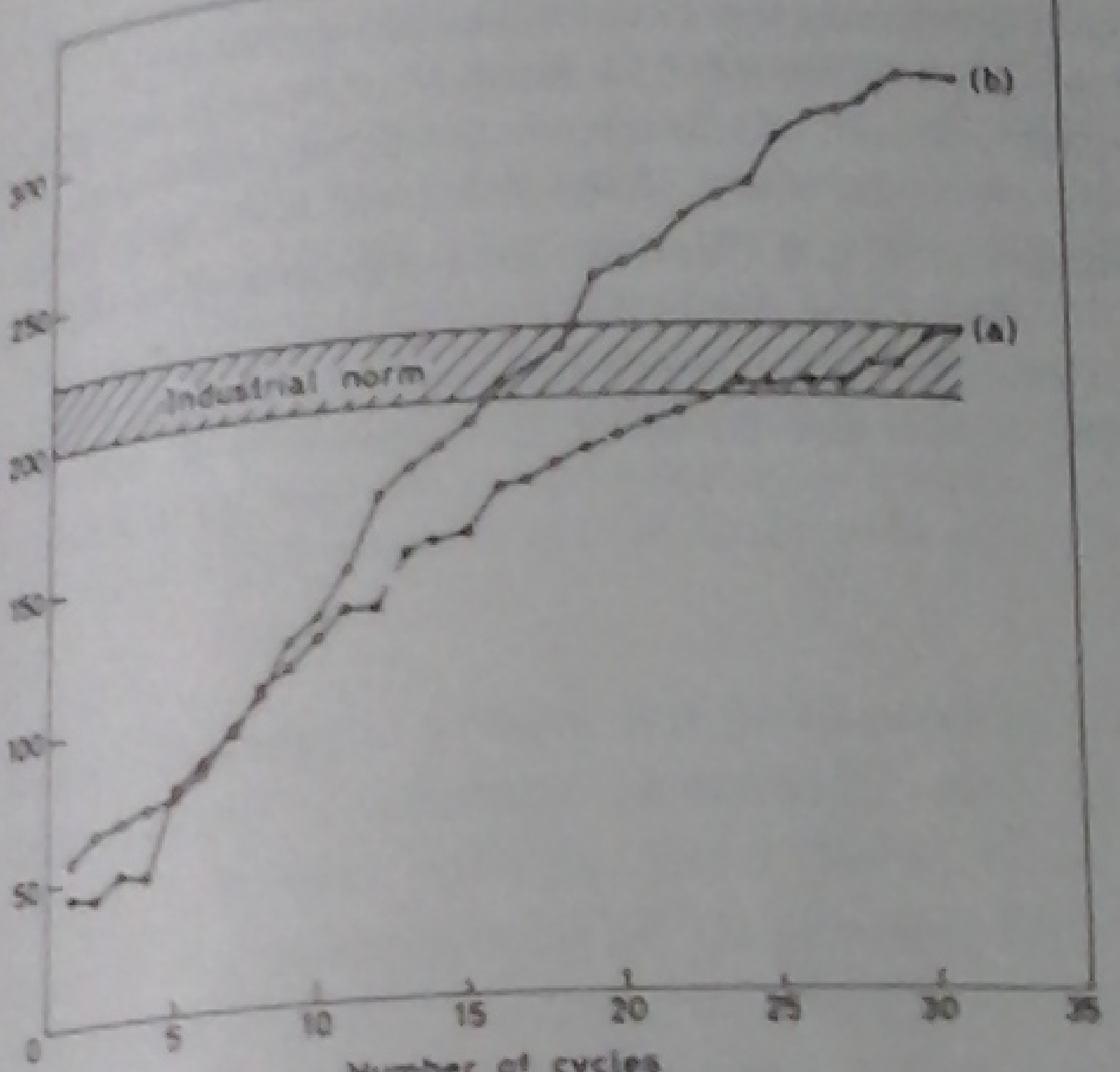

Fig. 1—Capacities up to −0.86 V vs Hg/HgO, OH^- during constant-current discharge for: (a) a pressed-plate iron electrode without optimization, and (b) an optimized F18 electrode as a function of the number of charge-discharge cycles

