Paste-Type Negative Plate for Alkaline Storage Batteries
—One Example of Random Combination Method

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Experimental design by the modern statistics especially orthogonal layout is widely applied in various fields in these days, but few of these⁽¹⁾ results have been published.

The author has attempted to ascertain whether this method is available or not in the field of his interest by applying this method in the maturing of negative plate of alkaline storage battery.

As the experiment has been designed for 17 factors in 3 levels a simple orthogonal layout L_{27} (3^{13}) for 13 factors does not suffice. Therefore, the two-step random combination method⁽²⁾ which can further accomodate several tests for interaction besides 17 factors in 3 levels by 27 samples was adopted. In principle, it is a random combination of the two sets of L_{27} (3^{13}), the analysis of variance being done at first independently in each set, and by modifying the effects of the larger factors of the set, then the variations of the other set re-calculated. By repeating such recalculations mutually between the two sets in sequence, the errors converged to constant values and the whole factors separated.

The details of the processes and factors referred to are shown in Tables 1 and 2. The sample plates were made in a size of about $40 \times 15 \times 2$ mm and each contained about 1.7 g of CdO. Initial capacity and durability

Table 1 Preparing Process of Paste-type
Negative Plate.

Table 2 The Factors and Their Conditions.

(A) 1st Part of Processes.

Factor		Conditions			Note
		1	2	3	
Conc. of Cd (NO ₃) ₂ soln.	(cc)	100	200	400	25 cc of original soln*. was diluted to leave
Vol. of FeCl ₃ soln.	(cc)	20	15	10	The vol. of original soln**. to be added
Shortage of NaOH soln.	(cc)	0	1	2	The vol. to be subtracted from the theoretical value.†
Conc. of NaOH soln.	(cc)	400	200	100	The vol. obtained above was diluted to leave
Temp. at precipitation	(°C)	100	60	20	±3°C
Time for standing	(h)	0	4	24	From precipitation to washing
Number of washing		1	2	1	Mother liquid was diluted to 1 l.
Temp. of heat treatment	(°C)	700	600	500	By siliconite furnace (±40°C)
Time for " "	(min.)	long	mid.	short	Refer to the foot-note‡

* 480 g Cd(NO₃)₂·4 H₂O per 1 l

** 235 g FeCl₃·6 H₂O per 1 l

† 12.3 cc of NaOH soln. (418 g/l) for 20 cc of original soln. of FeCl₃

11.0 " " " 15 " "

9.8 " " " 10 " "

Temp.	Time	Long	Middle	Short
	(°C)			
700	(°C)	30	15	7.5
600		60	30	15
500		120	60	30

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The original written in Japanese can be seen in J. Electrochem. Soc. Japan, 26, 125 (1958).

(B) 2nd Part of Processes

Factor	Conditions			Note
	1	2	3	
Sort of addition agent	Asbestos*	Lignine**	CdCO ₃ ‡	1% to original powder
Sort of conductive material	Nickel†	HgO‡	A-B§	10% " "
Mesh of network	14 (0.30 mm ϕ)	10 (0.35 mm ϕ)	10 (")	woven with nickel wire (40×15 mm)
Sp. gr. of pasting soln.	1.00	1.10	1.20	KOH soln.
Hardness of paste	medium	soft	hard	by hand.
Temp. at drying plate (°C)	100	60	20	±10°C
Sp. gr. of forming soln.	1.15	1.10	1.20	KOH soln. (the soln. was used also on testing.)
Current density at forming (A/dm ²)	0.10	0.40	0.20	For both surfaces

* For Gooch crucible

** Sulfonate from waste soln. in pulp production

† Powder metal reduced from its oxide

‡ Produced by ordinary method

§ Acetylene black

were tested with each of the test plates. Charge and discharge were carried out till 82 cycles, but as most of the samples lost their active material by shedding before that time, the durability was compared with the capacity at the 32nd cycle. Analyses of variance were made on each kind of the tests and the effects of the factors with significant variance are shown in Fig. 1.

Fig. 1 (A) PH after precipitation.

Fig. 1 (B) Apparent density of powder.

Fig. 1 (C) Volume of pasting solution.

Fig. 1 (D) Filter speed at washing.

Fig. 1 (E) Initial capacity.

Fig. 1 (F) Durability evaluated by capacity at 32nd charge and discharge cycle.

The admixing of HgO as conducting material was useful because the reduced Hg in charged plate aided binding action of powder of active materials. Lignin was useful as anti-shrinkage agent of the active materials. The combination of HgO and lignin was much effective. Through these results, the optimum conditions for electrode plate were determined as shown in Table 3 and the samples of the same size as before were made. This time, the shedding of the active materials was prevented by covering the surface of the plate with saran fabrics and by pressing a net of nickel on it adequately. Thus, the shedding was prevented almost completely and the plates withstood over 2,500 cycles of charge and discharge as shown in Fig. 2.

It has been recognized by this example that the orthogonal layout can detect the factor affecting large effect very efficiently out of many other factors and so the putting in practice of the conclusion will not cause any serious errors.

On the other hand, as minor factors are liable to be affected mutually or by other factors, a conclusion contrary to the fact may be obtained, but such an error in judgment will cause only a slight effect on the whole. An additional experiment by fixing larger factors at optimum conditions may be conducted if necessary. In the present experiment, the quantity of additional iron salt and the temperature at which the precipitate is made, may be counted as minor factors. If an adequate precaution be taken, the orthogonal layout is sure to be a very powerful aid for these experiments.

In summary, 17 factors in the preparation of paste-type negative plate for alkaline storage battery have been tested by the two-step random combination method and the following conditions were found to be satisfactory: (1) Heating of the raw hydroxides at about 600°C for 30~60 minutes, (2) Admixing of small amount of HgO and lignin, and (3) Covering the surface of the negative plate by alkaliproof materials such as saran.

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Literatures :

- (1) K. Sugita : *J. Electrochem. Soc. Japan*, 24, 300 (1956).
- (2) G. Taguchi : Determination of Common Difference, p. 67, JIS Association (1956).

Table 3 Most Suitable Procedure for Preparing
of Paste-type Negative Plate.

Process	Factor	Condition	Its Effect on	
			durability	initial capacity
Precipit.	Vol. of FeCl ₃	10 cc (Cd : Fe = 100 : 11)	*	**
	Conc. of NaOH	200~400 cc (12~21 gNaOH/l)	*	
	Temperature	below 60°C		
Standing	Time	soon after precipit.		?
Washing	Number	1 time		
Heat Treatment	Temperature	600°C		
	Time	30~60 min	**	
Pasting	Addition agent	Lignine	*	
	Conduct. material	HgO	**	**
	Pasting soln.	Sp. Gr.=1.20 KOH		**
Forming	Hardness of paste	Med. or Hard		**
	Current density	0.4 A/dm ²		

* : Significant ** : Extremely significant

Fig. 2 Results on the cycle test for the plates prepared by the most suitable procedure.