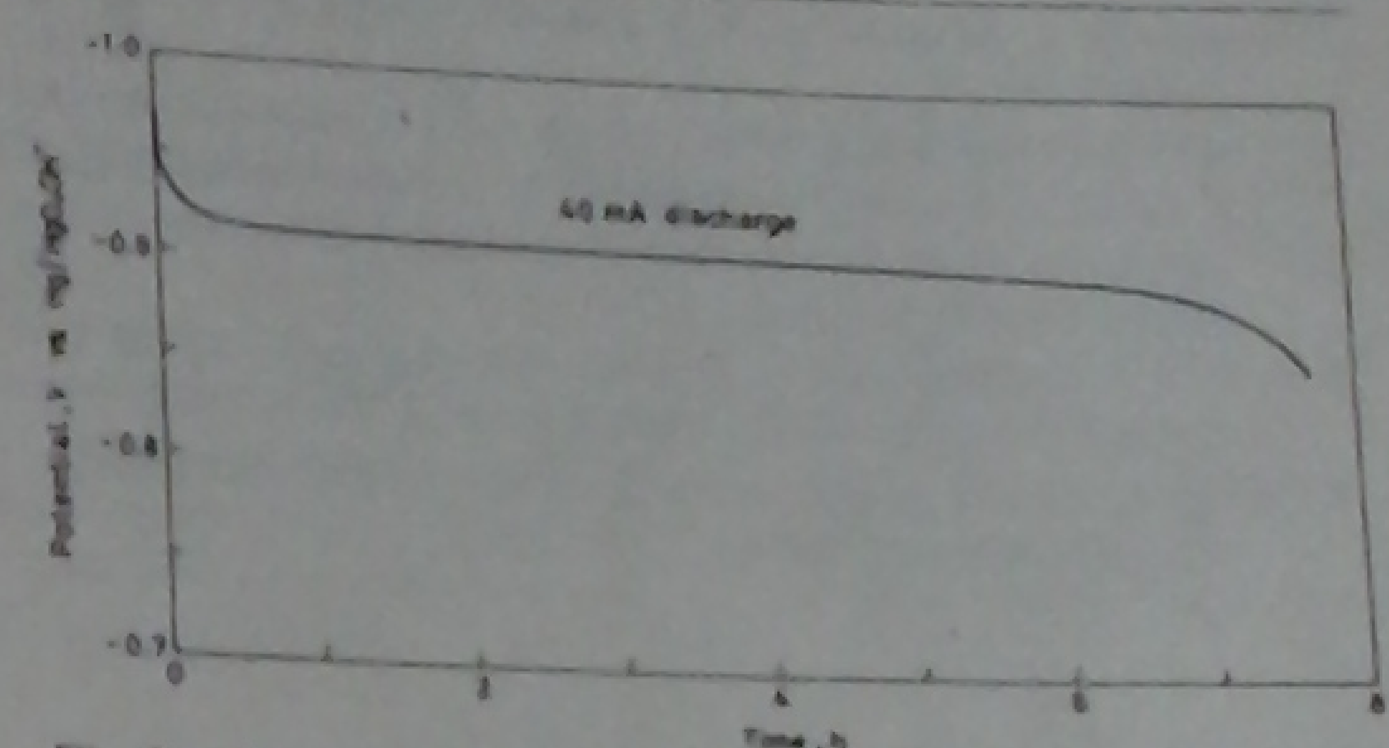

Fig. 2—A typical constant current-discharge curve for an optimized iron electrode (F18)

aliased with the second order interaction term *DEF* and has a positive mean effect of value of 14.2 (F8 of Table 2). It is therefore inferred that either the interaction term *DEF* or the parameter *C* contribute to the capacity of the electrodes. Since the second order interactions terms have been considered to be negligible, the analysis suggests that the parameter *C* should be increased from its mean value to reach the optimum. Yates' analysis assigns a mean effect value of 0.375 for the graphite composition (parameter-*D*) in the mixture (F2 of Table 2). In practice, this parameter is of no consequence so far as the electrode capacities are concerned, as it provides only a current conducting network.

The mean effect values for the compaction temperature (parameter-*E*) and compaction pressure (parameter-*F*) of the electrodes are −23.8 and −19.6 respectively (F3 and F5 of Table 3). The analysis suggests that both factors should be decreased from their mean values to optimize the capacity of the electrodes.

Lastly, the binder composition (parameter-*G*) has got a mean effect value of 11.37 (F9 of Table 2). This suggests that the binder composition should be increased from its mean value to achieve optimum capacity values of the electrodes. It is indeed an important parameter as it decides the hydrophobicity as well as the mechanical strength of the electrodes.

The optimum capacity value of the electrodes was achieved using the method of steepest ascent[15,17]. In this method, the mean effect values of various parameters have been employed. The parameters *A* and *D* have not been included as the capacity values do not show any apparent dependent on these. The remaining five parameters and the capacities of the electrodes have been taken to be the coordinates of a six-dimensional space to conduct the search plan. The slopes of the ascent through each of these coordinates were calculated using five steps relative to parameter *E*, as it happens to have the highest mean effect value of 23.8. Using these slopes, the final design of the electrodes was completed and accordingly a total of five electrodes were fabricated (Table 3). Electrode F17 could not be tested due to lack of mechanical strength. Of the remaining four electrodes, F18 gave the optimum capacity of 300±5 mAh/g. A comparison of the capacity of an F18 electrode with an electrode for which these parameters have not been optimized is shown in Fig. 1. It has been confirmed that the capacity of the electrode F18 lies within the contour of global optimum.

The reproducibility of the data was confirmed by fabricating a total of four electrodes with the optimal design F18. The stabilized capacity of these electrodes was found to be 300 ± 5 mAh/g of the active material (Fig. 2). From this study we can surmise that by a judicious choice of the input parameters of the pressed-plate iron electrodes, it is possible to optimize their capacity values by the statistical optimization technique.

References

1 Shukla A K, Manoharan R & Ramesh K V, *Bull Mat Sci*, **5** (1983) 267.

2 Sathyanarayana S & Sridharan L N, *Electrochemical energy storage systems for rural applications*, A report submitted to Department of Science and Technology, Government of India, New Delhi 1976.

3 Broadd R J, *Handbook of batteries and fuel cells*, edited by Linden D (McGraw-Hill Book Co., New York) 1984.

4 Ojefors L, *Electric vehicle exposition* (South Australian Energy Council, Adelaide) 1980.

5 Takahasi T, *Prog Batt Solar Cells*, **2** (1979) 15.

6 Sathyanarayana S, *The nickel-iron storage battery—A status report and techno-economic survey for India*, A report submitted to NRDC, Government of India, New Delhi (1983).

7 Tong C S, Wong S D, Wang Y Y & Wan C E, *J Electrochem Soc* **129** (1982) 1173.

8 Gentry K & Hudson R, *Proc 16th Intersociety Energy Conversion Engineering Conf.*, Vol. 1 (1981) 648.

9 Iofa Z A, *Z Prikl Khim*, **5** (1981) 1097.

10 Read C B, *Fuels, minerals and survival* (Ann Arbor Science Publishers, Michigan), 1978.

11 Ceynowa J & Wodzki R, *J Power Sources*, **1** (1977) 323.

12 Funk W & Goebe F, *Thin Solid Films*, **128** (1985) 45.

13 Duckworth W E, *Statistical techniques in technological research* (Methuen and Co., Ltd, London) 1968.

14 Marsh R A, Ryan D M & Nardi J C, *J Power Sources*, **3** (1978) 95.

15 Biles W E & Swain J J, *Optimization and industrial experimentation* (John Wiley and Sons, New York) 1980.

16 Cochran W G & Cox C M, *Experimental design* (John Wiley and Sons, New York) 1957.

17 Davies O L, *The design and analysis of industrial experiments* (Oliver and Boyd) 1957.